

Name	Index Number	Form Class	Tutorial Class	Subject Tutor
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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.

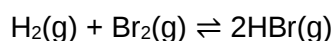


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Answer **all** the questions in the spaces provided.

- 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.



The reaction was carried out in a 250 m³ vessel at 334 °C.

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

[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.

[1]

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

Calculate the amount of bromine present at equilibrium.

[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.

[2]

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

.....
.....
.....
.....[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.

.....[1]

- (ii) When concentrated solutions of the two products formed in the above preparation react with each other, Br₂ is regenerated.

State and explain the type of reaction that HBr undergoes.

.....
.....[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.

[3]

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

.....[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*.

.....[1]

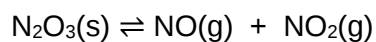
- (ii) Sketch a graph of the successive ionisation energies of all the electrons of a nitrogen atom.

[2]

- (iii) State and explain how the ionic radius of N^{3-} compares to that of P^{3-} .

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.....[2]

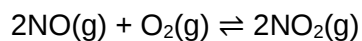
- (b) N_2O_3 is a pale blue solid at very low temperatures. As the temperature is raised, N_2O_3 dissociates to form colourless nitrogen monoxide gas, NO and brown nitrogen dioxide gas, NO_2 . The interesting feature of this reaction is that both products are molecular radicals, each with an unpaired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



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

[3]

- (c) NO is an air pollutant produced by cigarette smoke, automobile engines and power plants. It reacts with oxygen to form NO₂(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.

[4]

- (d) In Singapore, all petrol-driven vehicles are fitted with three-way catalytic converters which convert harmful emissions of NO and NO₂ 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.

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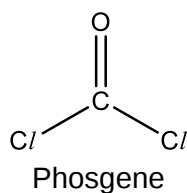
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.....[3]

[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.



- (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.

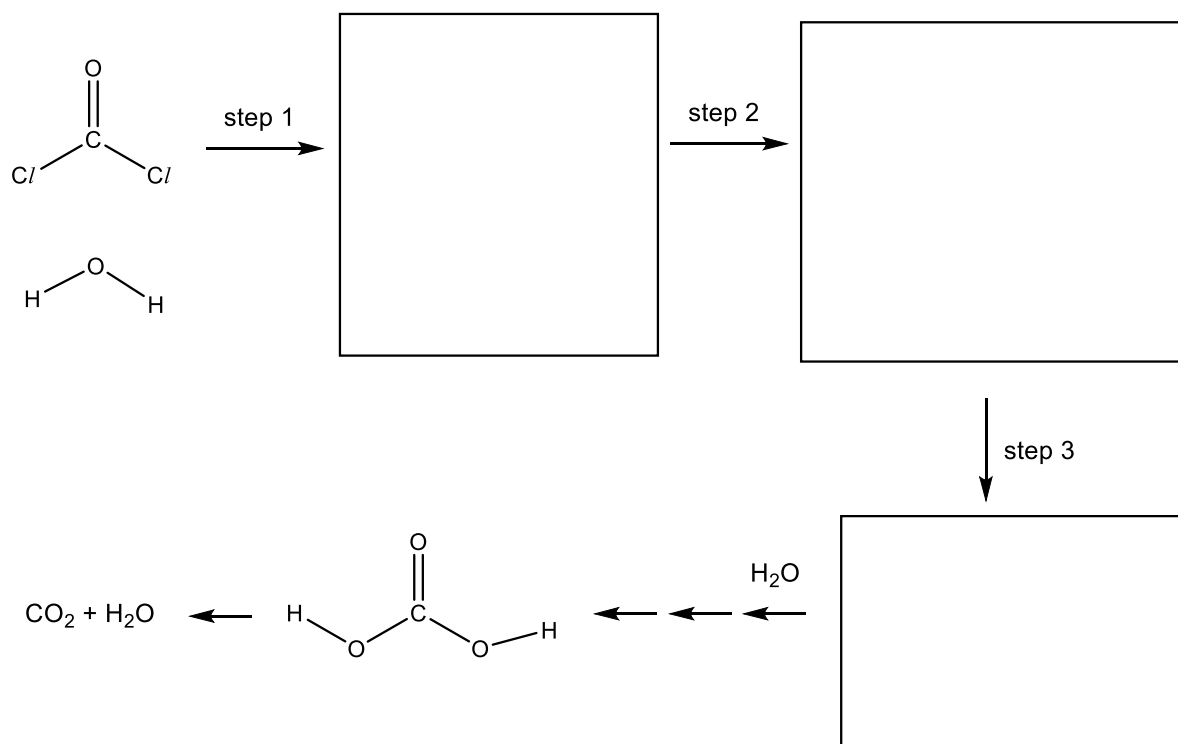
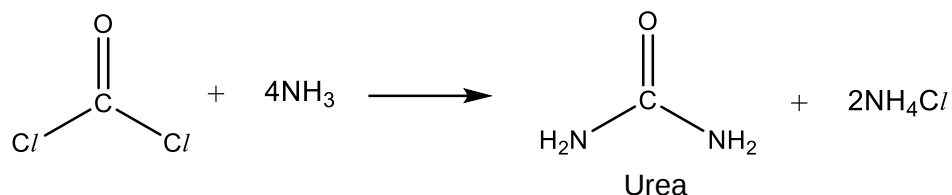


