Name		Index Number	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY

Higher 2

9729/02

Paper 2   Structured Questions

25 August 2021
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS CAREFULLY

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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

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

For Examiner's Use	
Question no.	**Marks**
1	/ 15
2	/ 15
3	/ 12
4	/ 5
5	/ 19
6	/ 9
Presentation of answers	
TOTAL	/ 75

This document consists of **25** printed pages and **1** blank page.

ANGLO-CHINESE JUNIOR COLLEGE
Department of Chemistry

[Turn over

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1   Hydrobromic acid, HBr, is one of the strongest mineral acids known and is even stronger than hydrochloric acid. Both the industrial and laboratory syntheses of HBr are well documented due to the usefulness of HBr in many chemical reactions.

(a) The primary industrial preparation of HBr involves the platinum-catalysed reaction between hydrogen and bromine at temperatures between 450 K to 700 K.

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$
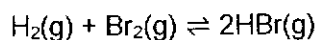
The reaction was carried out in a 250 m^3 vessel at 334 °C.

(i) Calculate the amount of HBr present at equilibrium, given that the equilibrium partial pressure of HBr is 2 atm.

PV = nRT

$n = \dfrac{PV}{RT}$

$n = \dfrac{(2 \times 101325)(250)}{8.31 \times 607}$

$n = 1.00 \times 10^4$ mol   [1]

(ii) At 334 °C, the equilibrium constant, K_p, for the above reaction is 2.50.
Write the expression for the equilibrium constant, K_p, for the above reaction.

$K_p = \dfrac{(P_{HBr})^2}{P_{H_2} P_{Br_2}}$ [1]

(iii) At equilibrium, the number of hydrogen molecules is ten times that of bromine molecules.

Calculate the amount of bromine present at equilibrium.

Let x be the number of moles of Br_2.
Number of moles of H_2 = 10x

$K_p = \dfrac{(P_{HBr})^2}{P_{H_2} P_{Br_2}} = \dfrac{(1 \times 10^4)^2}{(10x)(x)} = 2.50$

$x = 2.00 \times 10^3$ mol   [2]

(iv) Given that the equilibrium in (a) was established using hydrogen and bromine only, determine the mass of bromine (in kg) that was used.
Since only hydrogen and bromine were present in the vessel in the beginning, all the hydrogen bromide formed must have come from Br_2 initially.

Initial no. of moles of Br_2
= No. of moles of Br_2 at equilibrium + ½ x no. of moles of HBr
= 2 x 10^3 + ½ x (1.00 x 10^4)
= 7.00 x 10^3 mol

Mass of Br_2 = 7.00 x 10^3 x 79.9 x 2
                = 1118 kg ≈ 1120 kg   [2]

(v) Predict, with explanation, the effect on the equilibrium position if the volume was decreased at constant temperature.

In this reaction, there is **no change in the number of gaseous molecules** when the reactants form the products. Hence, changes of pressure have **no effect on the position of the equilibrium**. [1]

(b) The preparation of the acid, HBr, in the laboratory can be carried out by the reaction between bromine, sulfur dioxide and water **only**. The only by-product formed is also a strong acid.

(i) Write the equation for the above laboratory preparation of HBr.

$Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$ [1]

(ii) When concentrated solutions of the two products formed in the above preparation react with each other, Br_2 is regenerated.

State and explain the type of reaction that HBr undergoes.

Oxidation

Oxidation state of Br changes from -1 in HBr to 0 in Br_2.

[2]

(c) Inter and intramolecular bondings respectively can explain the trends in the volatility and thermal stability of the hydrogen halides.

(i) State and explain the trend in the volatility of hydrogen halides from HF to HI.

HC*l* to HI molecules: **Decreasing volatility from HC*l* to HBr to HI**
HF molecules: HF boiling point is exceptionally high. **Volatility lowest**.

HC*l* to HI molecules: As the **electron cloud size of halogen atom increases from C*l* to Br to I**, there is **greater ease of distortion/polarisation of the electron cloud of HX** leading to **stronger instantaneous dipole-induced dipole interactions** between the molecules. As the amount of energy required to overcome the forces increases, volatility decreases down the group.

HF molecules: Due to **hydrogen bonding** between HF molecules, HF has an exceptionally low volatility. [3]

(ii) State and explain the trend in the relative thermal stabilities of hydrogen halides from HF to HI.

Thermal stability of the halides decreases down the group as H—X bond energy/bond strength decreases.
As the size of halogen atom increases, its p orbitals become more diffused and overlap less effectively with the s orbital of the hydrogen atom resulting in longer and thus weaker H-X covalent bonds.

[2]

[Total: 15]

2 This question is about nitrogen and its oxides.

(a) **(i)** N^{3-} is *isoelectronic* with F^- and Na^+.

Define the term *isoelectronic*.

Same number of electrons [1]

(ii) Sketch a graph of the successive ionisation energies of all the electrons of a nitrogen atom.
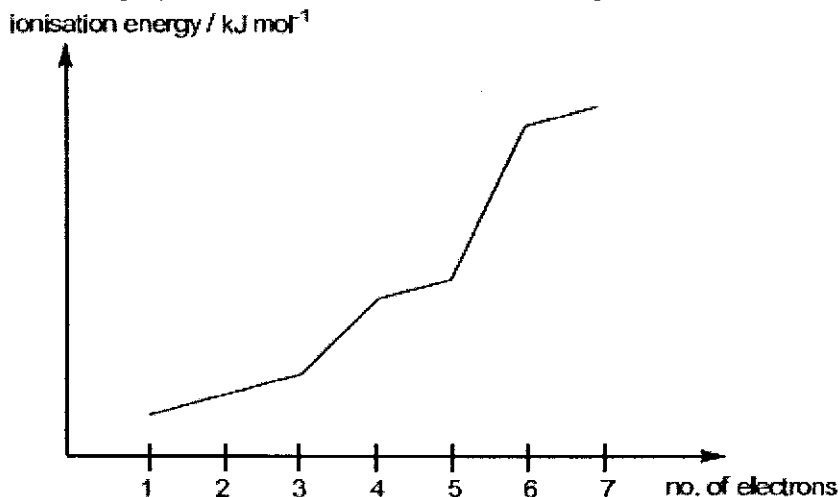
[2]

(iii) State and explain how the ionic radius of N^{3-} compares to that of P^{3-}.
Ionic radius of N^{3-} is smaller than P^{3-}.
P^{3-}: valence electrons are further away from the nucleus due to **increase in number of principal quantum shell**.
OR The valence electrons experiences weaker nuclear attraction due to **additional screening effect**.
Therefore, P^{3-} has a larger ionic radius. [2]

(b) N_2O_3 is a pale blue solid at very low temperatures. As the temperature is raised, N_2O_3 dissociates to form colourless nitrogen monoxide gas, NO and brown nitrogen dioxide gas, NO_2. The interesting feature of this reaction is that both products are molecular radicals, each with an unpaired electron on the nitrogen atom.

$$N_2O_3(s) \rightleftharpoons NO(g) + NO_2(g)$$

Draw the dot-and-cross diagram for N_2O_3, stating the shapes and bond angles about each N atom.

Bent about N, 118°
Trigonal planar about N, 120°
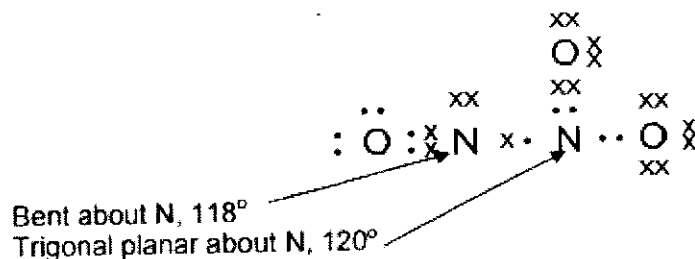
[3]

(c) NO is an air pollutant produced by cigarette smoke, automobile engines and power plants. It reacts with oxygen to form $NO_2(g)$.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$
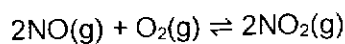
The kinetics of the reaction was studied and the following results were obtained.

experiment	initial concentrations / mol dm^{-3}		initial rate of formation of NO_2 / mol dm^{-3} s^{-1}
	[NO]	[O_2]	
1	0.001	0.001	7.0×10^{-6}
2	0.001	0.002	1.4×10^{-5}
3	0.002	0.003	8.4×10^{-5}

Use this data to deduce the order of reaction with respect to each of the reactants. Hence, write the rate equation for the reaction and calculate a value for the rate constant.

Comparing Experiment 1 and 2 where [NO] is constant.
When [O_2] doubles, the rate doubles
$\Rightarrow$ 1st order w.r.t O_2

Comparing Experiment 1 and 3,
$$\frac{8.4 \times 10^{-5}}{7 \times 10^{-6}} = \frac{(0.002)^m(0.003)}{(0.001)^m(0.001)}$$
$m = 2$

Order of reaction w.r.t NO $\Rightarrow$ 2nd order.

