Name	Index Number	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/02**
Higher 2

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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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

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

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

$n = 1.00 \times 10^4$ 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.

$$K_p = \frac{(P_{HBr})^2}{P_{H_2} P_{Br_2}}$$ [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 $H_2 = 10x$

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

$x = 2.00 \times 10^3$ 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
= $2 \times 10^3 + ½ \times (1.00 \times 10^4)$
= 7.00×10^3 mol

Mass of $Br_2 = 7.00 \times 10^3 \times 79.9 \times 2$
= 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]

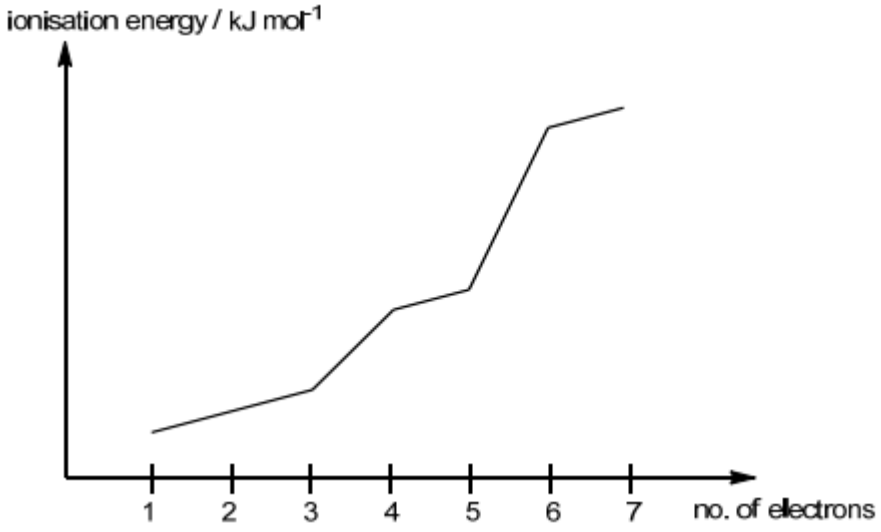
2 This question is about nitrogen and its oxides.

(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.



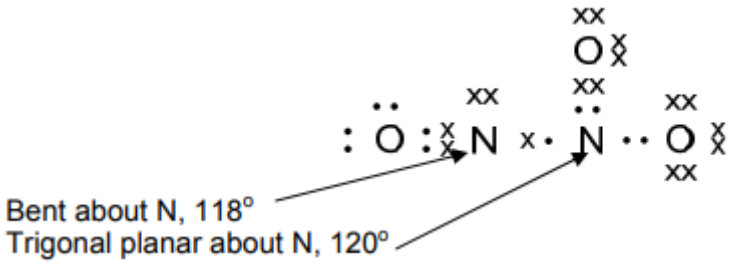
[2]

(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.



[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,

$$\frac{8.4\times10^{-5}}{7\times10^{-6}} = \frac{(0.002)^m(0.003)}{(0.001)^m(0.001)}$$

$$m = 2$$

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

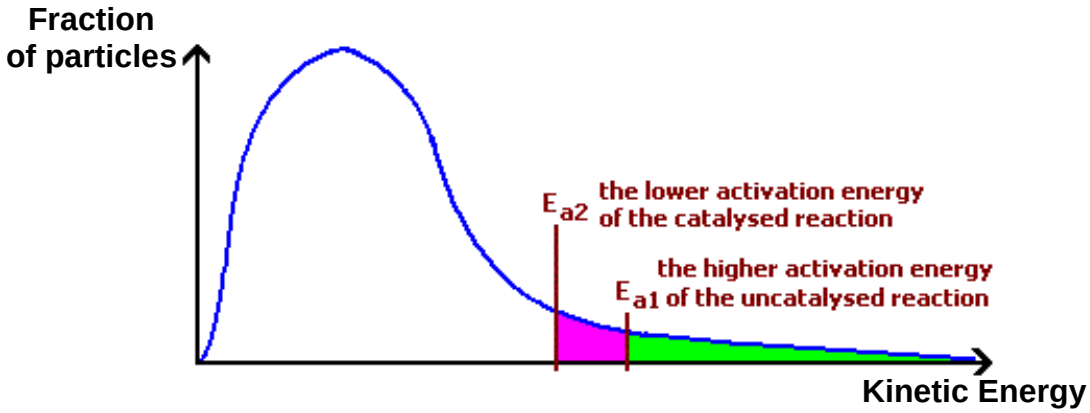
Rate equation: Rate = $k[NO]^2 [O_2]$

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.