Figure 1

[4]

- (b) Urea with the formula $\text{CO}(\text{NH}_2)_2$ 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.

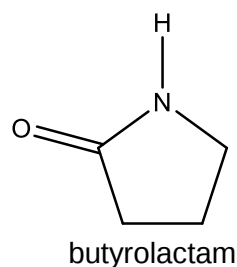
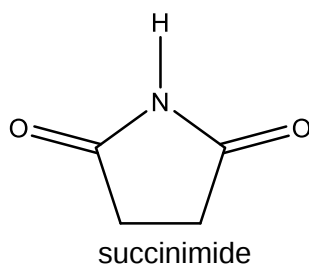
.....[1]

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

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[1]

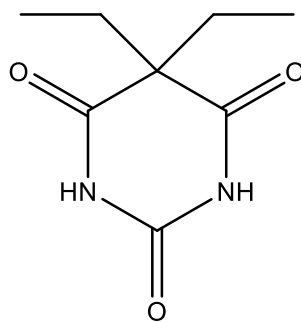
- (c) Explain why succinimide is able to form a salt with aqueous sodium hydroxide, but butyrolactam does not.



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[2]

(d) Veronal is a sleep-inducing drug.

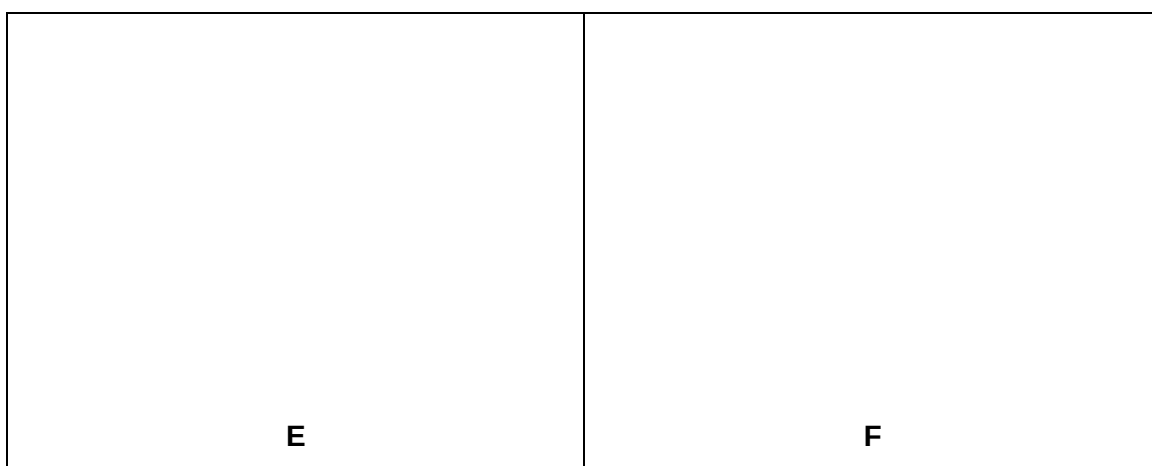
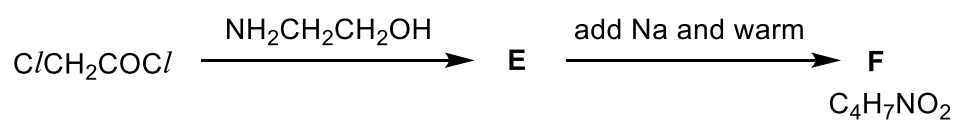


