VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY **9647/03**

Paper 3 Free Response **20 September 2016**

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

Additional Materials: Answer Paper
Data Booklet

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.

1 **(a)** At high temperatures NO reacts with H_2 to produce nitrous oxide, N_2O, a greenhouse gas.

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

To study the kinetics of this reaction at 820 °C, initial rates for the formation of N_2O were measured using various initial partial pressures of NO and H_2.

Experiment	Initial pressure / kPa		Initial rate of production of N_2O / kPa s^{-1}
	P_{NO}	P_{H_2}	
1	16	8	1.15×10^{-2}
2	8	8	2.87×10^{-3}
3	8	24	8.60×10^{-3}

(i) Deduce the rate equation in terms of partial pressure. [3]

(ii) Using the rate equation and the information in the table above, calculate a value for the rate constant, giving its units. [2]

(iii) Hence, calculate the initial rate at which NO reacts when 25 kPa of NO and 12.5 kPa of H_2 are mixed at 820 °C. [1]

(iv) Write the rate equation for the reaction when NO is used in large excess. Hence, determine the time elapsed to reduce the partial pressure of H_2 to half of its initial value, if 100 kPa of NO and 1 kPa of H_2 are mixed at 820 °C. [3]

(v) Two mechanisms, **A** and **B** are proposed below.

A: $2NO \xrightarrow{slow} N_2O_2$

$N_2O_2 + H_2 \xrightarrow{fast} H_2O + N_2O$

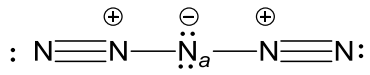
B: $2NO + H_2 \xrightarrow{slow} 2HNO$

$2HNO \xrightarrow{fast} N_2O + H_2O$

Which mechanism is consistent with the rate equation obtained in **(a)(i)**. Explain your answer. [1]

(b) Polynitrogen compounds have great potential for being used as high energy density materials. They are thermodynamically unstable. Huge amounts of energy are released from their decomposition or reactions leading to more stable products.

(i) The polynitrogen species, N_5^+ was first isolated in 1999. One of its resonance forms is shown below.



State the bond angle and molecular shape around nitrogen labelled *a*. [1]

(ii) The synthesis of a white ionic solid, $[N_5^+][AsF_6^-]$, was achieved by reacting $[N_2F^+][AsF_6^-]$ with hydrazoic acid, HN_3, in liquid HF at –78 °C.
Write a balanced equation for this reaction. [1]

(iii) $[N_2F^+][AsF_6^-]$ was first prepared by reacting N_2F_2 with the strong Lewis acid, AsF_5. N_2F_2 has the following structure and exhibits cis-trans isomerism.

$$F-N=N-F$$

Draw the cis-trans isomers of N_2F_2, including all lone pairs and suggest an appropriate hybridisation for each nitrogen atom in N_2F_2. [2]

(c) Nitrogen is found in all organisms, primarily in amino acids which made up proteins.

Isoleucine, $NH_2CH(CH(CH_3)CH_2CH_3)CO_2H$ is an α-amino acid where the amino group and carboxylic acid group are separated by one carbon. It is a constituent amino acid in many protein molecules. Isoleucine can exist as different stereoisomers.

(i) State the reagents and conditions needed to break protein down into its constituent amino acids. [1]

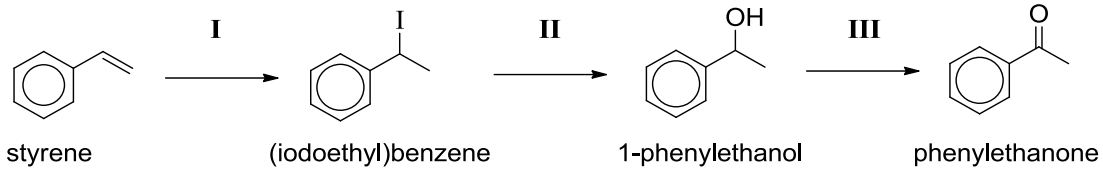
(ii) Define the term *stereoisomers*. [1]