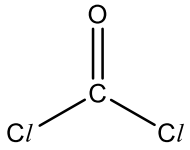


The catalyst increases reaction rate by providing an **alternative pathway with a lower activation energy.**
The **proportion of particles with kinetic energy ≥ E_a increases.**
This leads to an increase in the **frequency of effective collisions** between reactant particles.
Hence the rate of reaction 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.

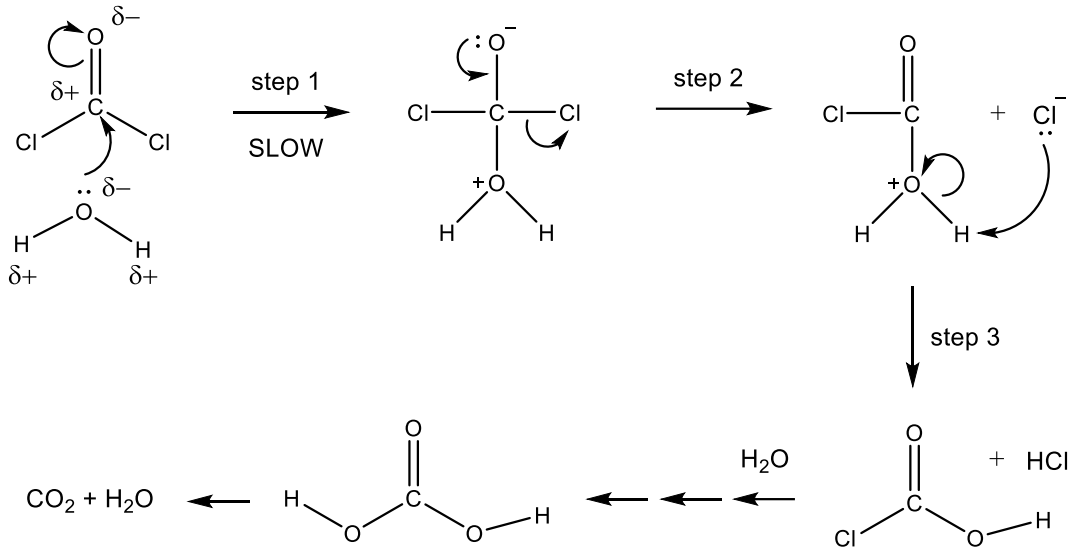
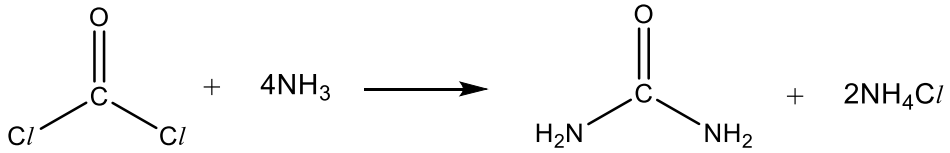


Figure 1

[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.



Urea

(i) State the type of reaction between phosgene and ammonia.

Nucleophilic Addition-Elimination / Condensation

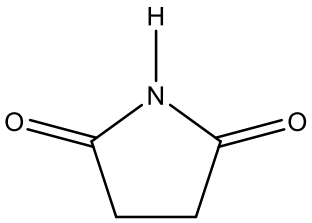
…… [1]

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

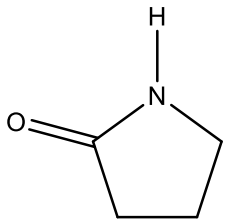
Water is a weak acid. It is not strong enough to have acid-base reaction with urea.
Nitric acid is a strong acid. It is strong enough to have acid-base reaction with urea.

…… [1]

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



succinimide



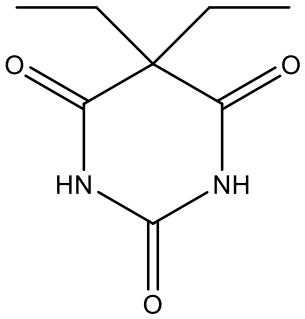
butyrolactam

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.

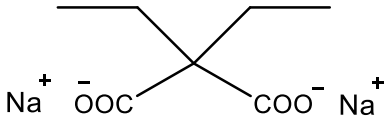
[2]

(d) Veronal is a sleep-inducing drug.