Rate equation: Rate = $k[NO]^2 [O_2]$

Using values for any experiment,
$k = 7000 \ mol^{-2}dm^6s^{-1}$

[4]

(d) In Singapore, all petrol-driven vehicles are fitted with three-way catalytic converters which convert harmful emissions of NO and NO_2 to less harmful products. A mixture of transition metals palladium, platinum and rhodium are used as catalysts.

Explain, with the aid of a Maxwell-Boltzman distribution curve, why a catalysed reaction has a higher rate of reaction than an uncatalysed reaction.
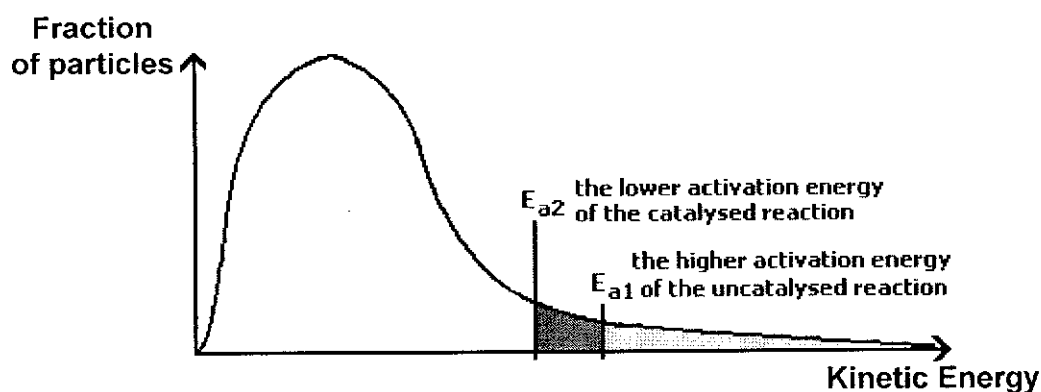
The catalyst increases reaction rate by providing an **alternative pathway with a lower activation energy.**
The **proportion of particles with kinetic energy** $\geq E_a$ **increases.**
This leads to an increase in the **frequency of effective collisions** between reactant particles. Hence the rate of reaction increases.

[3]

[Total: 15]

3   Phosgene with the formula $COCl_2$ is an important building block for many organic products. However it is a very poisonous gas and was used as a chemical weapon during the First World War.
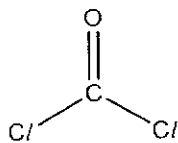
Phosgene

(a)   Phosgene is rapidly hydrolysed by water.

Complete the figure below to suggest a likely mechanism for this hydrolysis, showing the following:
   • **Displayed structures** of the intermediates in steps 1, 2 and 3.
   • All relevant charges.
   • Relevant lone pairs and movement of electron pairs using curly arrows.
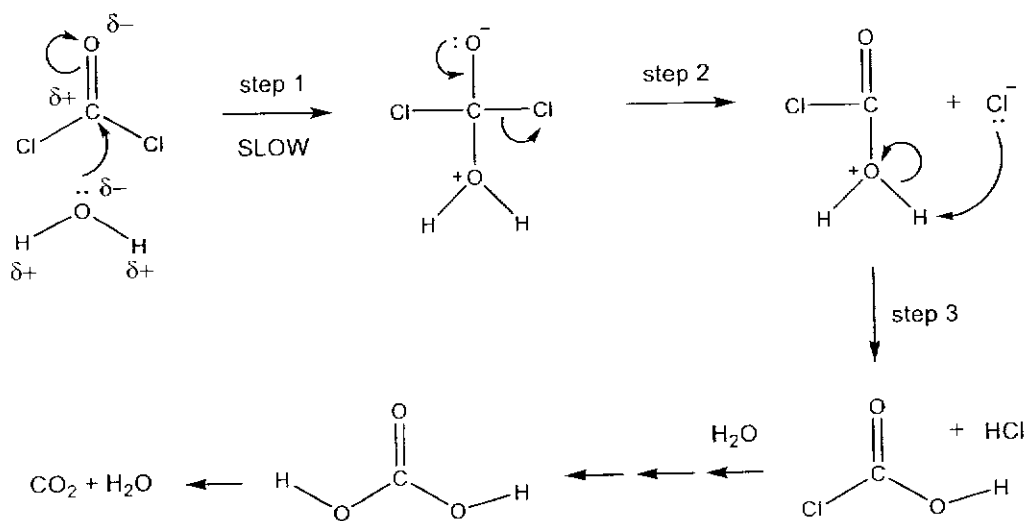
Figure 1

[4]

(b) Urea with the formula $CO(NH_2)_2$ is mainly used as a nitrogen-releasing fertilizer. It is also used to make skin care products that promote rehydration of the skin.

Urea can be made in the lab by reacting phosgene with excess ammonia.
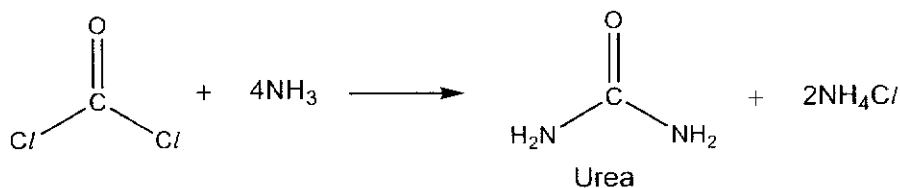
(i) State the type of reaction between phosgene and ammonia.

Nucleophilic Addition-Elimination / Condensation

.... [1]

(ii) Explain why urea is neutral in water, but it forms a salt with nitric acid.

Water is a weak acid. It is not strong enough to have acid-base reaction with urea. Nitric acid is a strong acid. It is strong enough to have acid-base reaction with urea.

.... [1]

(c) Explain why succinimide is able to form a salt with aqueous sodium hydroxide, but butyrolactam does not.
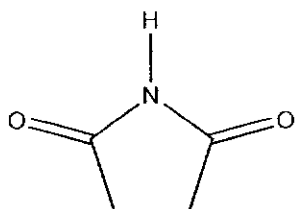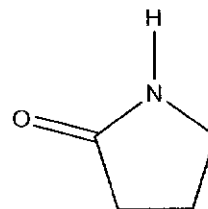
succinimide   butyrolactam

Succinimide has two powerful electron-withdrawing –CO groups that weaken the N–H bond to the extent that it breaks easily. Succinimide is acidic and reacts with NaOH(aq) to form a salt.

Butyrolactam has only one electron-withdrawing –CO group which does not weaken the N–H enough for it to break. Butyrolactam is neutral and does not reacts with NaOH(aq) to form a salt.

[2]

(d) Veronal is a sleep-inducing drug.
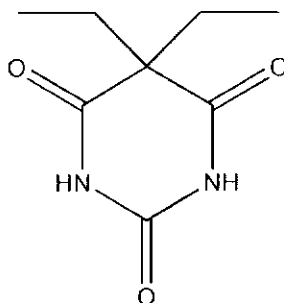
Veronal

Predict all products of hydrolysis of Veronal by aqueous sodium hydroxide.

Na₂CO₃ and NH₃ and

Na_2CO_3 and NH_3 and

[2]
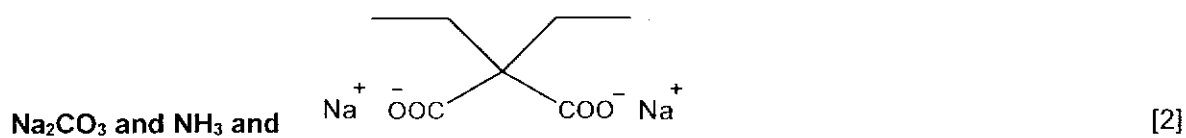
(e) Draw the structures of intermediate **E** and product **F** for the following transformation.

$$ClCH_2COCl \xrightarrow{NH_2CH_2CH_2OH} E \xrightarrow{\text{add Na and warm}} F$$
$$C_4H_7NO_2$$

E

F
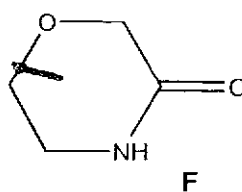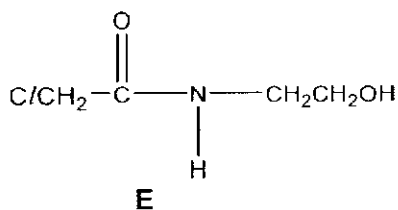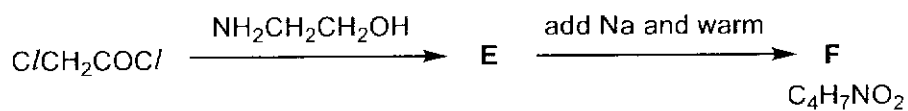
[2]

[Total: 12]

4 The Ellingham diagram is commonly used to show the variation in the Gibbs free energy change, ΔG, of a reaction with temperature. Since enthalpy change and entropy change are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines. The graph showing the relationship between the Gibbs free energy change and the temperature of some oxides, as well as the melting points of some elements, are provided below.