(iii) There are four optical isomers of isoleucine. Draw the structures of these four stereoisomers of isoleucine, indicating clearly the chiral centres. [2]

(d) 3-amino-3-methyl-1butyne, $CH{\equiv}CCNH_2(CH_3)_2$ is used as the starting material to make other chemicals.
Draw a labelled diagram to show the orbitals that form C≡C in an alkyne. [2]

[Total: 20]

2 **(a)** Styrene (phenylethene) is a useful organic intermediate used for the synthesis of many products. For instance, styrene is able to undergo the reaction shown below:



(i) State the reagents and conditions required for reactions **I**, **II** and **III**. [3]

(ii) By considering the substituent(s) attached to the carbonyl group, give two reasons for the lower reactivity of phenylethanone towards nucleophiles compared to propanone, CH_3COCH_3. [2]

(iii) Suggest a simple chemical test to distinguish between (iodoethyl)benzene and iodobenzene, C_6H_5I. State the observations for each compound. [2]

(iv) The solubility of (iodoethyl)benzene in water was found to be 32.1 mg dm^{-3}. Explain why (iodoethyl)benzene has such a low solubility in water. [2]

(b) (Iodoethyl)benzene exists as a pair of enantiomers **A** and **B.**

An optically pure sample containing only isomer **A** dissolved in hexane underwent a nucleophilic substitution reaction with a solution containing radioactive iodide ions, $^{131}I^-$. After the reaction, 75% of the (iodoethyl)benzene is incorporated with radioactive iodide.

An investigation into the kinetics of the reaction revealed that the rate of reaction was independent of the concentration of $^{131}I^-$.

(i) Describe the mechanism for the reaction of (iodoethyl)benzene with $^{131}I^-$. In your answer, clearly label the ^{131}I, and include any relevant charges, curly arrows and dipoles or lone pairs of electrons that you consider important in this mechanism. [2]

(ii) Calculate the percentage of (iodoethyl)benzene that exists as enantiomer **B** incorporated with ^{131}I in the product mixture. [1]

(c) The term 'tri-iodide' refers to molecules that contain three iodine atoms in their molecular formula, such as nitrogen tri-iodide, NI_3, and aluminium tri-iodide, AlI_3.

AlI_3 has a simple molecular structure. In the gas phase, it dimerises readily to form the dimer Al_2I_6. The two species are related by the equilibrium shown below.

$$Al_2I_6(g) \rightleftharpoons 2AlI_3(g) \qquad \Delta H > 0$$

(i) A 10.0 g sample of Al_2I_6 was allowed to vapourise in a 2 dm^3 vessel at 400 °C. Calculate the initial pressure of Al_2I_6. [2]

(ii) Given that the degree of dissociation (α) of Al_2I_6 was 0.35, find the K_p value for the equilibrium at 400 °C. [2]

(iii) Explain the effect on the degree of dissociation of Al_2I_6 for each of the changes below.

- The reaction was carried out at 300 ^oC.
- A sample of Ar(g) was introduced into a 1 dm^3 vessel containing AlI_3(g) and Al_2I_6(g) at 400 ^oC. [2]

(d) The table below shows the boiling points of PCl_3 and PF_5.

Compound	Boiling Point / ^oC
PCl_3	76.1
PF_5	– 84.6

Explain why PCl_3 has a higher boiling point than PF_5. [2]

[Total: 20]

3 **(a)** Lead(II) nitrate decomposes on heating in the same way as magnesium nitrate. By using relevant data from the *Data Booklet*, predict and explain which of the two nitrates, lead(II) nitrate or magnesium nitrate, would have a higher decomposition temperature. [2]

(b) The halogens are reactive elements and are involved in many reactions.