Veronal

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

[2]

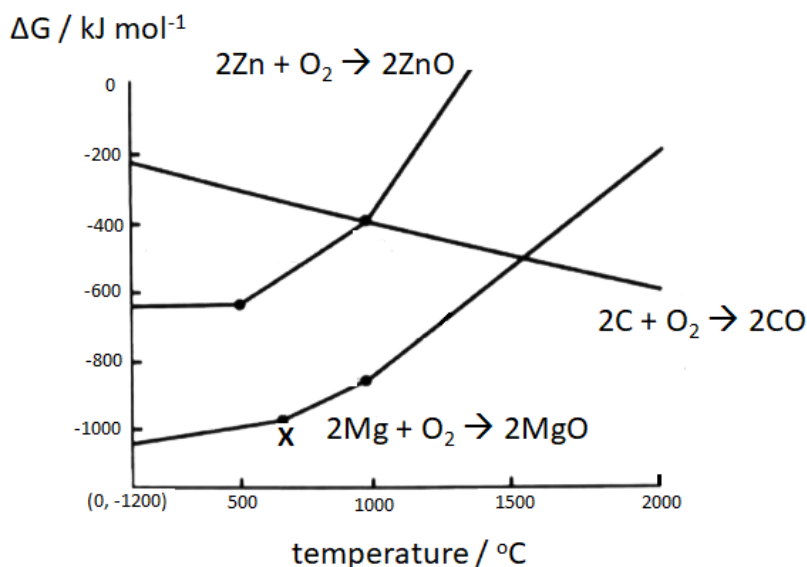
(e) Draw the structures of intermediate **E** and product **F** for the following transformation.



[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.



element	melting point / °C
zinc	420
magnesium	650

Table 1

- (a) Explain why the gradient for the reaction of $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$ is negative.

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.....[2]

- (b) By considering the significance of point X, explain why the gradient for the reaction of $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ becomes more positive at point X as temperature increases.

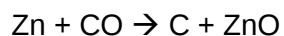
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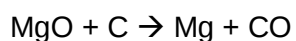
.....[1]

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



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.....[1]

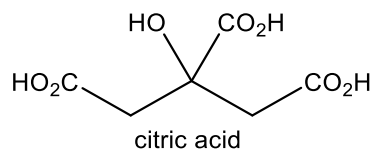
- (d) Estimate the range of temperatures for which the following reaction is spontaneous.



.....[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.



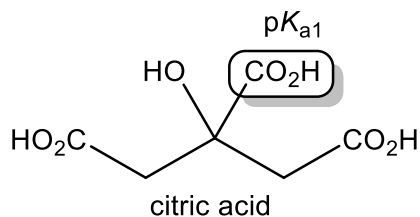
- (a) Calculate the standard enthalpy change of formation of citric acid using the following data.

	$\Delta H^\ominus / \text{kJ mol}^{-1}$
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.

[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.