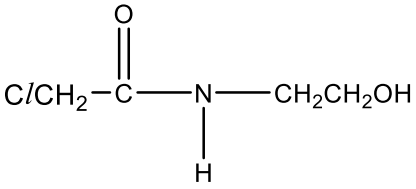
Veronal

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

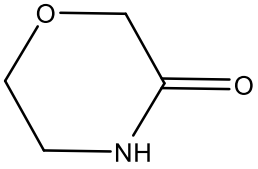
Na_2CO_3 and NH_3 and  [2]

(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

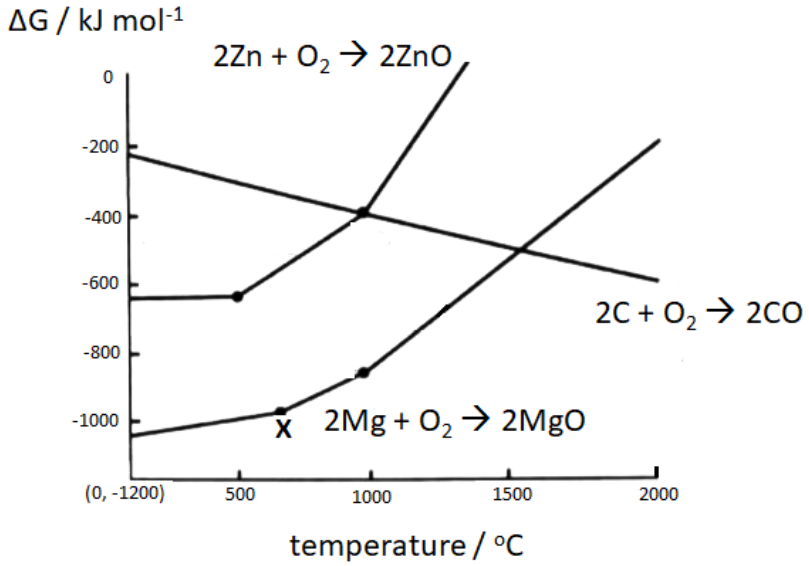


F

[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.



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 – ΔS, 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 ^{o}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.

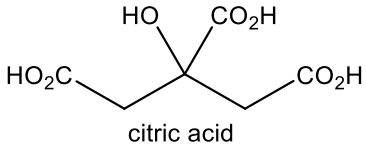
$$MgO + C \rightarrow Mg + CO$$

T > 1500 ^{o}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.

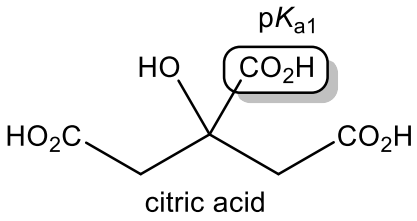
$C_6H_8O_7$ (s) + 4.5O_2 (g) → 4H_2O (l) + 6CO_2 (g)

ΔH_f (citric acid) ← **8O_2 (g) + 6C (s) + 4H_2 (g)** → **6ΔH_f (CO_2(g)) + 4ΔH_c (H_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.



citric acid

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

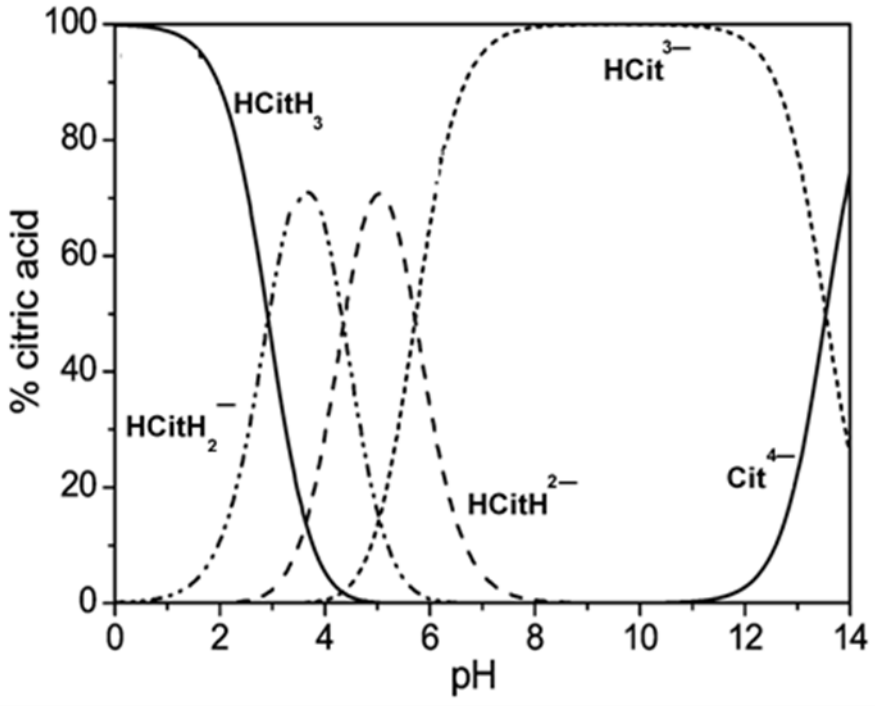
This carboxylic acid is the closest to the alcohol group.

