HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**13S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9647/02

Paper 2 Structured Questions

15 September 2014

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1) Write your **name**, **CT group, centre number** and **index number** clearly in the spaces at the top of this page.

2) Answer **all** questions in the spaces provided in this Question Paper.

INFORMATION FOR CANDIDATES

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

A Data Booklet is provided.

Do not use staples, paper clips, highlighters, glue or correction fluid.

You may use a calculator.

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

For Examiner's Use	
1	**/ 12**
2	**/ 12**
3	**/ 21**
4	**/ 12**
5	**/ 15**
Deductions	
Total	**/ 72**

Calculator Model:

For Examiner's use

1 Planning (P)

Passing an electrical current through an electrolytic cell can cause a non-spontaneous chemical reaction to occur. The number of moles of products formed is related to the number of moles of electrons that pass through the cell during electrolysis.

This technique can be used to determine the Avogadro's constant. When a current is passed through a solution of acidified aqueous potassium iodide, hydrogen gas will be produced at one electrode, while iodine will be formed at the other electrode. The amount of hydrogen produced can be determined from the volume of hydrogen gas collected by downward displacement of solution. The amount of iodine formed can be found by titration of a portion of the electrolyte with sodium thiosulfate.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

(a) Give the ion-electron equation, with state symbols, for the reaction which occur at the cathode.

……..... [1]

(b) Calculate the expected volume of hydrogen gas formed at r.t.p. if a current of 0.50 A is passed for 10 minutes.

[1]

(c) Using your answer to **(b)**, you are required to write a plan to determine the amount of hydrogen and iodine produced in the electrolysis of acidified aqueous potassium iodide, and hence, the Avogadro's constant.

You are provided with:

- 500 cm^3 of 0.500 mol dm^{-3} acidified aqueous potassium iodide;
- 0.0100 mol dm^{-3} aqueous sodium thiosulfate;
- common indicators;
- milliammeter (range 0 – 1.0 A);
- battery
- the apparatus and chemicals normally found in a school or college laboratory.

In your plan you should include:

- a fully-labelled diagram of the electrolytic setup, showing
  - how you collect the hydrogen gas,
  - your choice of electrodes;
- an outline of the procedure with essential experimental details, including
  - quantities of chemicals and appropriate apparatus to be used,
  - choice of a suitable indicator,
  - all measurements to be made;
- an outline of how you would process the titration results to determine the Avogadro's constant.

For Examiner's use

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For Examiner's use

[10]

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2 **(a)** Sodium fluoride is commonly added to toothpastes or mouth rinses to prevent tooth decay. However, in high concentrations, F^- is lethal. A person who has accidentally swallowed some toothpaste may be treated by drinking some *milk of magnesia* to form magnesium fluoride, MgF_2. The numerical value of the solubility product of MgF_2 at 25 °C is 5.16×10^{-11}.

(i) Write an expression for the K_{sp} of MgF_2, stating its units.

……

(ii) Calculate the minimum concentration of Mg^{2+} ions required to form a precipitate in a solution containing 1.0 mg dm^{-3} of F^- ions.

[3]

(b) **(i)** State the three products formed in the electrolysis of brine (concentrated sodium chloride solution).

……

(ii) Sodium chlorate(V), $NaClO_3$, an ingredient in weed-killer, can be obtained from the products of this electrolysis.

Write a balanced equation with state symbols to show how $NaClO_3$ can be formed.

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[2]

(c) Explain why hydrogen iodide cannot be prepared with sodium iodide and concentrated sulfuric acid. Support your answer with an appropriate equation.

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[2]

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(d) **(i)** State three ways in which an ideal gas differs from a real gas.