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

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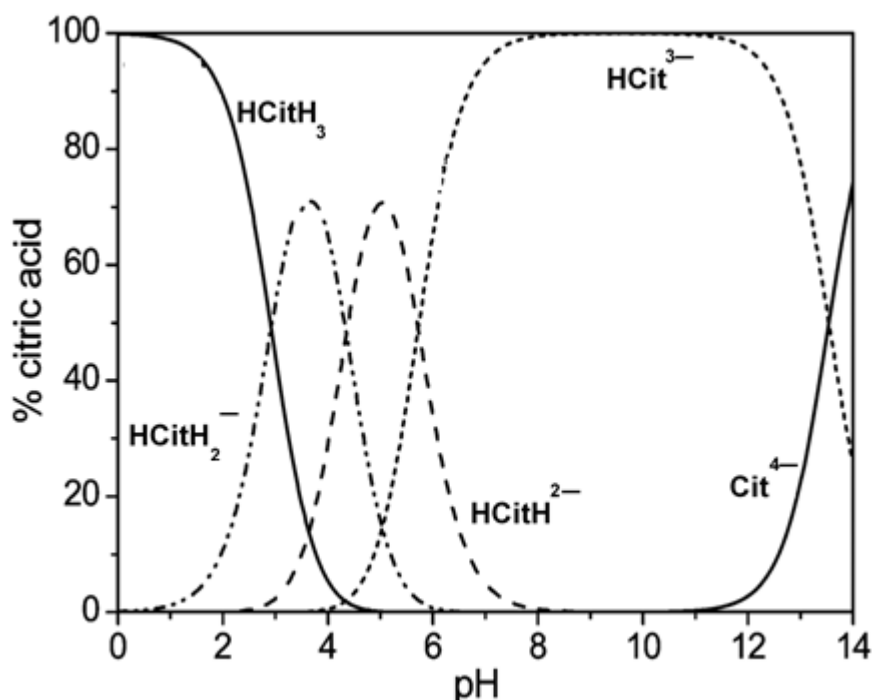
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.....[2]

- (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 “HCitH₃”, with the first H denoting the alcoholic hydrogen atom. Similarly, the tricarboxylate anion of citric acid is denoted as “HCit³⁻”.

- (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}

pK_{a3}

[2]

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

[1]

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

- (iii) Representing citric acid as “HCitH₃” and monosodium citrate as “NaHCitH₂”, write an equation to illustrate how a solution containing both species maintains fairly constant pH when small amounts of NaOH is added to it.

.....[1]

- (iv) A solution was prepared by dissolving 3.84 g of solid citric acid in 1 dm³ 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.

[3]

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

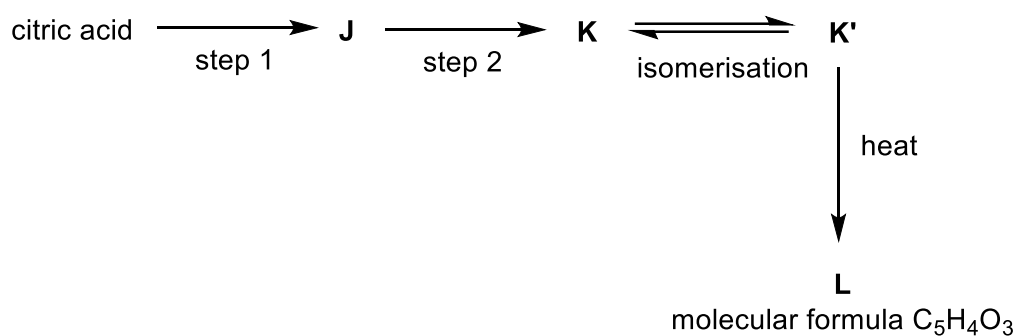
- (i) Isocitric acid is a constitutional isomer of citric acid. It exists in more than two stereoisomeric forms.

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.