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 [sqrt(0.120 times $10^{-3.0}$)] = 1.50 – ½ 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

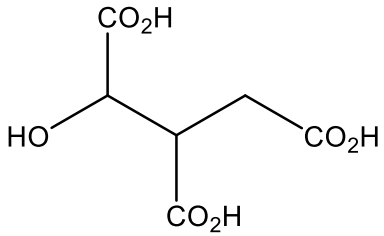
[3]

(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.

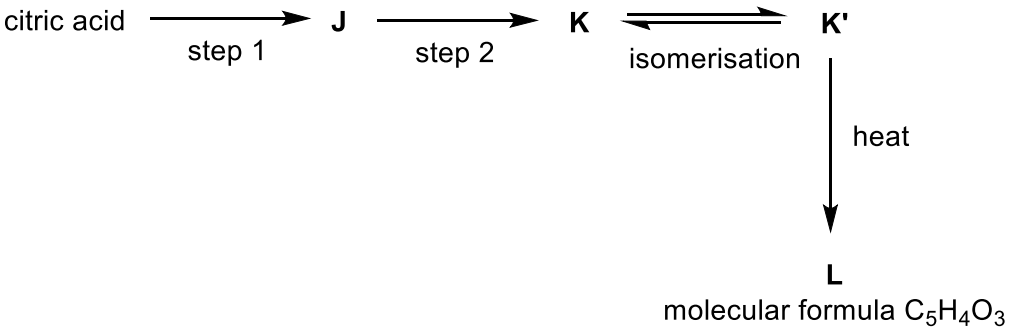
Equal volumes of carbon dioxide gas are obtained when excess sodium hydrogencarbonate is added to the same amount of each acid. Isocitric acid can be made by reacting a suitable aldehyde with HCN, followed by heating the product in aqueous sulfuric acid.

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.



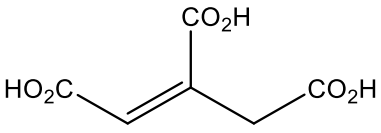
(ii) Compound **J** has relative molecular mass of 174.0. The **mass ratio** of carbon to hydrogen to oxygen is 12:1:16 in **J**.

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.

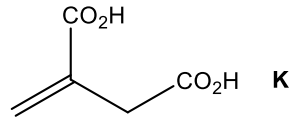


excess conc. H_2SO_4 & heat

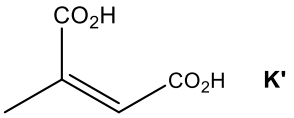
[2]

(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.

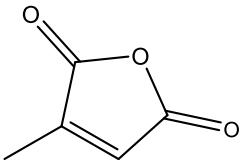
Find the structural formulae of **K**, **K'** and **L**.



K



K'