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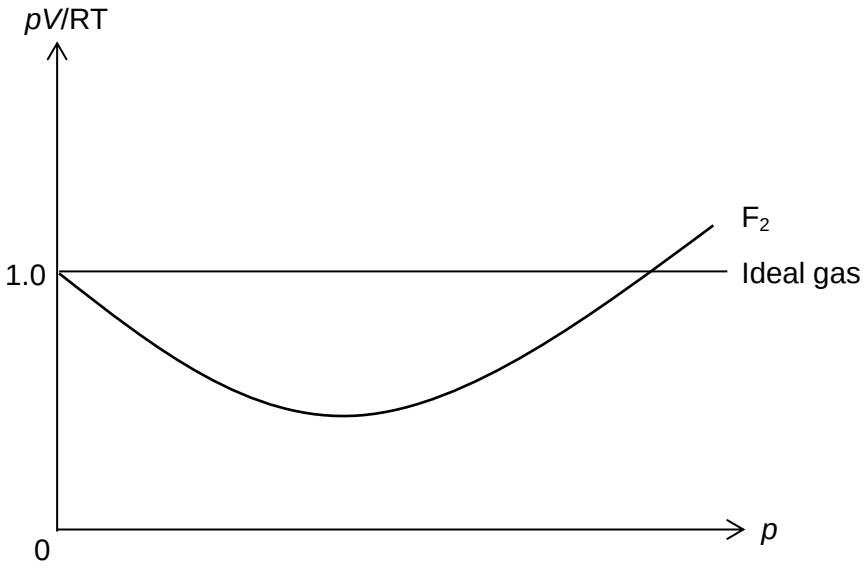
(ii) The value of pV/RT is plotted against p for one mole of an ideal gas and one mole of fluorine gas at 300 K, where p is the pressure and V is the volume of the gas.



On the same axes, sketch the variation of pV/RT against p for one mole of hydrogen fluoride, HF, at the same temperature of 300 K. Briefly explain your answer.

……

……

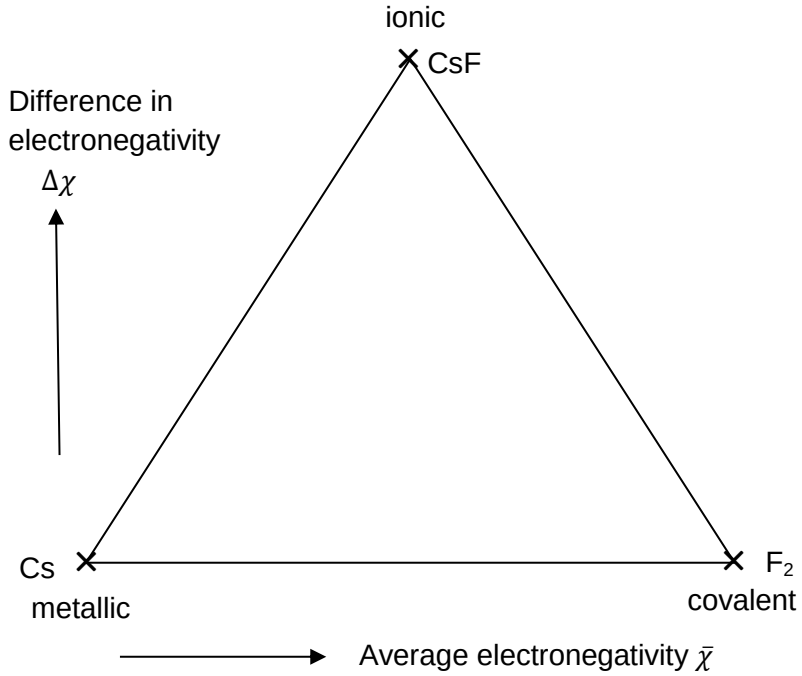
[5]
[Total: 12]

For Examiner's use

3 In this question, data from the *Data Booklet* and the information and answers derived in one part may be relevant to other parts of the question.

(a) The type of bonding present in a binary compound can be predicted from the electronegativities of the elements involved. This can be shown on a van Arkel-Ketelaar triangle, which plots the difference in electronegativity, $\Delta\chi$, on the y-axis against the average electronegativity of the two elements, $\bar{\chi}$, on the x-axis.

In this triangle, the three corners represent the extremes of metallic, ionic, and covalent bonding, with caesium (Cs), caesium fluoride (CsF), and fluorine (F_2) in these corners.



(i) State the type of bonding in sodium chloride (NaC*l*), aluminium chloride (A*l*Cl_3), and titanium-aluminium alloy (Ti-A*l*).

Type of bonding in NaC*l*: ……

Type of bonding in A*l*Cl_3: ……..

Type of bonding in Ti-A*l*: ……..

(ii) Mark the approximate positions of NaC*l*, A*l*Cl_3, and Ti-A*l* with crosses (x) in the van Arkel-Ketelaar triangle above, and label the crosses accordingly.

[3]

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(b) Lattice energies can be obtained from the experimental data in a Born-Haber cycle, and they can also be estimated using a pure ionic model represented by the Kapustinskii equation:

$$\Delta H_{latt} = \frac{k\ v\ z_+\ z_-}{r_+ + r_-}$$

where z_+ and z_- are positive or negative integers giving the charges on the ions, r_+ and r_- are the ionic radii in nm, v is the number of ions in the formula unit, and k is a constant with a value of 107.9 nm kJ mol^{-1}.