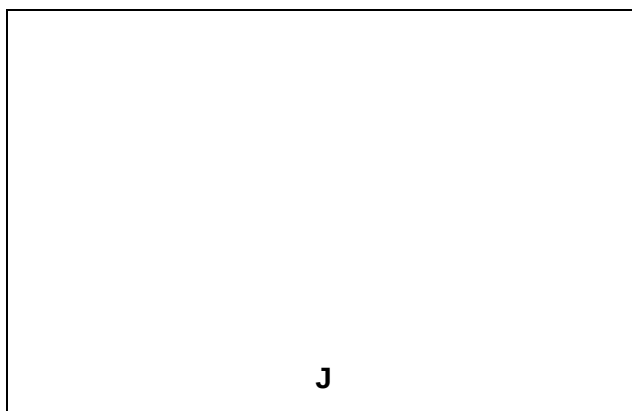
- (ii) Compound **J** has relative molecular mass of 174.0. The **mass ratio** of carbon to hydrogen to oxygen is 12:1:16 in **J**.

Find the molecular formula of **J**.

.....[1]

- (iii) Both compounds **J** and **K** can be reacted with hot acidified KMnO_4 to give 2-oxobutanedioic acid, $\text{HO}_2\text{CCOCH}_2\text{CO}_2\text{H}$.

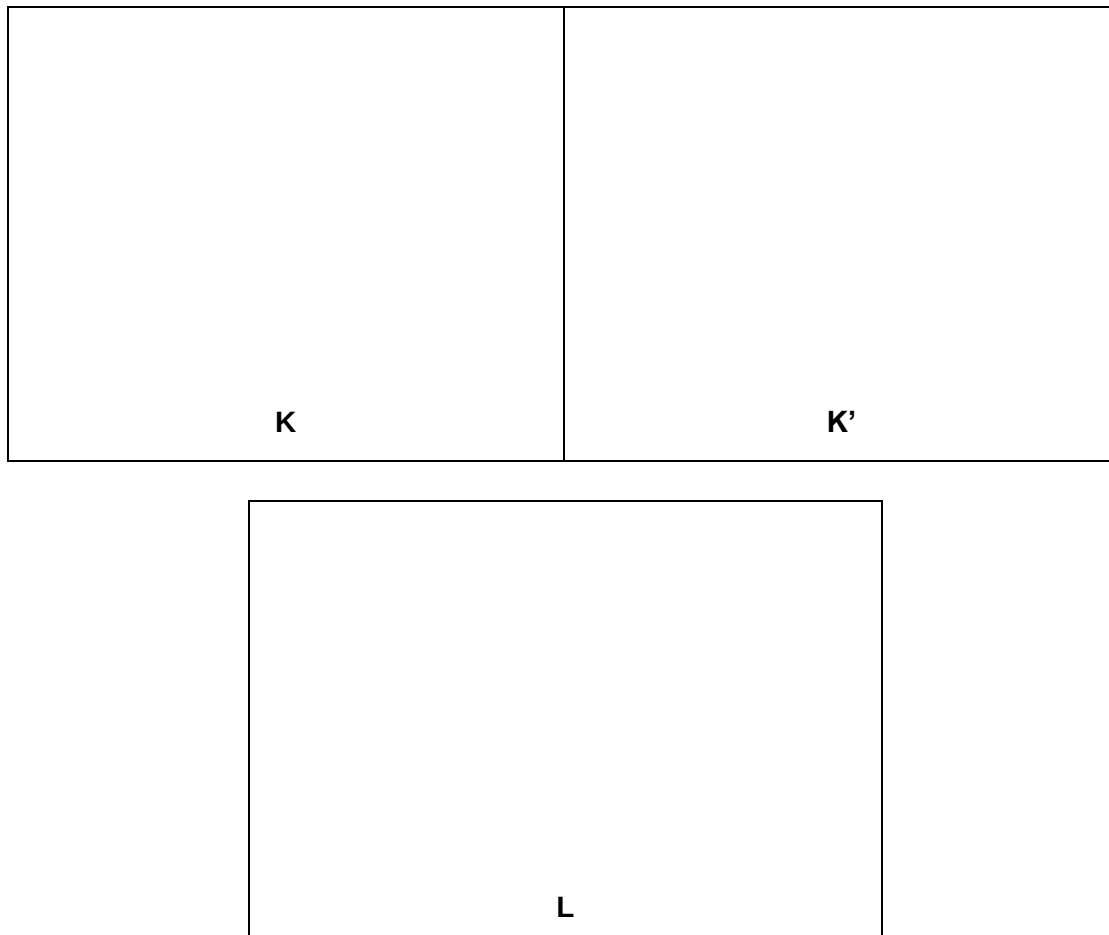
Deduce the structural formula of **J**. State the reagents and conditions used in step 1.



step 1 [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**.

