VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 2

**CHEMISTRY** **9647/03**

Paper 3 Free Response **22 September 2014**

Candidates answer on separate paper. **2 hours**

Additional Materials: Answer Paper
Data Booklet
Graph Paper

**READ THESE INSTRUCTIONS FIRST**

Write your name and CT group 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.
A Data Booklet is provided.
You are reminded of the need for good English and clear explanation in your answers.

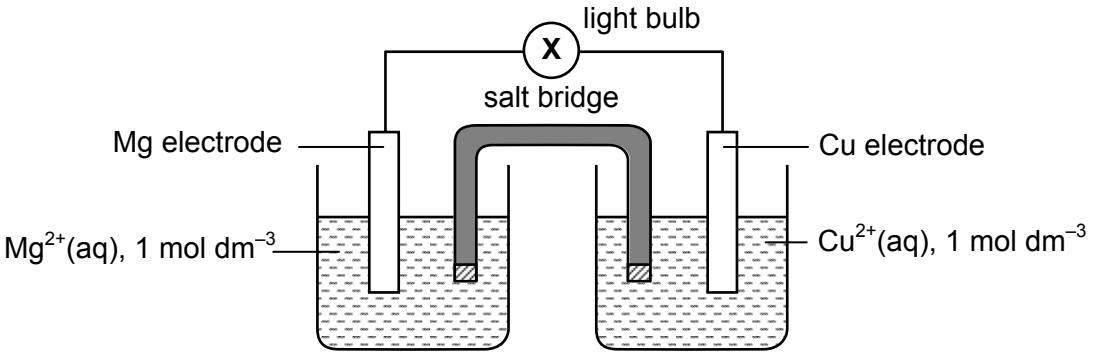
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

**Answer any four questions.**

**1 (a)** *Use of the Data Booklet is relevant in this question.*

The following cell has been used to light up a light bulb.




**(i)** Explain how the cell potential changes when the current has passed through for a while.

The electrode potential of the cell is related to the equilibrium constant by the following equation,

$$E^{\ominus} = \frac{RT}{zF} \ln K_c$$

where T is the temperature measured in Kelvin, $z$ is the number of moles of electrons transferred during the redox reaction and F is the Faraday constant.

**(ii)** Determine the equilibrium constant $K_c$ for the reaction between $Cu^{2+}$ and Mg.

**(iii)** Hence, determine the ratio $[Mg^{2+}]:[Cu^{2+}]$, when there is no current flowing in this cell.

**(iv)** Suggest the significance of the magnitude of your answer in **(a)(iii)**.

[5]

**(b)** Copper minerals often contain suifides of magnesium and silver as impurity. After minerals are reduced with carbon, the solid impure copper is purified by electrolysis.

**(i)** Describe the electrode reactions that take place during the electrolysis and explain in detail how each of the two impurity metals is removed from copper.

An impure copper rod is purified by electrolysis using a constant current. After 1 hour, mass of one electrode decreased by 19.0 g while mass of the other electrode increased by 17.8 g. The electrolyte was further analysed and found that the amount of $Cu^{2+}$ ions is reduced by 0.020 mol.

**(ii)** Calculate the current used for this process.

**(iii)** Determine the percentage composition by mass of the three elements.

**(iv)** Suggest how magnesium can be recovered as magnesium oxide near the end of the electrolytic process. Write balanced equations for any reactions involving magnesium that might occur.

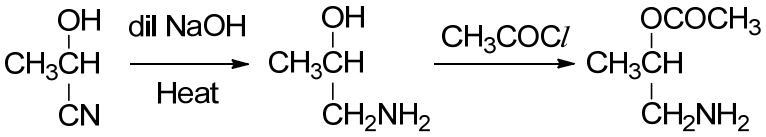
[11]

**(c)** The methods of synthesis shown below are faulty.

In each case

- Explain why this is so.
- Suggest how the synthesis from the initial reactant to the final product could be satisfactorily achieved.

**(i)** $CH_3CH(OH)CO_2C_2H_5 \xrightarrow[\text{Heat}]{\text{dil HCl}} CH_2{=}CHCO_2C_2H_5$

**(ii)** 


[4]

[Total: 20]

**2 (a) (i)** When $CHI_2CHO$ was warmed with alkaline aqueous iodine, two organic products are formed. Construct an equation for this reaction.