For example, using the Kapustinskii equation, the lattice energy of sodium chloride is calculated as follows:

$$\Delta H_{latt} = \frac{107.9 \times 2 \times (+1) \times (-1)}{(0.095 + 0.181)} = -782 \text{ kJ mol}^{-1}$$

(i) The table below shows numerical values of lattice energies for sodium chloride and two silver halides. These have been determined from experimental data or theoretically calculated.

compound	experimental value / kJ mol^{-1}	theoretical value / kJ mol^{-1}
NaC*l*	–781	–782
AgF	–967	–824
AgI	–889	–618

Explain the differences between the experimental and theoretical values of lattice energy for AgF and AgI.

……

……

……

(ii) Use the Kapustinskii equation to calculate the lattice energies of calcium(I) chloride and calcium(II) chloride. As calcium(I) chloride is not known to exist, assume that the ionic radius of Ca^+ is similar to that of the neighbouring ion K^+, which is 0.133 nm.

ΔH_{latt} of calcium(I) chloride, CaC*l*:

ΔH_{latt} of calcium(II) chloride, CaCl_2:

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(iii) Use the data below to construct a Born-Haber cycle in the grid provided to calculate the enthalpy change of formation of calcium(I) chloride, CaC*l*. Label each energy level of your cycle, and draw arrows representing the energy terms involved. Use symbols or numbers to represent these energy terms.

enthalpy change of atomisation of calcium = +178 kJ mol^{-1}
electron affinity of chlorine = –349 kJ mol^{-1}

energy

For Examiner's use

(iv) Construct an energy cycle to calculate the enthalpy change of the following disproportionation reaction:

$$2CaCl(s) \rightarrow Ca(s) + CaCl_2(s)$$

(v) Which of your answers, **(b)(iii)** or **(b)(iv)**, provides support for the argument that calcium(I) chloride does not exist? Explain your reasoning.

Provides support: ……

Explanation:

……

……

……

[11]

(c) **(i)** Write a balanced equation, including state symbols, for the decomposition of barium nitrate.

……

(ii) The corresponding compound in Group I, caesium nitrate, decomposes according to the equation:

$$2CsNO_3(s) \rightarrow 2CsNO_2(s) + O_2(g)$$

Explain why different products are formed in the decomposition of barium nitrate and caesium nitrate.

……

……

……

[3]

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(d) Aqueous metal cations exhibit varying degrees of Bronsted acidity. The ionic radii and pK_a values of some cations are given below.

Cation	Ionic radius /nm	pK_a at 25 ^{o}C
Al^{3+}(aq)	0.050	5.0
Fe^{3+}(aq)	0.064	2.2
Mg^{2+}(aq)	0.065	11.4
Na^{+}(aq)	0.095	14.2
Ca^{2+}(aq)	0.099	12.8
K^{+}(aq)	0.138	14.5

(i) Calculate the pH of a 0.100 mol dm^{-3} solution of aluminium nitrate.

(ii) The pK_a value of carbonic acid at 25 °C is 6.3. Identify one metal cation from the list above that will react with $NaHCO_3$. Explain your choice of cation with reference to the relevant pK_a values, describe what you expect to observe, and identify the products formed.

Cation: ……..

Explanation:

……..……

..……..……

Observations and products:

……..……

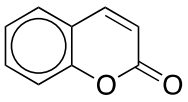
……..……

[4]
[Total: 21]

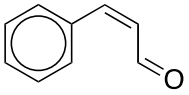
For Examiner's use

4 The spice cassia has been used in traditional Chinese medicine, where it is considered one of the 50 fundamental herbs.

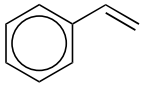
Each of the following four compounds, which are present in cassia, is toxic to humans if consumed in large amounts.



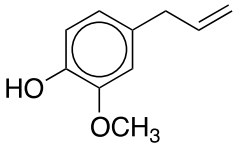
A



B



C



D

The group $-OCH_3$ which is present in compound **D** can be regarded as inert.

(a) Only **one** of the compounds **A**, **B**, **C** or **D** will react with **each** of the following reagents. In **each** case identify the compound concerned and draw the structural formula of the organic product formed.