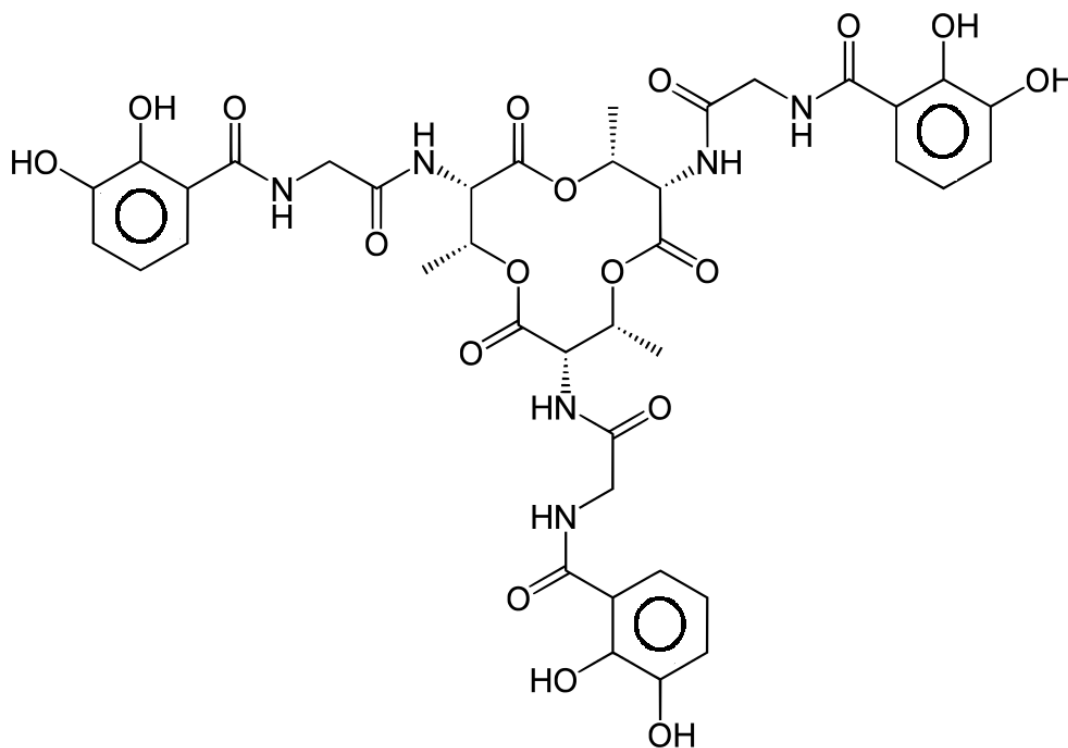


[3]

[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.

