TEMASEK JUNIOR COLLEGE

2025 JC2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME								
CENTRE NUMBER	S					INDEX NUMBER		

Chemistry **9729/03**

Paper 3 Free Response Questions **15 September 2025**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics class, centre number and index number 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. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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		
Paper 3	Q1	
	Q2	
	Q3	
	Q4	
	Q5	
	Total	/80

This document consists of **27** printed pages and **1** blank page.

Section A

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

1 Schweizer's reagent is used in purifying cellulose. This dark blue compound has the formula, $[Cu(NH_3)_4(H_2O)_2](OH)_2$ and contains the tetraamminediaquacopper(II) cation, $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

(a) Explain the origin of the dark blue colour of the tetraamminediaquacopper(II) cation. [3]

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(b) When a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ was gently heated, NH_3 gas was released. A precipitate of $Cu(OH)_2$ and NH_4^+ ions were also obtained as products.

The $Cu(OH)_2$ formed was purified and separated into two samples. One of the samples was added to concentrated hydrochloric acid, forming complex ion **X**.

The other sample of $Cu(OH)_2$ was added to dilute sulfuric acid, forming blue complex ion **Y**.

$[Cu(NH_3)_4(H_2O)_2]^{2+}$, **X** and **Y** are of different colours.

When $[Cu(NH_3)_4(H_2O)_2]^{2+}$ was strongly heated, a black solid **Z** is formed.

(i) Write an equation for the reaction when a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ was gently heated. [1]

(ii) Write an equation for the reaction of $Cu(OH)_2$ with concentrated hydrochloric acid, forming **X**. [1]

(iii) Suggest the identities of **Y** and **Z**. [2]

(iv) Explain why $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and **X** are of different colours. [1]

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(c) Tetraamminediaquacopper(II) cation, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, has two possible stereoisomers.

Draw the two stereoisomers. [2]

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[Turn over

(d) Copper based nanopesticides like $Cu(OH)_2$ and CuO, have been used to protect crops from bacteria induced diseases.

The minimum effective concentration for Cu^{2+} ion as a pesticide is 6.35×10^{-5} g dm^{-3}.

(i) Write the expression for the solubility product of $Cu(OH)_2$, giving its units. [1]

(ii) A sample of solid $Cu(OH)_2$ is added to water. Given that the value of the solubility product of $Cu(OH)_2$ is 2.20×10^{-20}, calculate the solubility of $Cu(OH)_2$ in mol dm^{-3}. [1]

(iii) Hence, deduce if the sample in part **(d)(ii)** is suitable for use as a pesticide. [2]

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(e) Gilman reagent is an organometallic reagent containing two R groups (alkyl or aryl), copper, and lithium. The general formula of Gilman reagents can be expressed as R_2CuLi.

The Gilman reagent, lithium dimethylcopper, can react with an acyl chloride via nucleophilic reaction to form a ketone. The steps of the reaction are shown in Fig. 1.1.

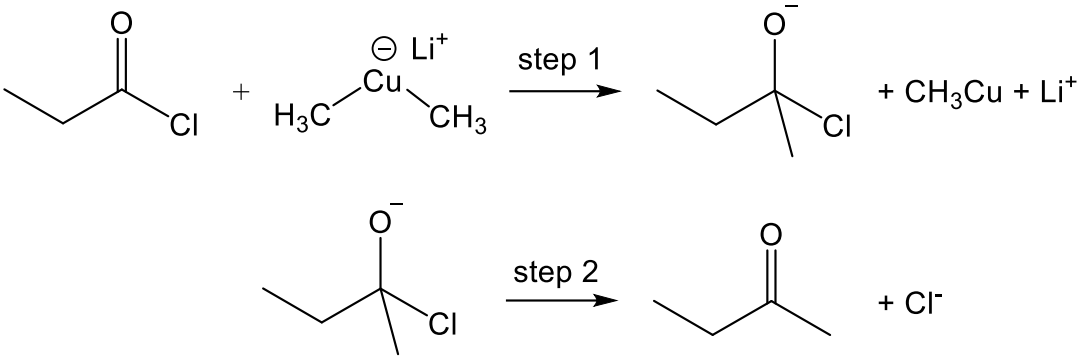
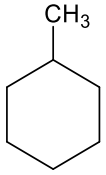


Fig. 1.1

(i) Draw four curly arrows on Fig. 1.1 to complete the mechanism. Include relevant lone pairs and partial charges. [2]

(ii) Lithium dimethylcopper can also react with alkyl halides. A product of this reaction is shown.



Suggest the structure of the alkyl halide that reacted with lithium dimethylcopper to give the product above. [1]

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(f) Transition elements like copper and iron are commonly used as catalysts.