**(ii)** There are suggestions on using $CF_3CH_2F$ to replace CFCs. One problem however is that $CF_3CH_2F$ can be converted to $CF_3CO_2H$, which is toxic when ingested. When $CF_3CH_2F$ eventually reaches the atmosphere, it is thought that $CF_3CH_2F$ is initially attacked by •OH radicals.

A student suggested the following equation to represent the above reaction:

$$CF_3CH_2F + \bullet OH \rightarrow CF_3\dot{C}H_2 + HOF$$

By considering the
- bonds broken and
- bonds formed

in the above reaction, explain why the above reaction will **not** occur.

**(iii)** In light of your answers to **(a)(ii)**, suggest a more appropriate equation for the reaction between $CF_3CH_2F$ and •OH.

**(iv)** Ethanedioic acid, $HO_2C\text{-}CO_2H$ is a dibasic acid, with $pK_{a1}$ = 1.3 and $pK_{a2}$ = 4.3. Methanoic acid is a monobasic acid with $pK_a$ = 3.7.

Account for the lower $pK_{a1}$ value of ethanedioic acid as compared to the $pK_a$ of methanoic acid.

[6]

**(b)** But-2-yne, $H_3CC{\equiv}CCH_3$ may undergo the addition of hydrogen at the surface of a metal catalyst to produce an alkene **X**. Draw relevant diagrams to illustrate how the metal catalyses this reaction. Give the structure of **X**.

[3]

**(c) (i)** Describe briefly how gaseous HC*l* can be made in the laboratory from NaC*l* and concentrated $H_2SO_4$.

**(ii)** Explain with relevant equations, if HBr and HI can be prepared in a similar method as in **(c)(i)**.

**(iii)** Silver chloride is soluble in aqueous ammonia while silver bromide is soluble in concentrated aqueous ammonia. Explain these observations.

[6]

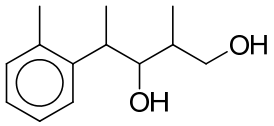
**(d)** **A** is one of the elements from Na to P in the third period of the Periodic Table. When **A** is boiled with aqueous sodium hydroxide, a colourless gas, **B** is formed together with a sodium salt, **C**. Gas **B** is weakly basic and reacts with hydrogen iodide to form a solid compound, **D**, which contains 19.1% of **A**, 2.5% of hydrogen and 78.4% of iodine by mass. The sodium salt **C** contains 26.1% of sodium, 2.27% of hydrogen, 35.2% of **A** and 36.4% of oxygen by mass. **A** also forms two chlorides which dissolve readily in water to produce strongly acidic solutions of pH 2.

Identify the element **A** and the compounds **B**, **C** and **D**. Write equations for all the reactions involved.

[5]

[Total: 20]

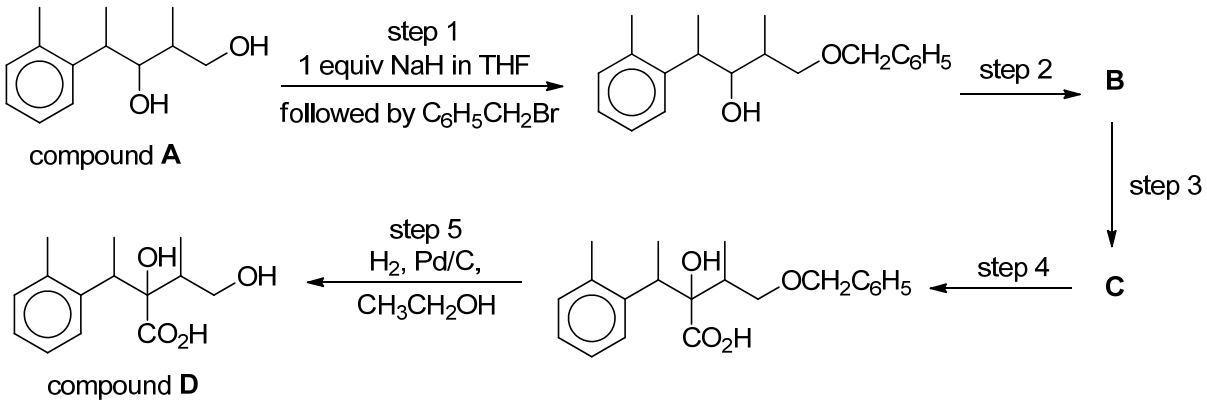
**3** Alcohols are very useful in organic synthesis and can be used to produce a wide variety of compounds. The structural formula of one such alcohol is shown below.