(i) When chlorine is bubbled through cold sodium hydroxide solution, followed by an excess of acidified silver nitrate solution, only $\frac{1}{2}$ of the chlorine which has dissolved is precipitated as silver chloride. When the sodium hydroxide solution is hot, up to $\frac{5}{6}$ of the chlorine can be precipitated. Explain the observations with the aid of relevant equations. [3]

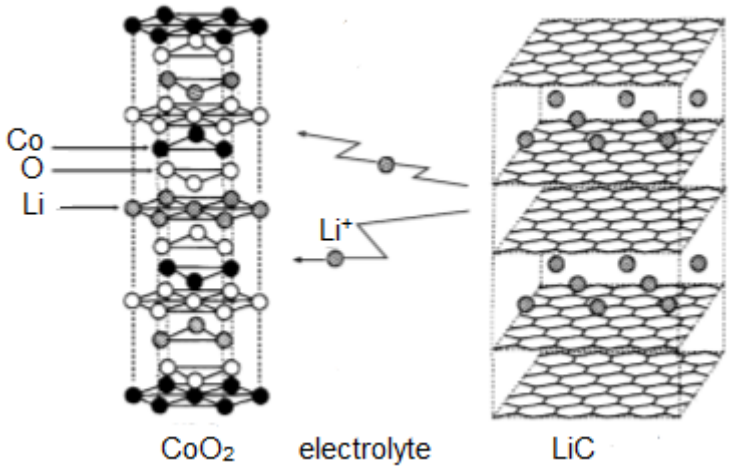
(ii) When chromium is made to react with chlorine, the main product of the reaction is $CrCl_3$. However, when chromium is made to separately react with other halogens such as fluorine and iodine, the main products are CrF_4 and CrI_2. By reference to relevant $E^{\ominus}$ values, what can you conclude about the relative oxidising ability of the halogens? [2]

The halogens also form many interhalogen compounds in which two different halogens are combined. Interhalogen compounds like BrCl have similar properties to the halogens.

(iii) Suggest an equation for the reaction that occurs between BrCl and aqueous KI. [1]

(iv) BrCl reacts with alkenes faster than the pure halogens such as Cl_2 and Br_2. Show the slow step of the reaction between BrCl and propene. [1]

(c) A lithium-ion battery is a rechargeable battery. In a fully charged battery, lithium ions occupy the tiny spaces in graphite to form LiC. During discharge, lithium ions are produced which migrate through the electrolyte while at the same time, graphite is being regenerated. In the other electrode, lithium ions react with CoO_2 to form $LiCoO_2$.



(i) Write equations for the electrode reactions occurring at the anode and cathode during discharge. [2]

(ii) Hence, write an equation for the overall reaction that occurs during discharge. [1]

(iii) By determining the oxidation numbers of the relevant elements, identify the elements that have been oxidised and reduced. [1]

(d) (i) With reference to the *Data Booklet*, draw a fully labelled diagram showing how you could measure the standard electrode potential for the Ag^+/Ag system. Indicate the direction of electron flow. [2]

(ii) The electrode potential, E and the concentration of silver ions in solution under non-standard conditions are related by the following equation.

$$E = 0.80 - 0.03 \lg \frac{1}{[Ag^+(aq)]^2}$$

The solubility product constant of AgC*l* is $K_{sp} = 1.8 \times 10^{-10}$ mol^2 dm^{-6}. Using the equation given above, calculate the electrode potential at 298 K of a half-cell formed by

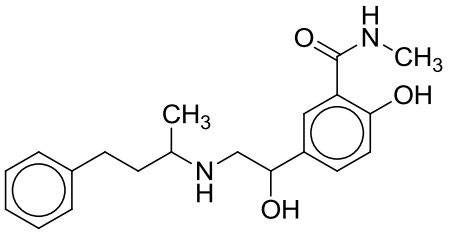
(I) a Ag electrode immersed in a saturated solution of AgC*l*.
(II) a Ag electrode immersed in a 0.5 mol dm^{-3} solution of KC*l* containing some AgC*l* precipitate.

[3]

(iii) A cell is made by connecting the half-cell in **(d)(i)** to a standard Cu^{2+}/Cu half-cell. By reference to relevant data from the Data Booklet, calculate the cell emf and write an equation (with state symbols) for the reaction that has occurred. [2]

[Total: 20]

4 **(a)** Compound **G** has the structure shown.



Give the structures of the organic compounds formed by compound **G** under the following conditions.