The reaction between $S_2O_8^{2-}$ ions and I^- ions is very slow. If a small amount of aqueous iron(II) ions is added to the mixture, the rate of reaction increases.

Write two equations to illustrate the catalytic role of Fe^{2+} in the $S_2O_8^{2-}$ / I^- reaction. [2]

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[Total: 19]

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2 Chlorine-containing organic compounds are widely used in both industrial and laboratory settings due to their diverse chemical properties and applications.

One such compound is 1-chloro-1-phenylethane, an aromatic halogenoalkane, which exhibits reactivity typical of benzylic halides. A typical reaction is the reaction between 1-chloro-1-phenylethane and hydroxide ions to produce 1-phenylethanol.

$$C_6H_5CHCl CH_3 + OH^- \rightarrow C_6H_5CH(OH)CH_3 + Cl^-$$

The rate of this reaction can be studied by measuring the amount of hydroxide ions that remained in the solution at a given time. The reaction can effectively be stopped if the solution is diluted with an ice-cold solvent.

(a) Briefly describe a suitable method for studying the rate of this reaction at a temperature of 40 °C. [3]

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(b) The reaction was studied by carrying out four experiments at different initial concentrations of the two reagents. Table 2.1 shows the results obtained.

Table 2.1

experiment	$[C_6H_5CHCl/CH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	relative rate
1	0.05	0.10	0.5
2	0.10	0.20	1.0
3	0.15	0.10	1.5
4	*x*	0.15	2.0

(i) Show that the overall order of the reaction is 1. Explain your reasoning. [2]

(ii) Write the rate equation for this reaction. [1]

(iii) Deduce the value of *x* in Table 2.1. [1]

(iv) Using your answer to **(b)(i)**, name and draw the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions. Include all relevant lone pairs, dipoles and curly arrows to show the movement of electron pairs. [3]

(v) With reference to the structure of relevant species in the mechanism, explain why the reaction would proceed via such a mechanism. [1]

(vi) This reaction was carried out using a single enantiomer of 1-chloro-1-phenylethane. Use your mechanism in **(b)(iv)** to predict whether the product will be optically active. Explain your answer. [2]

(vii) The reaction was contaminated with a small amount of benzene to give a side product, $C_{14}H_{14}$. Suggest the structure of the side product. [1]

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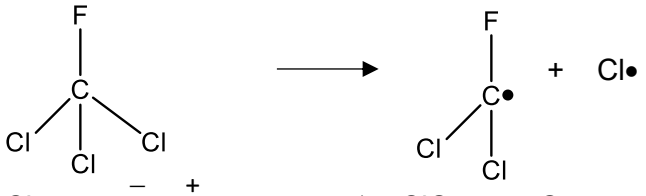
(c) Chlorofluorocarbons, CFCs, such as $CFCl_3$, are extremely stable. This extreme stability allows CFCs to slowly make their way into the stratosphere. However, when the CFCs come into contact with ultraviolet light, they can cause extensive damage to the ozone layer. One such process of ozone destruction is believed to be the reaction shown below.

step 1



step 2 $Cl\bullet + O{-}O{=}O \rightarrow ClO\bullet + O_2$

step 3 $ClO\bullet + O\bullet \rightarrow Cl\bullet + O_2$

step 4 $O_3 + O\bullet \rightarrow 2O_2$

(i) State the role of Cl•. Explain your answer. [1]

To address the problem of ozone destruction, material chemists have developed new hydrofluorocarbons (HFCs) such as CF_3CH_2F. The HFCs contain carbon–hydrogen bonds which are susceptible to homolytic cleavage caused by small amounts of hydroxyl radicals present in the lower atmosphere. This degradation occurs before the HFCs molecules have a chance to drift higher up to the stratosphere and damage the ozone layer. The organic degradation products are unstable and can easily degrade to harmless by-products.

(ii) Write an equation for the reaction of CF_3CH_2F with hydroxyl radical. Draw three curly arrows to illustrate the mechanism for the reaction. [2]

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[Total: 17]

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3 **(a)** Aqueous halogens react with methanoic acid to form hydrogen halides and an acidic gas.

(i) Suggest the chemical equation for the reaction between bromine and methanoic acid. [1]

(ii) With the use of relevant data from the *Data Booklet*, describe and explain the trend in the thermal stability of the hydrogen halides, HC*l*, HBr and HI. [2]

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(b) When iron is heated separately with chlorine and iodine, the respective iron halide is formed but each containing iron of a different oxidation state.