ΔG / kJ mol^{-1}

$2Zn + O_2 \rightarrow 2ZnO$

$2C + O_2 \rightarrow 2CO$

$2Mg + O_2 \rightarrow 2MgO$

temperature / °C
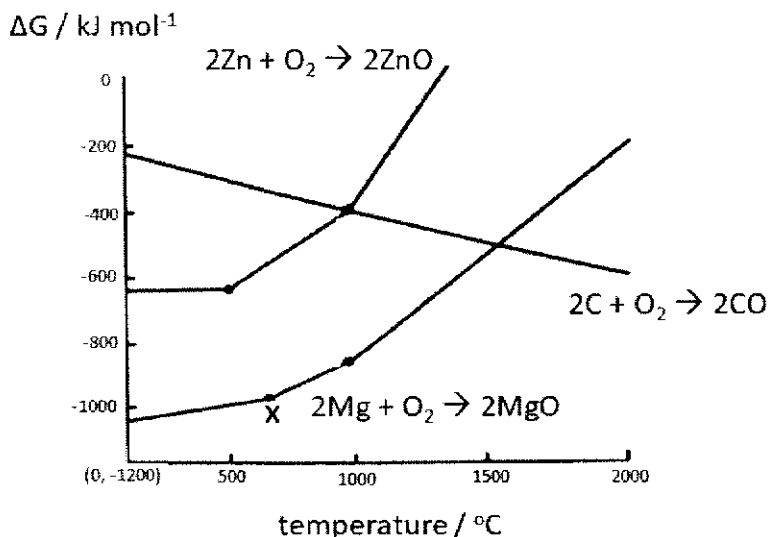
element	melting point / °C
zinc	420
magnesium	650

Table 1

(a) Explain why the gradient for the reaction of $2C + O_2 \rightarrow 2CO$ is negative.

There is an increase in amount of gas and hence the change in entropy is positive.
But as the gradient is $- \Delta S$, therefore the gradient is negative.

[2]

(b) By considering the significance of point **X**, explain why the gradient for the reaction of $2Mg + O_2 \rightarrow 2MgO$ becomes more positive at point **X** as temperature increases.

Instead of starting off as solid magnesium, it starts off as molten/liquid magnesium, as a result the change in entropy becomes greater, hence ΔS becomes more negative, which translates to a more positive gradient.

[1]

(c) Explain how it can be deduced from the Ellingham diagram that below 1000 °C, the following reaction is spontaneous.

$$Zn + CO \rightarrow C + ZnO$$
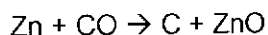
In this temperature range, the ΔG for the Zn-oxygen reaction is more negative, hence it is more spontaneous than the C-oxygen reaction.
As such, Zn will be oxidised to ZnO by CO, while CO itself will be reduced to carbon.

[1]

(d) Estimate the range of temperatures for which the following reaction is spontaneous.

$$MgO + C \rightarrow Mg + CO$$
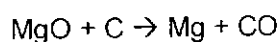
T > 1500 °C

[1]

[Total: 5]

5 Citric acid (molecular formula $C_6H_8O_7$) is an important compound that occurs naturally in citrus fruits like lemons and oranges. It plays a central role in the Krebs cycle, which is a series of chemical reactions in all aerobic organisms to release stored energy. It is a solid at standard conditions.
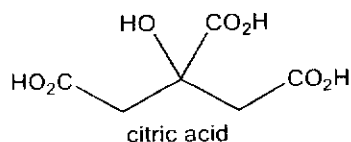
citric acid

(a) Calculate the standard enthalpy change of formation of citric acid using the following data.

	$\Delta H^\ominus$ / kJ mol^{-1}
Standard enthalpy change of combustion of citric acid	−1960
Standard enthalpy change of combustion of hydrogen	−286
Standard enthalpy change of formation of carbon dioxide	−394

For simplicity, you may choose to use the molecular formula of citric acid to represent citric acid.

$$C_6H_8O_7 (s) + 4.5O_2 (g) \rightarrow 4H_2O (l) + 6CO_2 (g)$$

ΔH_f (citric acid)

$6\Delta H_f (CO_2(g)) + 4\Delta H_c (H_2(g))$

$$8O_2 (g) + 6C (s) + 4H_2 (g)$$
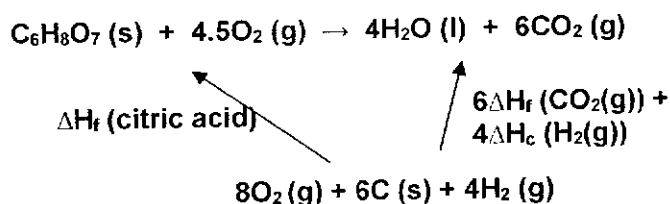
ΔH_f (citric acid) = 1960 − 6(394) − 4(286) = -1550 kJ mol^{-1} (3 s.f.)

[3]

(b) As citric acid is a tricarboxylic acid, it has three pK_a values, denoted by pK_{a1}, pK_{a2} and pK_{a3}, arranged in increasing order.

$$pK_{a1}$$

HO $\quad$ $\boxed{CO_2H}$

HO_2C $\qquad$ CO_2H
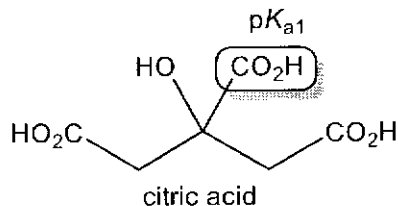
citric acid

Explain why the boxed carboxylic acid group has the lowest pK_a value out of the three carboxylic acids in citric acid.

This carboxylic acid is the closest to the alcohol group.

As alcohol groups are electron-withdrawing, the negative charge of that carboxylate group will be the most dispersed compared to the two other carboxylate groups.

As a result, this carboxylic acid will be the strongest acid out of the three, hence having the lowest pK_a.

[2]

(c) A graph showing the correlation between the composition of the different ionic forms of citric acid (y-axis) and the pH of the solution (x-axis) is shown below.
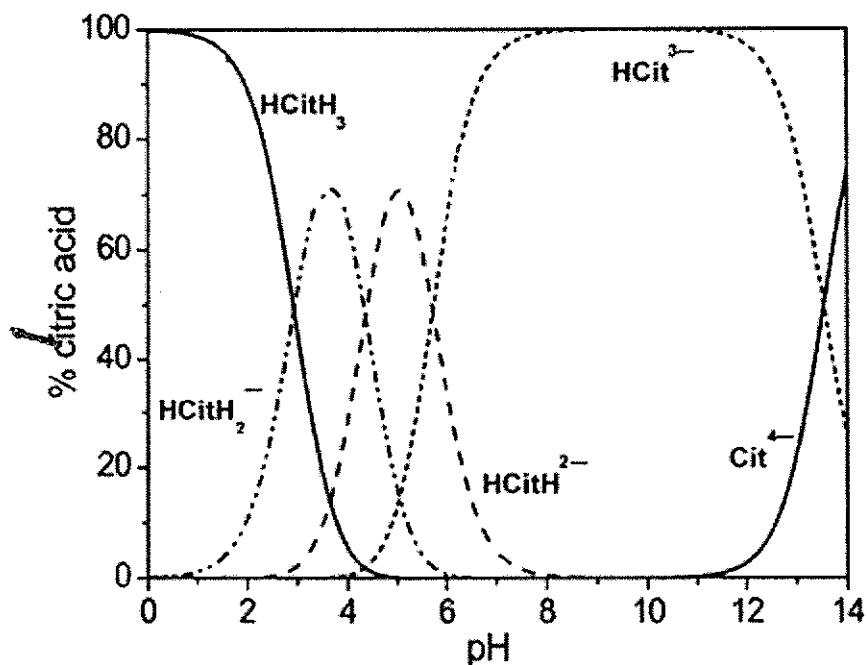
The fully protonated form of citric acid is denoted as "$HCitH_3$", with the first H denoting the alcoholic hydrogen atom. Similarly, the tricarboxylate anion of citric acid is denoted as "$HCit^{3-}$".

(i) Given that pK_{a1} of citric acid is approximately 3.0, estimate the values of pK_{a2} and pK_{a3} from the above graph. You are to show your working clearly on the graph.

pK_{a2} is about 4.1.
pK_{a3} is about 6.0.

[2]

(ii) Assuming that citric acid is a weak monobasic acid, calculate the pH of a 0.120 mol dm^{-3} solution of citric acid.

$pH = - \log [\text{sqrt}(0.120 \text{ times } 10^{-3.0})] = 1.50 - \frac{1}{2} \log 0.12 = 1.96$

[1]

Citric acid and its salts are used to make buffers of varying pH values.

(iii) Representing citric acid as "$HCitH_3$" and monosodium citrate as "$NaHCitH_2$", write an equation to illustrate how a solution containing both species maintains fairly constant pH when small amounts of NaOH is added to it.

$HCitH_3 + OH^- \rightarrow HCitH_2^- + H_2O$
or
$HCitH_3 + NaOH \rightarrow NaHCitH_2 + H_2O$
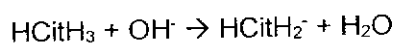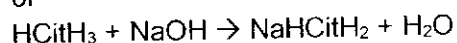
[1]

(iv) A solution was prepared by dissolving 3.84 g of solid citric acid in 1 dm^3 of water.

Calculate the volume of 0.500 mol dm^{-3} NaOH(aq) that needs to be added to the above solution to prepare a buffer of pH 2.7.