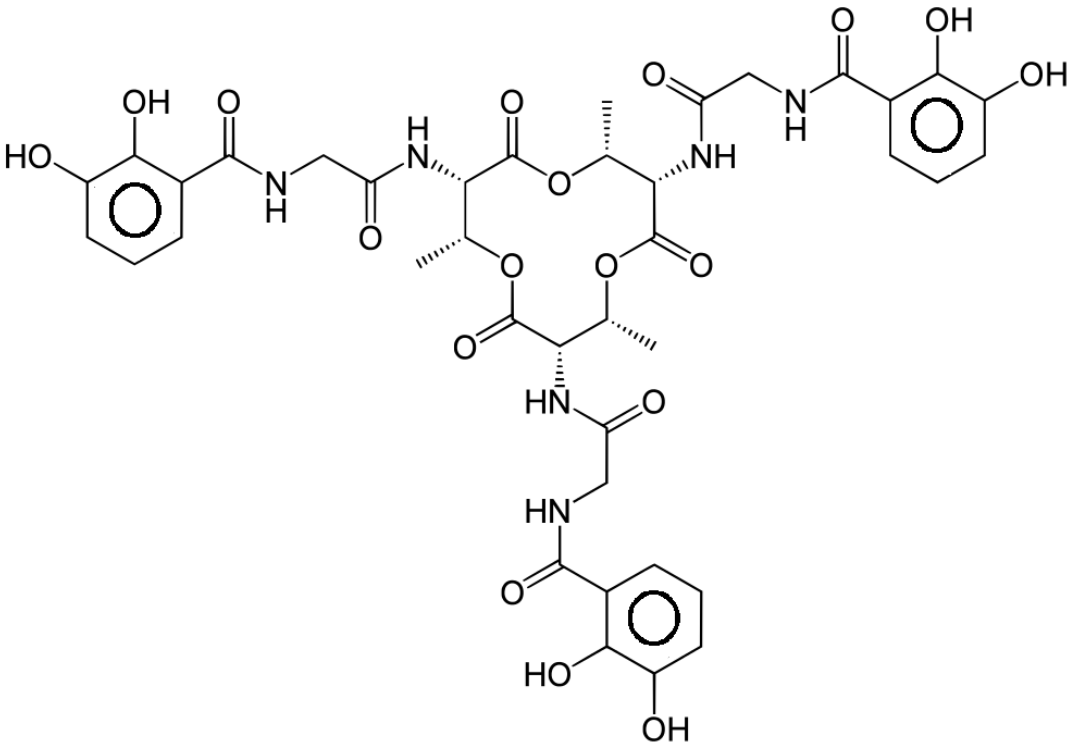
L

[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

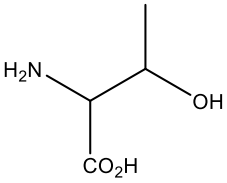
(i) Bacillibactin binds to iron(III) ions via its oxygen atoms. This process facilitates the transportation of iron(III) ions into the interior of a cell.

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]

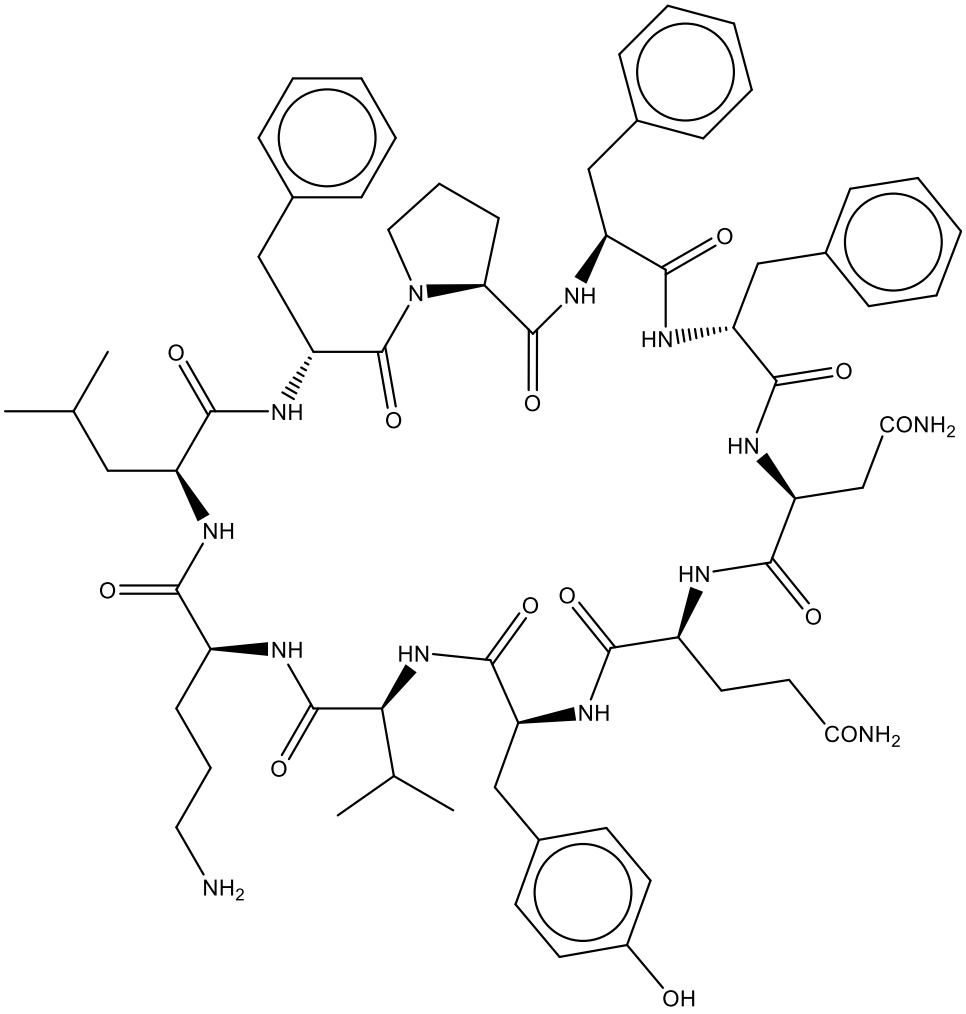
(ii) Draw the structures of the two α-amino acids formed when bacillibactin is hydrolysed.