(i) NaOH(aq), reflux [2]

(ii) Excess CH_3COCl, room temperature [2]

(b) Lactic acid can be used in food products as pH regulators or as a food preservative. It can also be used as a flavouring agent.

(i) Suggest reagents and conditions needed to convert propene into 2-hydroxypropanoic acid (commonly known as lactic acid) in no more than 3 steps. Give the structures of the intermediates.

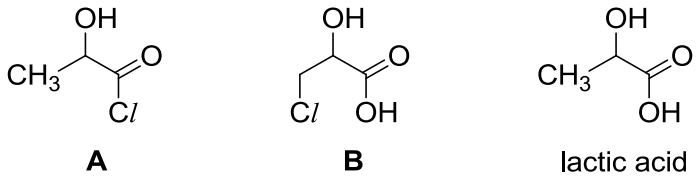
$CH_3CH{=}CH_2$ ⟶ $CH_3CH(OH)CO_2H$

propene lactic acid

[3]

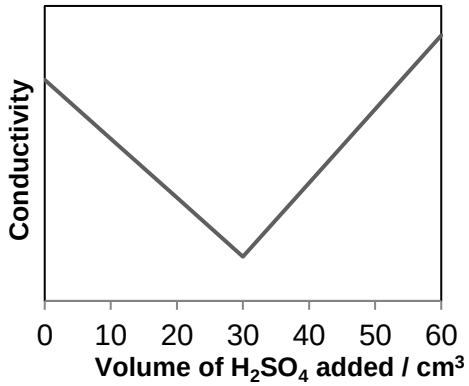
(ii) When lactic acid is refluxed with concentrated sulfuric acid, compound **H** with the molecular formula of $C_6H_8O_4$ is formed. It does not react with sodium. Give the structural formula of **H**. [1]

(iii) Describe and explain the relative acidity of the following three compounds.



A **B** lactic acid [2]

(c) Experiment 1 is conducted in which the conductivity of 25 cm^3 of $Ba(OH)_2$ solution is monitored as it is titrated with 0.10 mol dm^{-3} of aqueous H_2SO_4. The data collected from the experiment is plotted in the graph below.



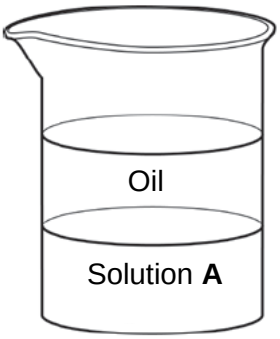
(i) The conductivity of the $Ba(OH)_2$ solution decreases as the volume of 0.10 mol dm^{-3} H_2SO_4 is added from 0 cm^3 to 30 cm^3.

Identify the chemical species that enable the solution to conduct electricity as the first 30 cm^3 of H_2SO_4 (aq) is added. Hence explain why the conductivity decreases. [2]

(ii) Using the information in the graph, calculate the initial concentration of $Ba(OH)_2$. [1]

(d) In Experiment 2, another 25 cm^3 sample of 0.10 mol dm^{-3} aqueous $Ba(OH)_2$ is mixed with 80 cm^3 of 0.10 mol dm^{-3} of ethanoic acid to form solution **A**. Barium ethanoate, $Ba(CH_3CO_2)_2$ is the product of the reaction. The acid dissociation constant, K_a, of ethanoic acid is 1.7×10^{-5} mol dm^{-3}. Calculate the pH of the solution **A**. [3]

(e) Half of the solution **A** formed in **(d)** is added to beaker **X** where there is a layer of colourless oil as shown in the figure below.



Beaker **X**

The indicator HIn is a weak acid with a pK_a value of 6.0. It reacts with water as represented in the equation below.

$$\underset{\text{yellow}}{HIn(aq)} + H_2O(l) \rightleftharpoons \underset{\text{blue}}{In^-(aq)} + H_3O^+(aq)$$

A small amount of indicator HIn is added into beaker **X**. The mixtures are stirred well and the two layers are allowed to separate.

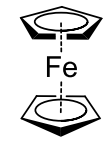
Assume the pH of solution **A** is unaffected by the presence of colourless oil.