compound **A** ($C_{13}H_{20}O_2$)

**(a)** When compound **A** is heated with an excess of concentrated sulfuric acid, a mixture of two isomeric hydrocarbons, **P** and **Q** are produced. Draw the structures of **P** and **Q**. [2]

**(b)** Compound **D** can be formed from compound **A** via a five-step synthesis.




**(i)** State the reagents and conditions required for steps 2 to 4 and the structural formulae of the two intermediates **B** and **C**.

**(ii)** Step 1 involves the 'protection' of one of the alcohol groups to convert it into an ether, which is inert. Suggest a reason why this step is necessary.

**(iii)** Suggest the type of reaction in step 5.

[6]

**(c)** Nitrosyl bromide, NOBr, is a red gas and can be formed by the reversible reaction of nitric oxide with bromine.

**(i)** Explain why nitrosyl bromide has a boiling point of 14 $^{o}$C whereas nitrosyl chloride, NO*Cl* boils at −5 $^{o}$C.

NOBr decomposes to NO and $Br_2$ as shown below.

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$$

**(ii)** Given that the bond energy of N−Br is 120 kJ mol$^{-1}$, use the data from the *Data Booklet* to calculate the enthalpy change of decomposition of nitrosyl bromide, NOBr.

**(iii)** Standard enthalpy changes of formation of nitrosyl bromide and nitrogen monoxide are given below.

| compound | $\Delta H_f$ / kJ mol$^{-1}$ |
|---|---|
| NOBr(g) | +82 |
| NO(g) | +90 |

With the aid of an energy cycle, use your answer in **(c)(ii)** and data above to calculate the enthalpy change of vaporisation of bromine.

**(iv)** Predict and explain the 'sign' of entropy change for the decomposition of nitrosyl bromide.

[6]

**(d)** A calorimeter containing 300 cm$^3$ of water at 25 °C was calibrated as follows.

**(i)** 10 kJ of heat energy from a heating coil was used to increase the temperature of water by 7.5 °C. Calculate the heat capacity of the empty calorimeter.

**(ii)** A solution containing 0.040 mol $Ag^+$(aq) was mixed with a second solution containing 0.050 mol $Br^-$(aq) in this calorimeter, causing AgBr(s) to precipitate. The temperature increased by 2.4 °C. Calculate the equilibrium concentrations of $Ag^+$(aq) and $Br^-$(aq) present in the final voiume of 320 cm$^3$.
[$K_{sp}$ of AgBr = 5 x 10$^{-13}$ mol$^2$ dm$^{-6}$]

**(iii)** Hence, calculate the enthalpy change of solution of AgBr(s).
[You may assume that the density of all solutions is 1 g cm$^{-3}$.]

[6]

[Total: 20]

**4 (a)** Sulfuryl dichloride, $SO_2Cl_2$, is a compound of industrial, environmental and scientific interest, widely used as a chlorinating or sulfonating agent. At room temperature, $SO_2Cl_2$ is a colourless liquid with a pungent odour.

An empty container is filled with $SO_2Cl_2$. Its decomposition to $SO_2$ and $Cl_2$ is followed by monitoring the change in total pressure at 375 K. The following data are obtained.

| time/ hour | 0 | 1 | 3 | 6 | 10 | 14 | 18 |
|---|---|---|---|---|---|---|---|
| $P_{total}$ / atm | 1.000 | 1.076 | 1.211 | 1.378 | 1.547 | 1.670 | 1.760 |
| $P_{SO_2Cl_2}$ / atm | 1.000 | **p** | **q** | 0.622 | **r** | 0.330 | 0.240 |

**(i)** Determine the values of **p**, **q** and **r**. Show your working clearly.

**(ii)** Hence, by plotting a suitable graph, show that the decomposition of $SO_2Cl_2$ is a first order reaction.

**(iii)** Calculate the rate constant, stating its unit.

**(iv)** Calculate the concentration of $SO_2Cl_2$, in mol $dm^{-3}$ after 18 hours.
You may assume ideal gas conditions.