Each compound may be used once, more than once, or not at all.

reagent	compound **A**, **B**, **C** or **D**	structural formula of the organic product
dilute HNO_3		
Na		
dilute H_2SO_4, heat		
Fehling's reagent		

[4]

(b) A student was asked to prepare compound **A** using 2-vinylphenol as the starting material. He suggested the following synthetic scheme.

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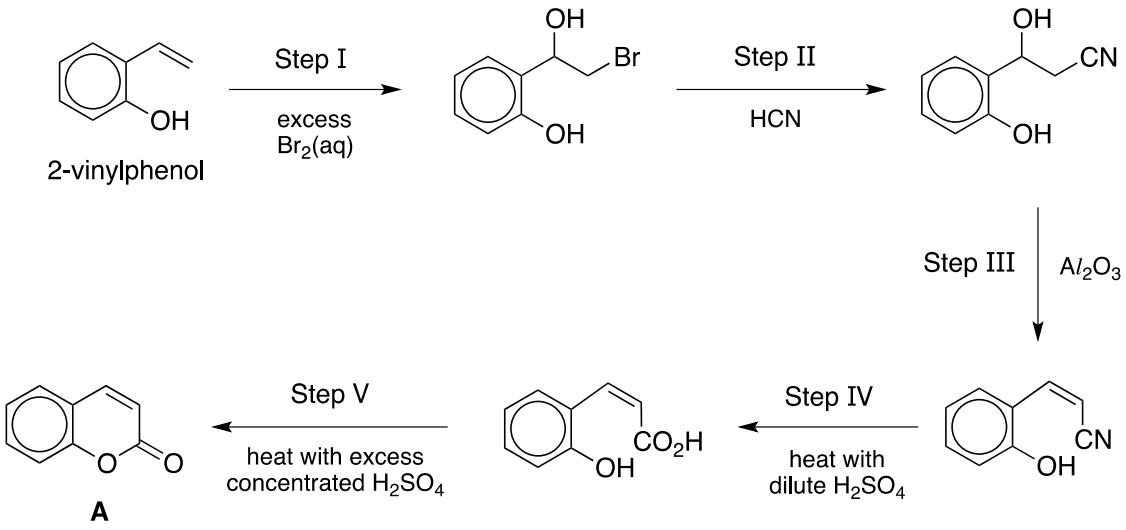

Steps I, II and V are unsatisfactory in his proposed synthesis. For each step that is unsatisfactory, explain why the reaction does not give a good yield of the desired product. Suggest an alternative method to obtain the desired product in steps II and V.

Step I:

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Step II:

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Step V:

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……

……

[6]

(c) Assuming compound **A** can be prepared from 2-vinylphenol via a 5-step synthesis route, with each step giving a yield of 80.0 %, calculate the mass of 2-vinylphenol needed to make 10.0 g of compound **A**. (M_r of compound **A**: 146)

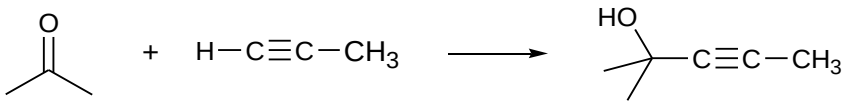
For Examiner's use

[2]

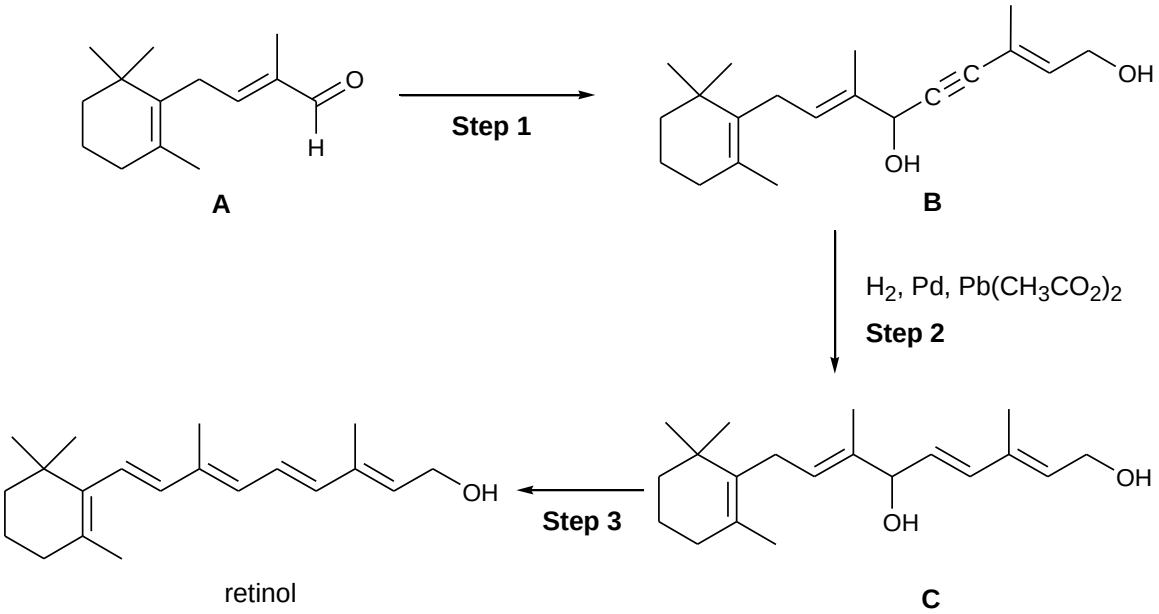
[Total: 12]