[citric acid] = 0.0200 mol dm^{-3}

$2.7 = 3.0 + \log [x/(0.0200 - x)]$
$0.3 = \log [(0.0200 - x)/x]$
$\rightarrow x = 6.677 \times 10^{-3}$
Volume of NaOH required = $(6.677 \times 10^{-3}/0.500)$ dm^3 = 13.4 cm^3

[3]

(d) Citric acid is used as the starting material for various other organic compounds, whether through metabolism or chemical synthesis.

(i) Isocitric acid is a constitutional isomer of citric acid. It exists in more than two stereoisomeric forms.

Equal volumes of carbon dioxide gas are obtained when excess sodium hydrogencarbonate is added to the same amount of each acid. Isocitric acid can be made by reacting a suitable aldehyde with HCN, followed by heating the product in aqueous sulfuric acid.

Give the structural formula of isocitric acid.
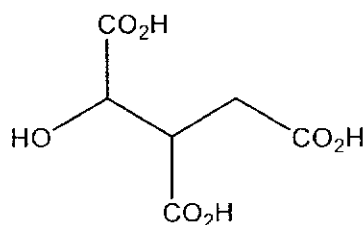
[1]

J, K, K' and L can be synthesised from citric acid through the synthetic route shown below.
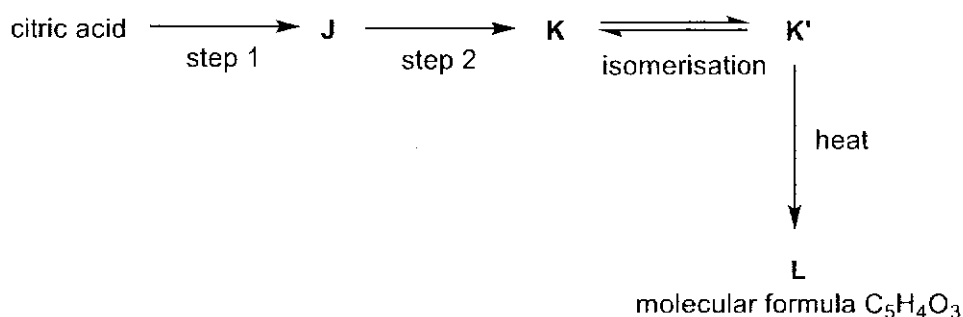
(ii) Compound **J** has relative molecular mass of 174.0. The **mass ratio** of carbon to hydrogen to oxygen is 12:1:16 in **J**.

Find the molecular formula of **J**.

$C_6H_6O_6$ [1]

(iii) Both compounds **J** and **K** can be reacted with hot acidified $KMnO_4$ to give 2-oxobutanedioic acid, $HO_2CCOCH_2CO_2H$.

Deduce the structural formula of **J**. State the reagents and conditions used in step 1.
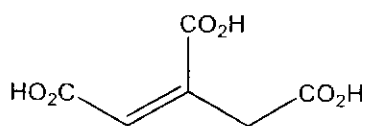
excess conc. H_2SO_4 & heat

[2]

(iv) Compounds **K'** and **K** are a pair of positional isomers. They have a molecular formula of $C_5H_6O_4$. While **K'** can exhibit cis-trans isomerism, **K** does not show any form of stereoisomerism. Only the *cis*- form of **K'** forms **L**, which is a neutral compound.

Find the structural formulae of **K**, **K'** and **L**.
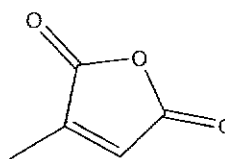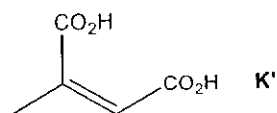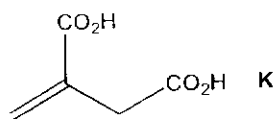
[3]

[Total: 19]

6 Microorganisms synthesise and secrete organic molecules called siderophores to increase the total concentration of available iron in the surrounding medium.

(a) Bacillibactin is a siderophore produced by bacteria.
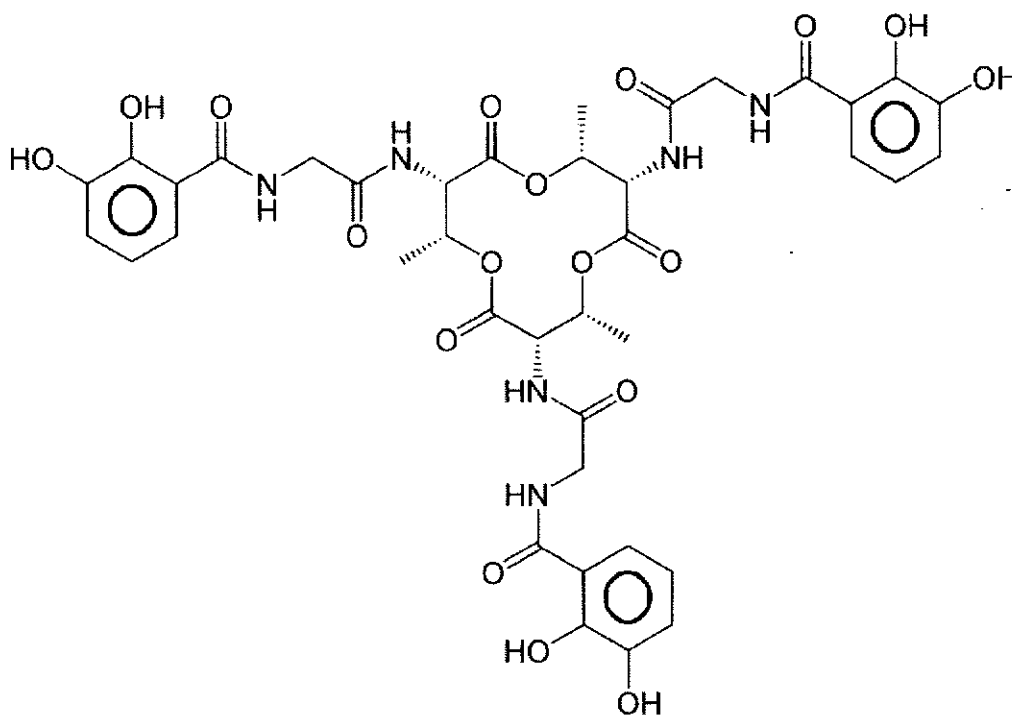
Bacillibactin

(i) Bacillibactin binds to iron(III) ions via its oxygen atoms. This process facilitates the transportation of iron(III) ions into the interior of a cell.

Suggest what bonds are formed during this process and why iron(III) does not bind to nitrogen atoms in bacillibactin compounds.

Ion-dipole interactions/Dative bonding
Because the lone pair on the nitrogen atoms are delocalised into the C=O group hence they are incapable of hydrogen bonding.

[2]

(ii) Draw the structures of the two α-amino acids formed when bacillibactin is hydrolysed.

and H_2NCH_2COOH
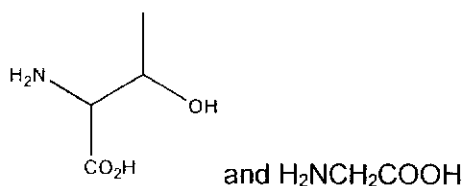
[2]

(b) Tyrocidine was the first commercially available antibiotic. Like bacillibactin, tyrocidine is also produced by bacteria. Tyrocidine has been found to be toxic towards human blood and reproductive cells.
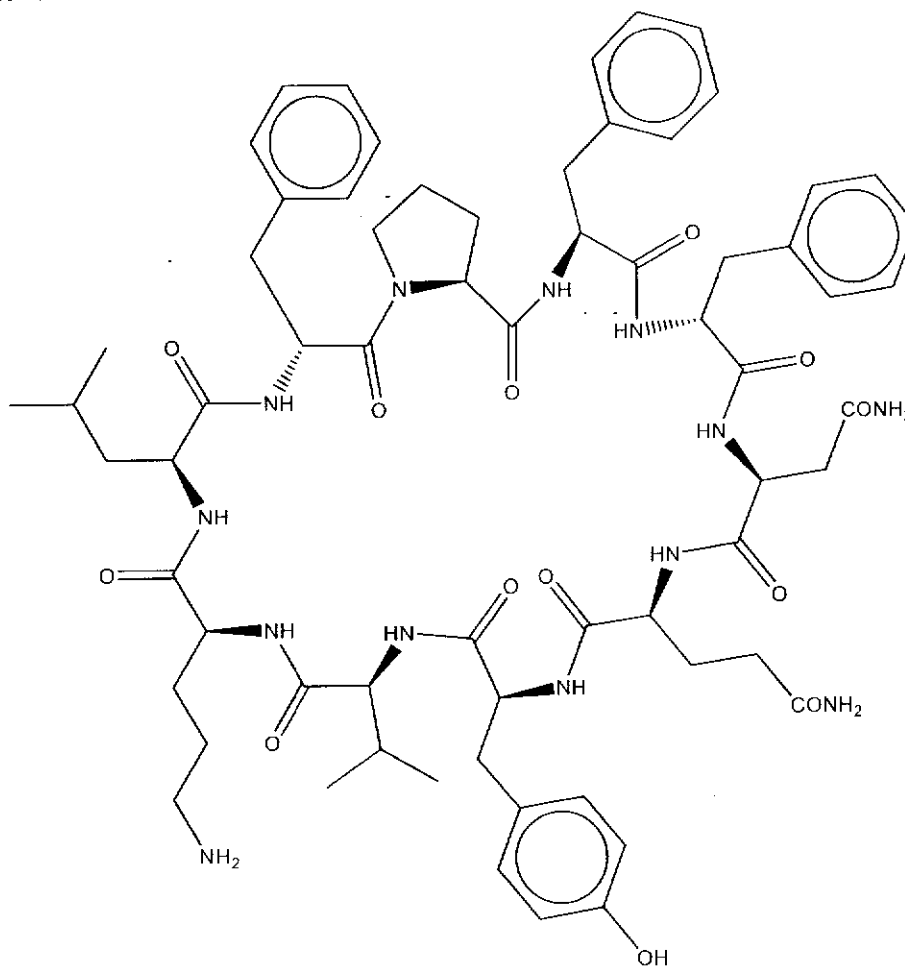
Tyrocidin

(i) Amongst the many amino acids that make up tyrocidine, there is one pair of amino acids where the side chains have the same functional group.