(i) State the colour observed in the oil layer of beaker **X**. Explain the observation in terms of acid-base equilibrium and inter-molecular interactions. [2]

(ii) A few drops of aqueous sodium hydroxide and hydrochloric acid are added to the beaker **X** successively and stirred well. Explain with the aid of equation(s) why there is no change in the colour of the oil layer after each addition. [2]

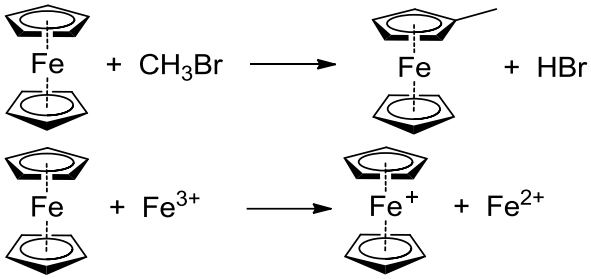
[Total: 20]

5 **(a)** Ferrocene, $Fe(C_5H_5)_2$, is an orange solid. In this complex, $C_5H_5^-$ is the ligand and it donates π electrons from the ring to the vacant 3d orbital of Fe. The structure of ferrocene is given below.



ferrocene

Ferrocene can undergo a series of different reactions and some are analogues of organic reactions. Two reactions of ferrocene are shown below:

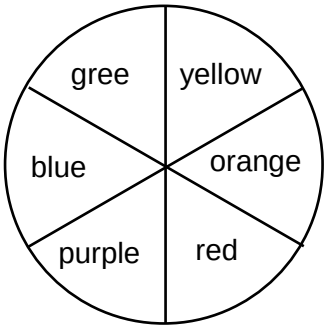


(i) State the types of reaction for reactions **I** and **II**. [1]

(ii) State the oxidation number of Fe in ferrocene and hence its electronic configuration. [1]

(iii) Suggest why Ferrocene is a coloured complex. [2]

(iv) The complementary colours are illustrated with the following colour wheel.



Aqueous Fe^{2+} ion is green in colour. Suggest and explain if water causes a larger split between the two groups of 3d orbitals as compared to $C_5H_5^-$. [2]

(v) By considering reaction **II**, suggest if $E^{\ominus}(Fe(C_5H_5)_2^+|Fe(C_5H_5)_2)$ is more positive or less positive than $E^{\ominus}(Fe^{3+}|Fe^{2+})$. Explain your answer. [1]

(vi) The reaction between $S_2O_8^{2-}$ and I^- is slow in the absence of catalyst. Ferrocene can be a suitable catalyst for this reaction between $S_2O_8^{2-}$ and I^-.

Explain with the aid of equations how it works. You may use $Fe(C_5H_5)_2$ to represent ferrocene. [2]

(vii) By considering your answers to **(v)** and **(vi)**, suggest a range of values for $E^{\ominus}(Fe(C_5H_5)_2^+|Fe(C_5H_5)_2)$. [1]

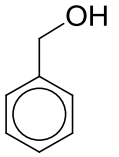
(b) Ephedrine, $C_{10}H_{15}NO$, is a drug used to prevent low blood pressure during spinal anaesthesia. It is optically active and has 2 chiral centres.

When Ephedrine is heated with acidified potassium manganate(VII), it gives benzoic acid, $C_6H_5CO_2H$ as one of the products. When it is heated with acidified potassium dichromate(VI), it gives **P**. **P** gives an orange precipitate when treated with 2,4–dinitrophenylhydrazine but it has no reaction with Tollens' reagent.

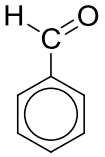
When Ephedrine is heated with equimolar CH_3Cl, it gives **Q**, $C_{11}H_{17}NO$ as the major product. When it is heated with excess CH_3Cl, it gives **R**, $C_{12}H_{20}NOCl$ as the major product.

Deduce the structures of Ephedrine, **P**, **Q** and **R**. Explain your answer. [7]

(c) Draw a labelled diagram to show how benzaldehyde can be synthesised from phenylmethanol in a laboratory.



phenylmethanol



benzaldehyde

[3]

[Total: 20]