For Examiner's use

5 (a) Alkynes are hydrocarbons with a carbon-carbon triple bond. When treated with a suitable strong base, alkynes with a hydrogen bonded to the carbon on the triple bond can act as a strong nucleophile that reacts with ketones or aldehydes. For example, propyne reacts with propanone as shown in the reaction below.



The following reaction scheme shows the final steps in the synthesis of retinol (a form of vitamin A).



(i) State the type of stereoisomerism that compound **A** can exhibit and describe how such stereoisomerism can arise.

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(ii) Draw the structure of the alkyne that is used in **Step 1**.

In **Step 2** of the reaction, compound **B** was heated with hydrogen gas in the presence of palladium and lead(II) ethanoate, $Pb(CH_3CO_2)_2$.

(iii) What type of reaction takes place in this step?

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(iv) What is the role of palladium in this step? Explain what feature of palladium makes it suitable for its role.

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(v) Suggest why this step cannot be achieved using hydrogen gas and nickel.

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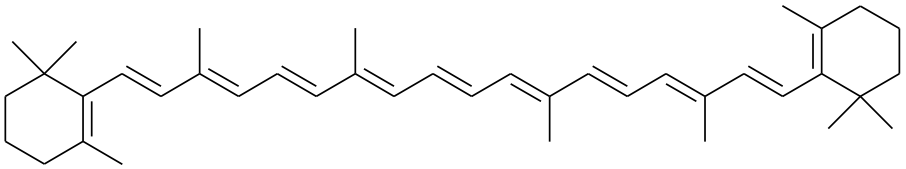
[7]

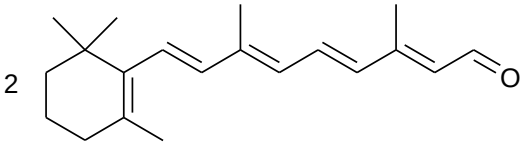
For Examiner's use

(b) *β*-carotene, a red-orange pigment found in carrots and papayas, is converted in our body by the enzyme beta-carotene monooxygenase (BCO) to retinal, which is a precursor of retinol.



β-carotene

BCO



retinal

A student attempts to carry out the same conversion in the laboratory using hot acidified potassium manganate(VII), but finds that different products are obtained

(i) Draw the structures of the two organic products formed when *β*-carotene is treated with an excess of hot acidified potassium manganate(VII).

(ii) Suggest why the enzyme BCO is able to convert *β*-carotene to retinal, but this conversion cannot be achieved in the laboratory using excess hot acidified potassium manganate(VII).

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For Examiner's use

(iii) In the conversion of *β*-carotene to retinal in the body, the substrate *β*-carotene must first bind to the active site of BCO. This involves favourable interactions between *β*-carotene and the amino acid residues in the active site.

amino acid	formula of side chain (R in $RCH(NH_2)CO_2H$)
glutamic acid	$-CH_2CH_2CO_2H$
serine	$-CH_2OH$
phenylalanine	$-CH_2C_6H_5$

Explain which of the above amino acids is most likely to be present in abundance in the active site of BCO.

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(iv) BCO's catalytic activity drops significantly in the presence of a strong base. Explain briefly what aspect of BCO's structure is altered when

I: BCO is mixed with aqueous sodium hydroxide at room temperature;

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II: BCO is heated under reflux with aqueous sodium hydroxide for several hours.

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[8]

[Total: 15]

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