Draw one amino acid from the pair in which the side chain is polar.

Either
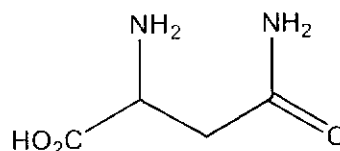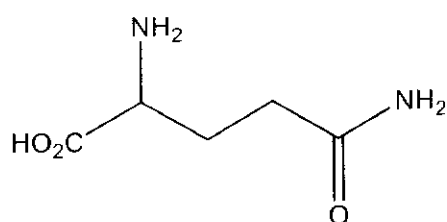
[1]

Ornithine is one of the α-amino acids found in tyrocidine.
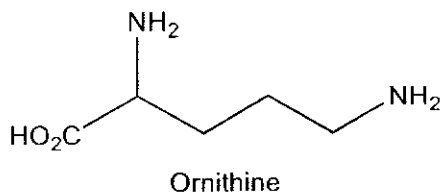
Ornithine

The three pK_a values of ornithine are 2.17 (the carboxylic acid), 9.04 (the α-amino group) and 12.48.

(ii) Draw the zwitterionic form of ornithine.

[1]
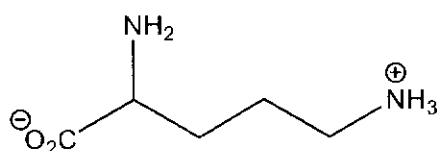
(iii) Calculate the pH at which ornithine exists solely in its zwitterionic form.

pH = ½ (9.04 + 12.48) = 10.76

[1]

(iv) Eflornithine is a drug that is structurally similar to ornithine, as its name implies. It is used to treat sleeping sickness and excessive hair growth on the face in women.
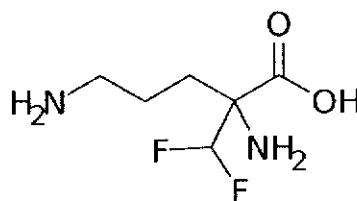
Eflornithine

Extensive studies have been done on the metabolic products of eflornithine. It has been suspected that **Z** is the main metabolic product of eflornithine.

Z
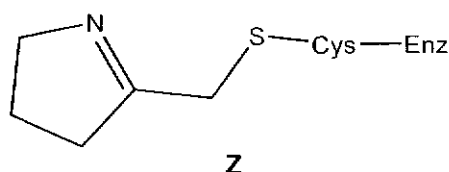
To confirm that **Z** is indeed formed from the metabolism of eflornithine, chemists conducted two tests on it and studied the products, **Z'** and **Z"**.

For the two tests, you may assume that the $-CH_2-S-Cys-Enz$ is inert.

Z' is obtained by reacting **Z** with $NaBH_4$. The relative molecular mass of **Z'** is 2 units larger than that of **Z**. The relative molecular mass of **Z''** is 4 units smaller than that of **Z'**.

Suggest the structural formulae of **Z'** and **Z''**.
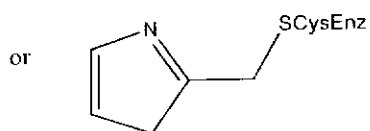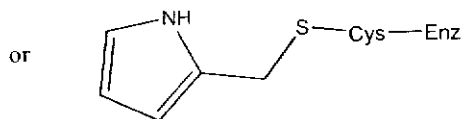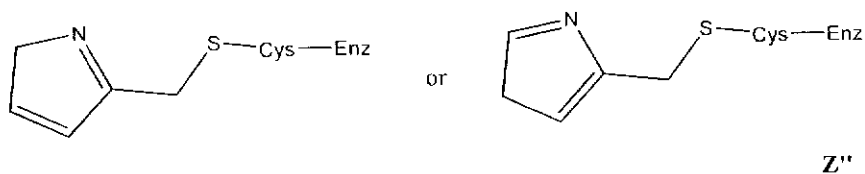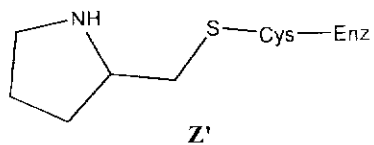
Z'

or

Z''

or

or

[2]
[Total: 9]

JC2 H2 Prelim 2021

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/03

Paper 3   Free Response

30 August 2021
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS CAREFULLY

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer **all** questions in the spaces provided on the Question Paper.

Section A   Answer all the questions.

Section B   Answer one question.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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

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

Section	Question No.	For Examiner's Use Marks
A	1	
A	2	
A	3	
A	4	
B		
Presentation of answers		
	TOTAL: 80 m	

This document consists of **31** printed pages and **1** blank page.

Section A
Answer **all** the questions in this section.

1 (a) Describe the reactions, if any, when separate samples of the oxides Na_2O, Al_2O_3 and P_4O_{10} are added to water. Write equations where appropriate and suggest the pH of any aqueous solution formed.

[4]

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(b) Phosphorus pentachloride, PCl_5, is a white, moisture-sensitive solid. It is a dangerous substance as it reacts violently with water.

(i) PCl_5 reacts completely with a large excess of water to form phosphoric acid, H_3PO_4. Write a balanced equation for this reaction. State the approximate pH value of the resulting solution.

[2]

The structural formula of phosphoric acid is shown below.
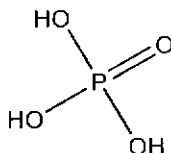
Two molecules of phosphoric acid can undergo a condensation reaction producing diphosphoric acid, $H_4P_2O_7$, and water. The reaction involves an –OH group from each H_3PO_4 molecule forming an oxygen bridge between the two phosphoric acid units.

(ii) Draw the structure of diphosphoric acid.

[1]

(iii) This condensation reaction may continue to give triphosphoric acid, $H_5P_3O_{10}$, and tetraphosphoric acid. Give the molecular formula of tetraphosphoric acid.

[1]

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(c) Phosphorus pentachloride can be used to convert alcohols into chloroalkanes. For example,

$$\wedge\!\!\text{OH} \; + \; PCl_5 \quad \longrightarrow \quad \wedge\!\!Cl \; + \; POCl_3 \; + \; HCl$$

Phosphoryl chloride, $POCl_3$, is formed as a side-product.

(i) The structure of $POCl_3$ is shown below.
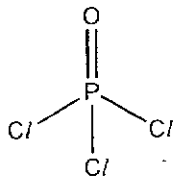
As there are four bond pairs and zero lone pairs on the phosphorus atom, VSEPR theory predicts that Cl-P-Cl bond angle is 109.5°. However, based on experimental evidence, the actual bond angle is only 103°. Suggest a reason why the actual bond angle is smaller than the predicted one.

[1]

(ii) Phosphoryl chloride can be synthesised by reacting PCl_5 with ethanedioic acid in equimolar amounts. Two moles of HCl is formed per mole of PCl_5, together with two other gases, one polar, the other non-polar. Identify the polar gas and the non-polar gas and write a balanced equation of this reaction.