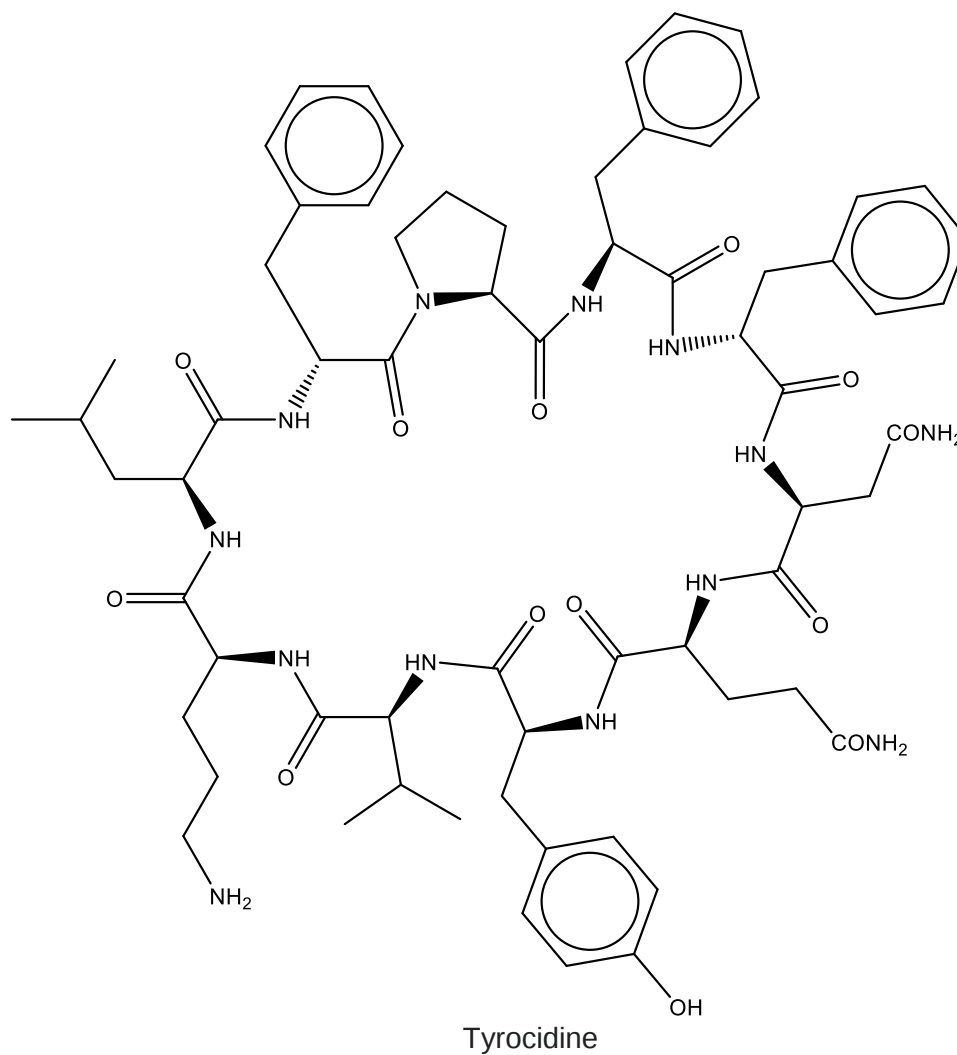
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[2]

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

[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.

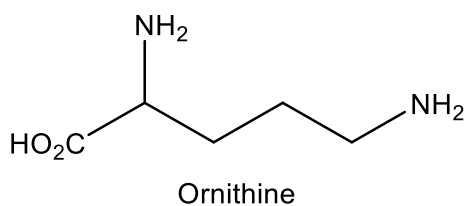


- (i) Amongst the many amino acids that make up tyrocidine, there is one pair of amino acids where the side chains have the same functional group.

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

[1]

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



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

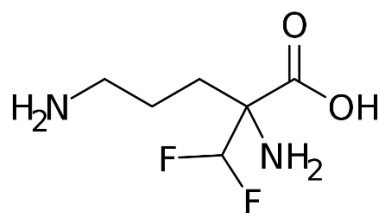
(ii) Draw the zwitterionic form of ornithine.

[1]

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

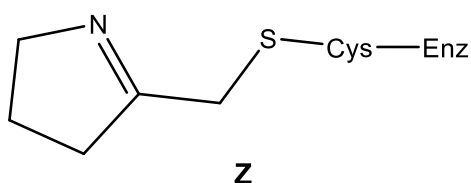
[1]

- (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 $-\text{CH}_2-\text{S}-\text{Cys}-\text{Enz}$ 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'	Z''
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[2]

[Total: 9]

Additional answer space

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

This image shows a full page of a handwriting practice worksheet. It consists of multiple rows of horizontal dotted lines spaced evenly down the page, providing a guide for letter height and placement. The background is plain white, and there are no other markings or text present.