**(v)** In another experiment, the decomposition reaction is repeated at 375 K with initial total pressure of 2 atm of $SO_2Cl_2$.

Use the graph drawn in **(a)(ii)** to estimate the time taken for partial pressure of $SO_2Cl_2$ to fall by 20% in this experiment. Explain your answer.

**(vi)** There will be a negligible amount of $SO_2Cl_2$ (g) in the reaction vessel after a long period of time. Therefore, the content of the vessel might be considered to be a mixture of $SO_2$ and $Cl_2$ gases.

A possible way to separate $SO_2$ and $Cl_2$ from each other is to pass the mixture over solid CaO which will convert all the $SO_2$ to $CaSO_3$, a strong electrolyte. Calculate the pH of a 0.020 mol $dm^{-3}$ $CaSO_3$ solution.
[For $H_2SO_3$ $K_{a1} = 1.7\times10^{-2}$ mol $dm^{-3}$ and $K_{a2} = 6.4\times10^{-8}$ mol $dm^{-3}$.]

[12]

**(b)** Compound **G** has a sweet smell. When heated with an excess of acidified concentrated manganate(VII) ions, it forms initially three products **H**, **J** and **K**.

$$\underset{C_{13}H_{20}O_2}{\mathbf{G}} \xrightarrow{MnO_4^- / H^+} \underset{C_6H_8O_3}{\mathbf{H}} + \underset{C_5H_{10}O_2}{\mathbf{J}} + \underset{C_2H_2O_4}{\mathbf{K}}$$

- When compound **G** was mixed with liquid bromine at room temperature, $C_{13}H_{20}O_2Br_4$ was obtained.
- Compound **J** evolves $CO_2$ with $NaHCO_3$. **J** also reacts with $LiAlH_4$ to give a compound which does not react with concentrated sulfuric acid.
- Compound **H** gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent. **H** has no reaction with Tollens' reagent. When 1 mol of **H** reacts with an excess of alkaline aqueous iodine, 2 mol of yellow precipitate are produced.

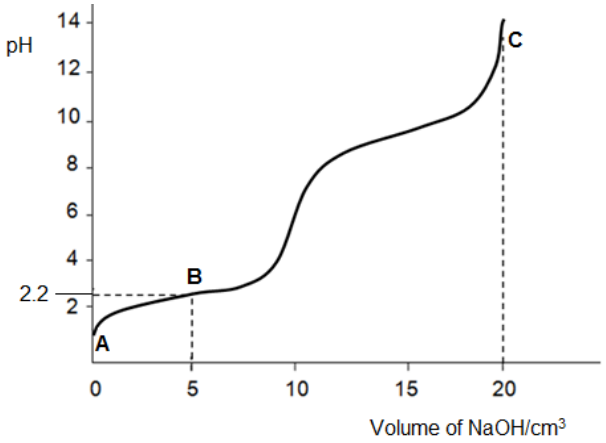
Use the information above to deduce the structures for compounds **G**, **H**, **J** and **K**.

[8]

[Total: 20]

**5** Amino acids are critical to life, and they serve as building blocks of proteins.

**(a)** Lysine is an alpha amino acid which shows both acidic and basic properties. The R group of lysine is $-(CH_2)_4NH_2$. In acidic solution, lysine is completely protonated. 10.0 $cm^3$ of completely protonated lysine is titrated with 1.00 mol $dm^{-3}$ sodium hydroxide solution. Its titration curve is shown below.




**(i)** Calculate the first dissociation constant $K_{a1}$ of fully protonated lysine.

**(ii)** Identify the two species at point **B**. Write an equation to show how the species present at point **B** can resist change in pH when a small amount of base is added.

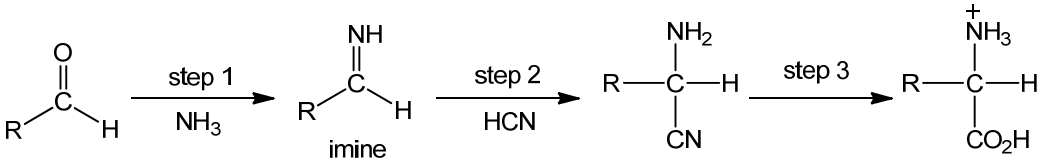
**(iii)** Calculate the pH when 10.0 $cm^3$ of 0.0200 mol $dm^{-3}$ sodium hydroxide is added to the solution at point **B**. (You may represent the fully protonated lysine as HA.)