[3]

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(c) (iii) The Vilsmeier–Haack reaction involves the use of phosphoryl chloride and a substituted amide to produce an aryl aldehyde or aryl ketone. An example of the Vilsmeier–Haack reaction is shown below.
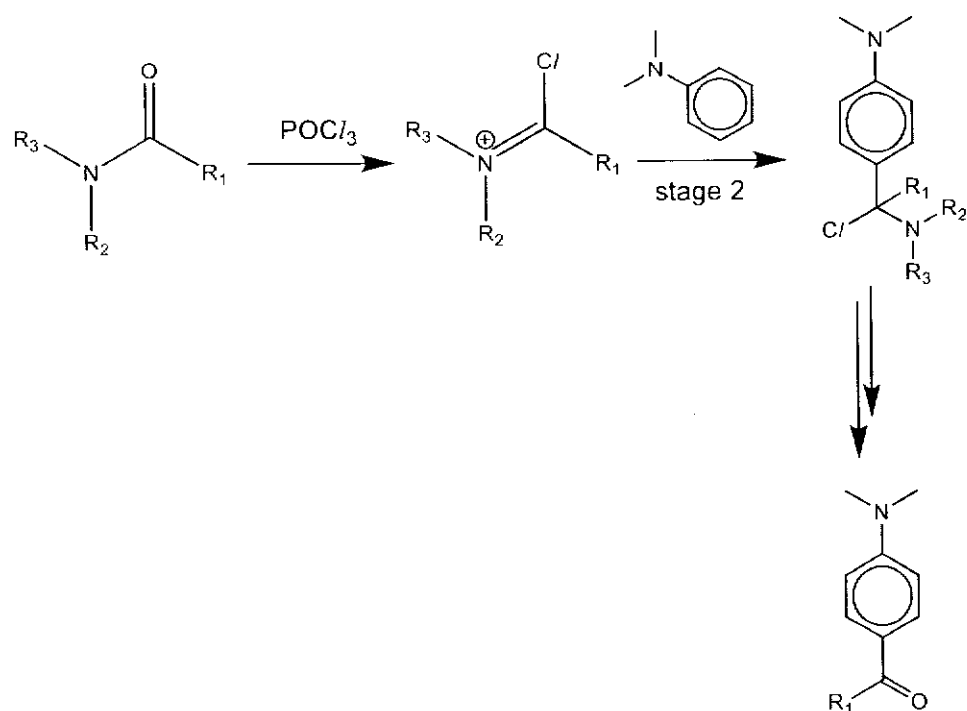
The mechanism of stage 2 consists of two steps. Using curly arrows and showing all relevant charges, propose the mechanism for stage 2.

[3]

[Total: 15]

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2 Magnesium reacts with pure nitrogen to form magnesium nitride, Mg_3N_2, which can be considered as a possible intermediate in the 'fixing' of nitrogen to make ammonia-based fertilisers.

$$3Mg + N_2 \longrightarrow Mg_3N_2$$
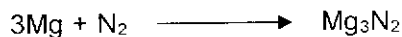
Nitrogen is an essential macronutrient needed by all plants to thrive. It is an important component of many structural, genetic and metabolic compounds in plant cells.

(a) When water is added to Mg_3N_2, a colourless gas which turns moist red litmus paper blue is produced.

This gas reacts with chlorate(I) ion, ClO^- in a 2:1 mole ratio to form a colourless liquid A with empirical formula NH_2. The reaction of A with sulfuric acid in a 1:1 mole ratio produces a salt B, $O_4N_2SH_6$, which contains one cation and one anion per formula unit.

Explain the role of the nitride ion when water was added to Mg_3N_2.

Deduce the structures of compounds A and B.

[3]

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(b) Another type of ammonia-based fertiliser contains urea, NH_2CONH_2, and has a large percentage by mass of nitrogen.

The nitrogen content of a urea-containing fertiliser can be determined by boiling a sample of known mass of the fertiliser with an excess of $NaOH(aq)$, absorbing the gas evolved in water, and titrating the resulting aqueous solution with hydrochloric acid of a known concentration.

$$NH_2CONH_2 + 2OH^- \rightarrow 2NH_3 + CO_3^{2-}$$

$$NH_3 + HCl \rightarrow NH_4Cl$$
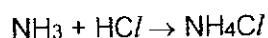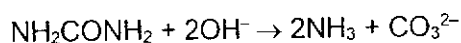
When 0.100 g of this fertiliser was subjected to this procedure, the resulting solution of ammonia required 15.0 cm^3 of 0.200 mol dm^{-3} HCl for complete neutralisation.

(i) Calculate the percentage by mass of nitrogen in the urea-containing fertiliser.
[2]

(ii) Hydrogen peroxide-urea (UHP) is a white crystalline solid which dissolves in water to give free hydrogen peroxide, H_2O_2. It offers a higher stability and better controllability than liquid hydrogen peroxide when used as an oxidising agent. UHP is used by dentists as a teeth-whitening agent.

A molecule of UHP is made up of one molecule each of hydrogen peroxide and urea held together by hydrogen bonding in a seven-membered ring. Draw a fully labelled diagram of a molecule of UHP.
[2]

(c) Ammonia is used in the synthesis of **F** from **D** as shown below.
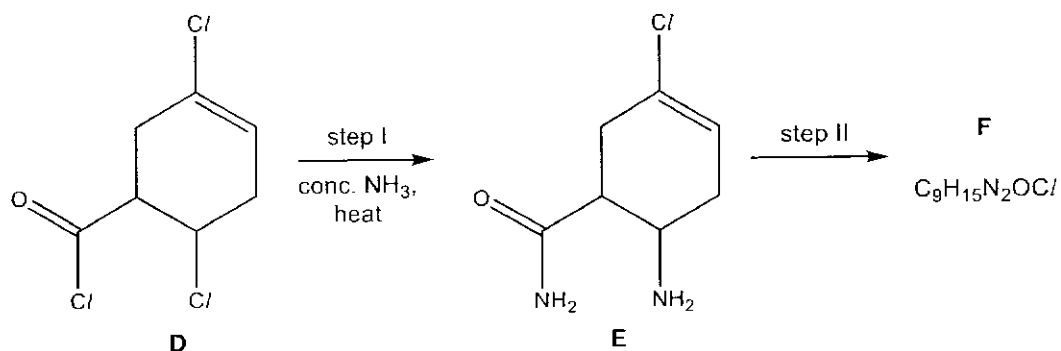
(i) Give the reagents and conditions for step II and hence suggest the structure of **F**.

[2]

(ii) One of the three chlorine atoms in **D** is inert towards hot concentrated NH_3. Explain why this is so.

[1]

(iii) Suggest a simple chemical test to differentiate between **D** and **E**. State the observations.

[2]

[Total: 12]

3 Calcium ethanedioate (CaC_2O_4) is the primary constituent of the common kidney stones, and is believed to form due to inappropriate diets.

Napoleon Bonaparte and Napoleon III were suffering from bladder stones and had severe symptoms, probably affecting their military decisions. Today, historians still debate over what might have happened in his Russian campaign in 1812 if Napoleon Bonaparte had not had a bladder stone. Similarly, the course of European history might have changed if Napoleon III was treated with modern surgical techniques during the Franco-Prussian War of 1870.

(a) The value of the solubility product of calcium ethanedioate is 2.32×10^{-9} at 25 °C.

  (i) Write an expression for the solubility product of calcium ethanedioate and state its units.

[2]

  (ii) Calculate the solubility of calcium ethanedioate in pure water at 25 °C.

[1]

  (iii) Calculate the solubility of calcium ethanedioate in a 0.30 mol dm^{-3} of calcium nitrate at 25 °C.

[2]

(b) Calcium ethanedioate decomposes at a higher temperature than magnesium ethanedioate. Explain this difference in their decomposition temperatures.

[2]

　　　　　9729/03/Prelim/2021　　　　　**[Turn over**

(c) Thermogravimetric analysis (TGA) is a technique where the mass of a sample in a controlled atmosphere is recorded as a function of temperature as the temperature of the sample is increased.

A sample of lithium pentaborate pentahydrate ($LiB_5O_8.5H_2O$) was subject to TGA and the graph obtained is shown below. The relative molecular mass of $LiB_5O_8.5H_2O$ is 278.9.
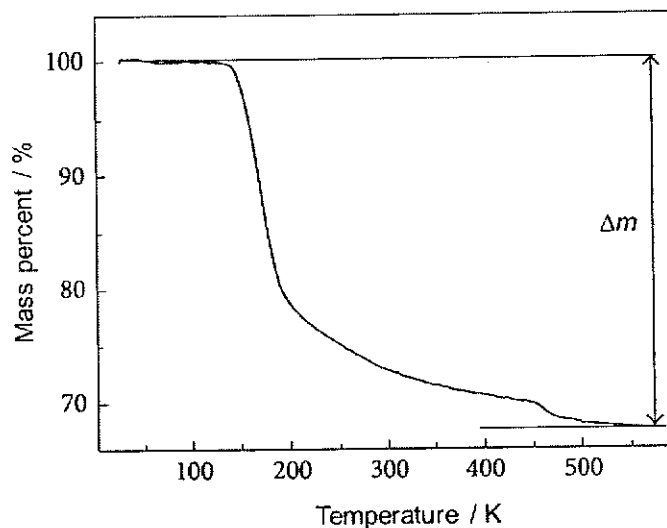
(i) Suggest an explanation, supported with relevant calculations, for the loss in mass (Δm) of $LiB_5O_8.5H_2O$ observed in the graph.

[2]

(ii) The sample of $LiB_5O_8.5H_2O$ used in **(i)** was synthesised from Li_2O, B_2O_3 and H_2O in the laboratory. Deduce the molar ratio of $Li_2O : B_2O_3 : H_2O$ used to produce a pure sample of $LiB_5O_8.5H_2O$.

[1]

(iii) Aqueous sodium hydroxide can be used to react with B_2O_3 to determine its actual amount in the sample.

Given that B_2O_3 and Al_2O_3 have similar reactions with aqueous sodium hydroxide under appropriate conditions, write a balanced equation for the reaction between B_2O_3 and aqueous sodium hydroxide.

[1]

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(d) Lithium peroxide, Li_2O_2, is a white solid.