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.

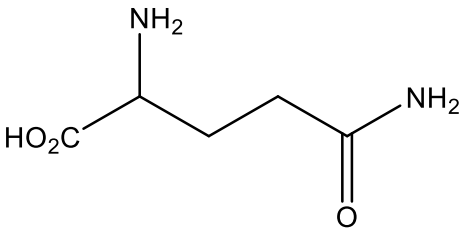


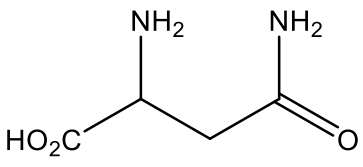
Tyrocidin

(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.

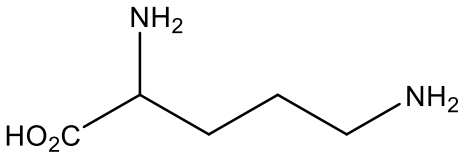
Either





[1]

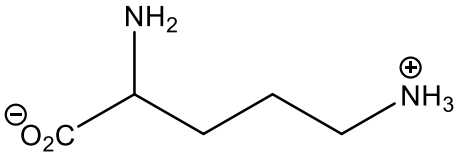
Ornithine is one of the α-amino acids found in tyrocidine.



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.



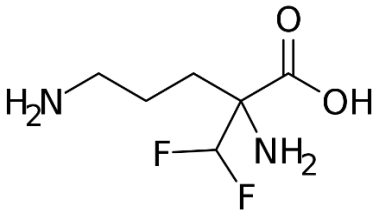
[1]

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

pH = ½ (9.04 + 12.48) = 10.76

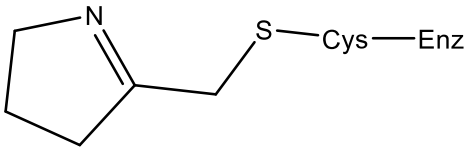
[1]

(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.



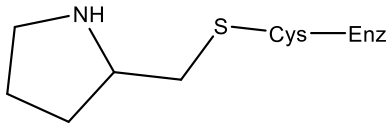
Z

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''**.

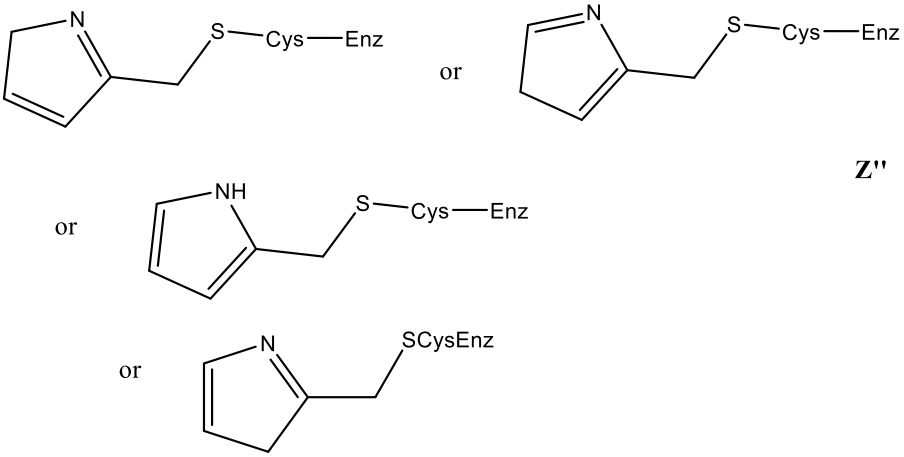
For the two tests, you may assume that the –CH_2–S–Cys–Enz is inert.

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'



Z''

[2]
[Total: 9]