**(iv)** State the predominant species at point **C**. Explain why it has a high melting point.

**(v)** State the type of isomerism in the species at point **C** and draw its isomers.

[8]

**(b)** The first known synthesis of an amino acid occurred in 1850 in the laboratory of Adolf Strecker.




**(i)** Name the type of reaction in step 1.

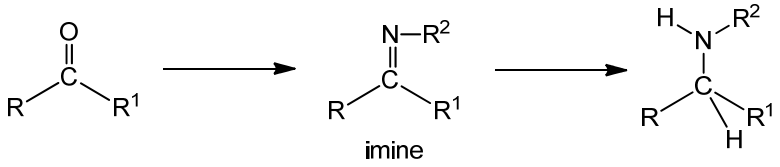
**(ii)** Suggest suitable reagents and conditions for step 3.

**(iii)** In step 2, the reaction proceeds via two stages:

(I) acid-base reaction between the N atom in imine and HCN
(II) nucleophilic attack on C by $CN^-$

Write the mechanism for step 2, showing clearly the movement of electrons and partial charges.

**(iv)** An imine intermediate is also formed in preparing secondary amines from ketones.




With reference to the Adolf Strecker synthesis, suggest the synthetic route by giving the reagents, conditions and intermediates for the preparation of $(CH_3)_2CHNH(CH_2CH_3)$.

**(v)** Another amine **X**, $CH_3CH(NH_2)CH_2NH_2$ reacts with ethanedioyl dichloride $(COCl)_2$ to produce compound **Y** with molecular formula $C_5H_8N_2O_2$. Suggest the structure for compound **Y** and write the equation between **X** and ethanedioyl dichloride.

[8]

**(c)** A polypeptide **H** was analysed and found to contain the following amino acids.

| **amino acid** | aspartic acid | glycine | serine | tyrosine | valine |
|---|---|---|---|---|---|
| **abbreviation** | asp | gly | ser | tyr | val |
| **number of residues** | 1 | 1 | 2 | 1 | 1 |

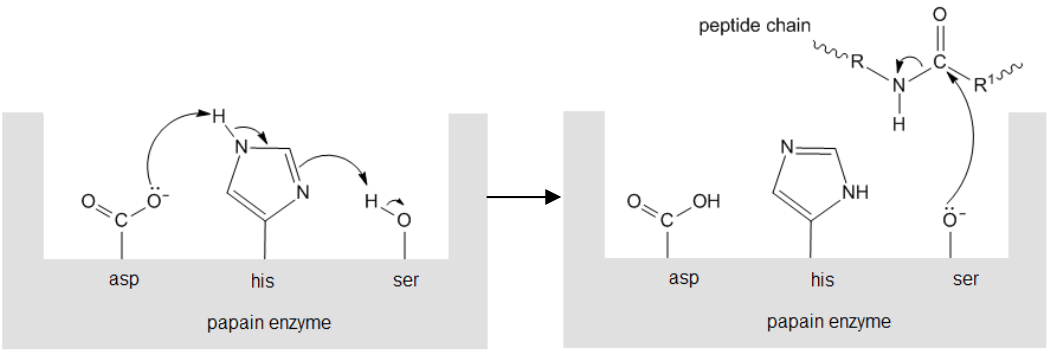
Analysis gave the following results:

- The N-terminus was shown to be ser.
- On reaction with the enzyme chymotrypsin, which hydrolyses at the carboxylic acid end of tyr, **H** gave two tripeptides.
- On reaction with a special reagent which digests at the carboxylic end of val, **H** gave two peptides. One of these two was a dipeptide of sequence gly-ser.

Determine the amino acid sequence of polypeptide **H**. Briefly justify your answer.
[You should use the same 3–letter abbreviations as shown above to write out the amino acid sequence].

[2]

**(d)** Papain, an enzyme in fresh papaya juice is used as a meat tenderiser. The three main amino acids involved in the catalytic activity of papain are his, asp and ser. Part of the mechanism of the action of papain is illustrated in the figures below.




(I) (II)

With reference to figures (I) and (II) above, explain why the action of this enzyme would be inhibited if the pH was too low.

[2]

[Total: 20]