(i) Li_2O_2 has been used to remove CO_2 from the atmosphere in spacecraft. It reacts with carbon dioxide according to the equation shown below. This is a disproportionation reaction.

$$2Li_2O_2(s) + 2CO_2(g) \rightarrow 2Li_2CO_3(s) + O_2(g)$$
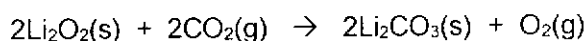
Explain the term *disproportionation* with reference to the changes in the oxidation numbers of the appropriate element in the above reaction.

[2]

(ii) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$ is given by the following equation.

$$\Delta G^{\ominus}_{ppt} = 2.303 \, RT \, \log_{10} K_{sp}$$

The value of the K_{sp} of lithium carbonate is 8.15×10^{-4} at 298 K.

Use the equation given above to deduce if lithium carbonate is soluble in water at 298 K. Explain your answer.

[2]

[Total: 15]

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4 The use of the *Data Booklet* is relevant for this part.

A quinhydrone half-cell comprises a platinum electrode immersed in a solution which is prepared by dissolving a mixture of quinone and hydroquinone in acid.

quinone   hydroquinone
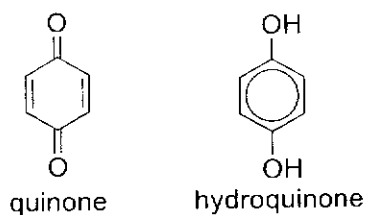
The standard reduction potential, $E^\ominus$, of the quinone-hydroquinone system is +0.70 V.

An electrochemical cell, which consists of a standard quinone-hydroquinone half-cell and a standard Ag^+/Ag half-cell, was set up.
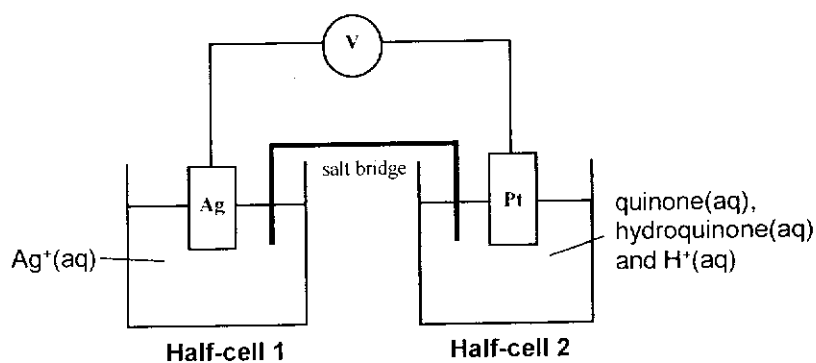
(a) **(i)** Write the half-equations of the reactions which occur at the cathode and anode.
[2]

(ii) State the reading on the voltmeter, when the above electrochemical cell is set up.
[1]

(a) (iii) Calculate the standard Gibbs' free energy change of this electrochemical cell.

[2]

(iv) Some aqueous ammonia was added in excess to the Ag^+/Ag half-cell. Predict the effect of this change on the reading on the voltmeter. You are to include the structural formula of the complex formed in your answer.

[4]

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(b) Blattellaquinone is a sex pheromone of the German cockroach. It is secreted by females to attract male cockroaches.

The molecular formula of blattellaquinone is $C_{12}H_{14}O_4$. As the suffix suggests, it is a quinone derivative.

On reaction with lithium aluminium hydride in dry ether, 3-methylbutan-1-ol and **Q** (molecular formula $C_7H_{10}O_3$) are formed.

Using the structures on page 14, deduce the structures of blattellaquinone and **Q**.

[2]

(c) For alkenes to be useful starting materials for synthesis of organic chemicals, it is important to synthesise alkenes with the carbon-carbon double bonds at specific positions with no ambiguity.

In 1954, a German chemist Georg Wittig reported a method of synthesising alkenes from ketones and aldehydes using a reagent known as triphenyl phosphonium ylide, $Ph_3P=CRR'$, which is also known as the Wittig reagent. The phenyl group is abbreviated as 'Ph'.

triphenyl phosphonium ylide
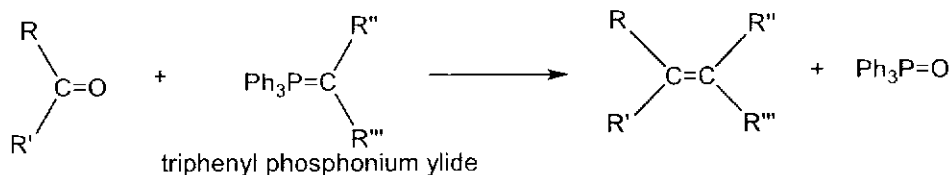
Wittig reagents can be produced by the reaction of alkyl halides with triphenylphosphine in the following two-step processes.

triphenyl phosphonium ylide
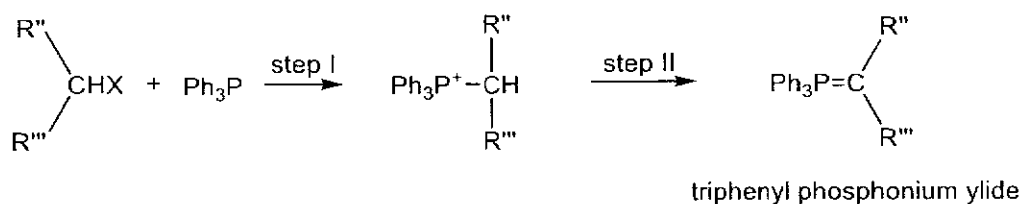
(i) Identify the types of reaction in steps I and II.

[2]

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(c) **(ii)** The conversion of hex-3-ene to 3,4-diethylhexa-2,4-diene involves three steps. Steps I and II are oxidation reactions. A Wittig reagent is used in one of the steps.

hex-3-ene

Step I ⟶ C Step II ⟶ D

Step III

3,4-diethylhexa-2,4-diene
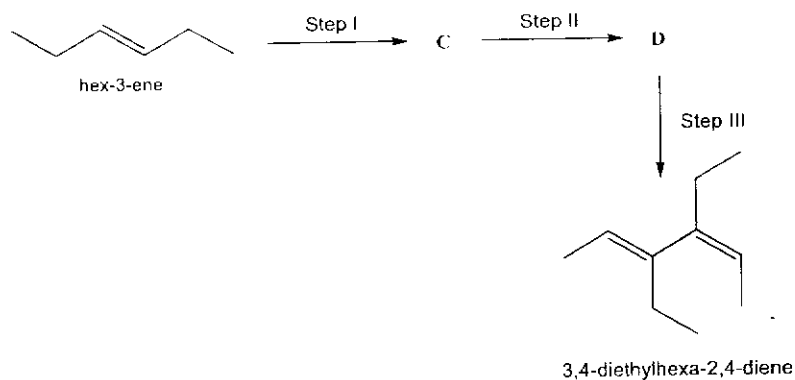
Deduce the structures of the intermediates **C** and **D** and the Wittig reagent involved.

[3]

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(iii) State the number of stereoisomers 3,4-diethylhexa-2,4-diene exists in.   [1]

(iv) Draw the skeletal formula of the constitutional isomer of hex-3-ene in which all the carbon atoms are sp^3 hybridised, and forms only one mono-chlorinated product on reaction with limited chlorine in the presence of ultraviolet light.

[1]

[Total: 18]

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Section B
Answer **one** question from this section.

5 Copper was the first metal to be worked by man, along with gold and meteoritic iron. This is because these metals were among the few that can be found in a relatively pure form in nature.

(a) Write the electronic configuration of the outermost shell of Cu^+.

[1]

(b) An example of a copper-containing enzyme is superoxide dismutase (SOD).

It aids in the disproportionation of the strongly oxidising superoxide ion, O_2^- to oxygen and hydrogen peroxide, thereby protecting the body from harm.

$$2O_2^- + 2H^+ \xrightarrow{\text{SOD}} O_2 + H_2O_2$$
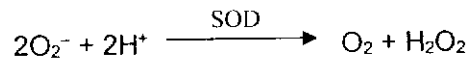
The activity of SOD hinges on the active site Cu^{2+} ion which can be reduced to Cu^+.

By referring to the following $E^\ominus$ data, suggest a mechanism for the catalysis of the disproportionation of O_2^- by SOD.

	$E^\ominus / V$
$O_2 + e^- \rightleftharpoons O_2^-$	−0.33
$O_2^- + e^- + 2H^+ \rightleftharpoons H_2O_2$	+0.89
$SOD{-}Cu^{2+} + e^- \rightleftharpoons SOD{-}Cu^+$	+0.42

You may represent the oxidised and reduced forms of the enzyme as $SOD{-}Cu^{2+}$ and $SOD{-}Cu^+$.

[3]

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(c) Another copper–containing enzyme is tyrosinase which catalyses the oxidation of phenols to quinones. **X** and **Y** are two intermediate species in the catalytic cycle of tyrosinase. The conversion of **X** to **Y** involves an electrophilic substitution mechanism.

1,2-benzoquinone, a quinone
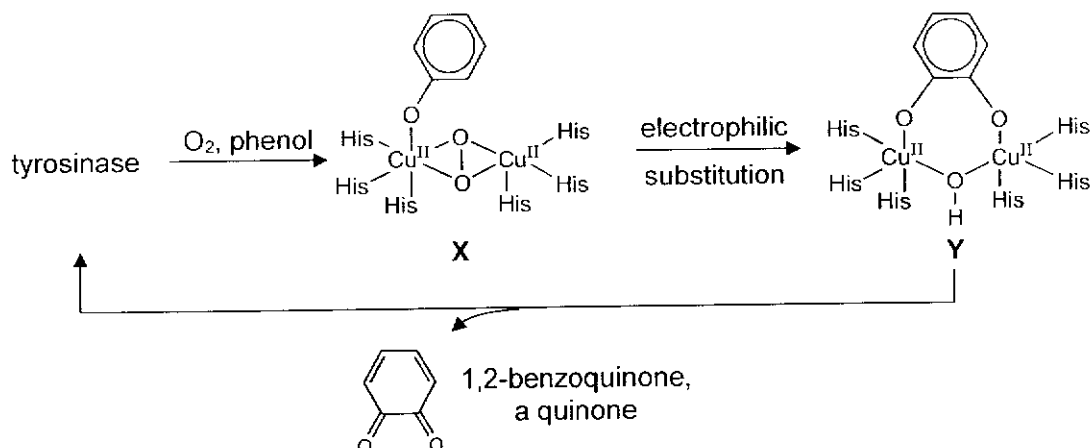
(i) Experiments were conducted using different phenol substrates and the relative rates of reactions are shown below.

phenol substrate	**I**	**II**
relative rate	7.9	0.02

Account for the different relative rates of reactions.

[2]

(ii) In the phenol substrate **III** below, the hydrogen atoms on the phenyl ring are replaced with deuterium (D = $^2_1$H). The bond dissociation energy of the C–D bond is greater than that of the C–H bond.

III
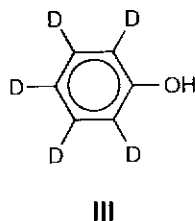
Predict and explain how the relative rate of reaction for substrate **III** would compare to that of substrate **I**.

[1]

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(d) The quinone product from **(c)** can undergo the following reaction.

$$\text{quinone} \xrightarrow{\text{stage 1}} \underset{\text{molecular formula } C_6H_8O_2}{\textbf{J}} \xrightarrow[\text{(COC}l)_2]{\text{stage 2}} \textbf{K}$$
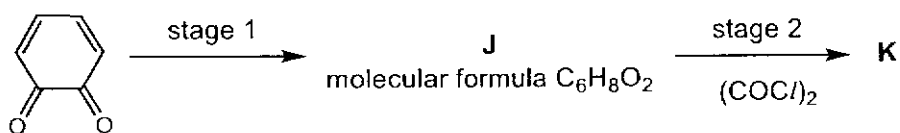
(i) Suggest the structural formulae of **J** and **K**, given that 2,4-dinitrophenylhydrazine can distinguish between the quinone starting material and **K**.

[2]

(ii) Suggest, in no more than three steps, how butanedioic acid can be obtained from 1,4-dimethylcyclohexa-1,3-diene.
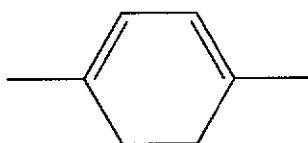
1,4-dimethylcyclohexa-1,3-diene

You are to include the structural formula(e) of all the intermediate(s).

[3]

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(e) Fehling's solution can be prepared by mixing copper(II) sulfate and aqueous potassium sodium tartrate with aqueous sodium hydroxide.

The condensed structural formula of D–erythose is $HOCH_2CH(OH)CH(OH)CHO$.

State what would be observed when a few drops of Fehling's solution is introduced to D-erythose solution. Write the balanced equation between Fehling's solution and D–erythose, showing the structure of the organic product.

[3]

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(f) When fluorine gas is passed over a heated mixture of potassium chloride and copper(II) chloride, a pale green solid, **J**, containing only potassium, copper and fluorine is formed.

When 1.00 g of **J** was reacted with water, 20.4 cm³ of oxygen (measured at 293 K and 1 atm) were evolved and a blue acidic solution was formed. The resulting solution was divided into two equal parts. Titration of one part with 0.100 mol dm⁻³ NaOH required 17.00 cm³ for neutralisation. The other part was electrolysed and 0.108 g of copper metal was deposited at the cathode.

    (i) Calculate the number of moles of oxygen molecules, copper(II) ions and hydrogen ions formed in the reaction with water.

                               [3]

    (ii) The oxidation state of copper in **J** is +3. Assuming that 1 mol of **J** contains 1 mol of copper atoms, deduce its relative formula mass and hence its formula.

                                 [2]

[Total: 20]

6 Iron is one of the most abundant element found on earth. It comprises about 5.6% of the earth's crust and almost all of the earth's core. It is also commonly found in both humans and plants.

(a) **(i)** Iron exists in many oxidation states.

An oxoanion of iron has the formula FeO_x^{2-}. In acidic conditions, FeO_x^{2-} is a strong oxidising agent and is reduced to Fe^{3+}. In an experiment, a 30 cm³ of 0.200 mol dm⁻³ of FeO_x^{2-} completely oxidised 30 cm³ of 0.600 mol dm⁻³ of Fe^{2+} to Fe^{3+}. Determine the value of x.

[3]

The most common oxidation states of iron are +2 and +3. Both iron(II) and iron(III) ions form complexes with H_2O and CN^-.

(ii) Draw a fully labelled diagram to describe how the standard reduction potential of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ half-cell can be measured using a standard hydrogen electrode.

[3]

(iii) By quoting relevant data from the Data Booklet, explain why aqueous iron(III) iodide does not exist while aqueous iron(III) chloride exists.

[2]

(iv) In the presence of iron(III) chloride, phenol does not undergo Friedel-Crafts alkylation with halogenoalkanes. This is because the phenol reacts with iron(III) chloride in an acid-base reaction to form a neutral compound. Suggest the structure of this product.

[1]

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(b) **(i)** Write a balanced equation of the reaction between $SiCl_4$ and water.

[1]

Trimethylsilyl chloride, $(CH_3)_3SiCl$, is closely related to $SiCl_4$. It is a colourless liquid that is stable in the absence of water.

It reacts with water according to the following equation.

$$2(CH_3)_3SiCl + H_2O \rightarrow 2HCl + (CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$$

(ii) The above reaction is slower than the reaction in **(i)**. Give two reasons for the difference in reaction rates.

[2]

(iii) The bond energy of the Si-C bond is commonly quoted as $+ 318$ kJ mol^{-1}.
Using additional data from the *Data Booklet*, calculate the enthalpy change of the above reaction.

[2]

(iv) The calculated value in **(iii)** is different from the experimentally determined value. Give a reason for the difference.

[1]

One of the hydrated forms of iron(III) chloride has a molecular formula of $FeCl_3.6H_2O$.

Heating hydrated iron(III) chloride does not yield anhydrous iron(III) chloride. Instead, the solid decomposes on heating.

(v) Anhydrous iron(III) chloride can be obtained by reacting hydrated iron(III) chloride with trimethylsilyl chloride. Write a balanced equation of this reaction.

[1]

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(c) British astronomer and photographer John Hershel used iron-based reagents to obtain a blue pigment (known as Turnbull's Blue) to develop the blue printing technique in 1842. Now, blue printing can be easily carried out using the photochemical redox chemistry of potassium iron(III) ethanedioate.

The molecular formula of potassium iron(III) ethanedioate is $K_3Fe(C_2O_4)_3$. Its relative formula mass is 437.1.

To confirm the molecular formula, 0.250 g of potassium iron(III) ethanedioate sample was added to 25 cm³ of 4.00 mol dm⁻³ H_2SO_4. After heating this solution, it was titrated with 0.0196 mol dm⁻³ $KMnO_4$ till the light pink colour was obtained. The titration reading was **x** cm³.

After this titration, an excess of zinc powder was added to the same flask that led to effervescence in the solution. When the effervescence subsided, the solution was boiled for fifteen minutes. The flask was cooled to room temperature and was titrated with the same $KMnO_4$ solution. The titration reading was 5.10 cm³.

(i) Find the value of **x**.

[3]

(ii) The anionic complex exists as a pair of enantiomers, as shown below.
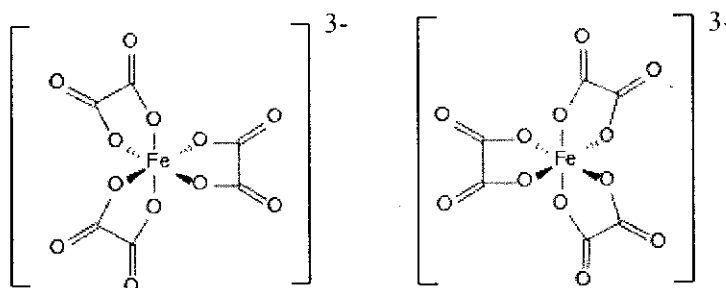
State the structural feature of the complex which is responsible for such a phenomenon.

[1]

[Total: 20]

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Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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