Using $E^{\ominus}$ values from the *Data Booklet*, suggest the formula of the final iron halide formed for each reaction. [3]

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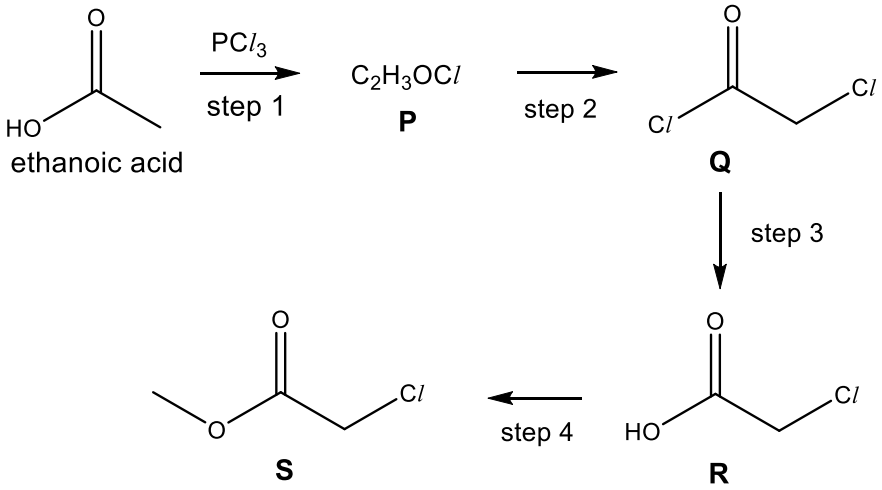
(c) Halogenated esters are used as intermediates in pharmaceutical drugs.

The reaction scheme below shows how a chlorinated ester, **S**, can be made from ethanoic acid.

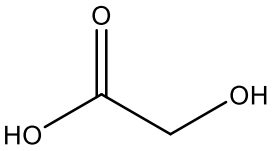


(i) Suggest the structure of intermediate **P** formed in step 1. [1]

(ii) State the reagents and conditions for step 4. [1]

(iii) Compare and explain the relative acidity of aqueous solutions of ethanoic acid, **Q** and **R**. [3]

(iv) Steps 1 and 2 need to be carried out carefully to prevent the formation of compound **T**.



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If **T** is present in the reaction mixture of step 3, a different compound **U** will also be formed in the final reaction mixture. Compound **U** has two identical functional groups.

The infrared spectrum of **U** shows strong absorptions at these wavenumbers, 1100 cm^{-1} and 1745 cm^{-1}, but no absorption due to O–H bonds.

Use the *Data Booklet* to identify the chemical bonds responsible for the absorption at these wavenumbers and deduce the functional group present in **U**. Hence, state the type of reaction that has taken place to form **U**. [2]

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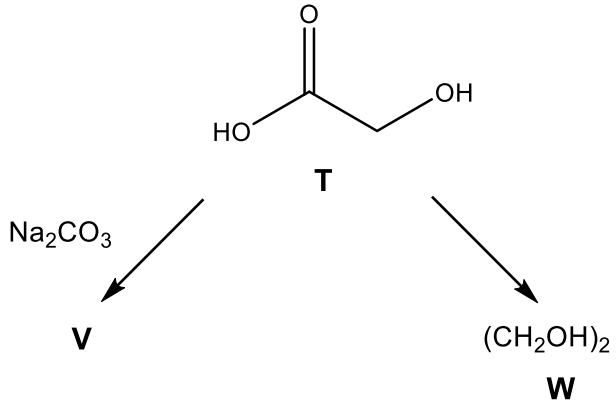
(d) Some further reactions of compound **T** are shown below.



(i) Draw the structure of compound **V**. [1]

(ii) Explain why $NaBH_4$ cannot be used in place of $LiAlH_4$ to form **W** from **T**. [1]

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(e) Compound **K**, C_4H_9ClO, is optically active. Upon heating with excess sodium metal, **K** produces effervescence and compound **L**, C_4H_8O. Compound **L** is optically inactive and does not decolourise bromine water and does not produce an orange precipitate with 2,4-DNPH.

K gives a yellow precipitate with hot alkaline aqueous iodine and organic compound **M**, which produces $C_2H_2O_4$ after acidifying the mixture.

Deduce the structures of **K** to **M**, explaining clearly the reactions involved. [9]

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Section B

Answer **one** question from this section.

4 The Gibbs free energy change, ΔG, is related to temperature, T, by the equation:

$$\Delta G = \Delta H - T\Delta S$$

Fig. 4.1 shows the Ellingham diagram which is a plot of ΔG against T and is used to evaluate the ease of reduction of oxides. The diagram shows how ΔG changes with T from 300 K to 2000 K for the following reactions.

reaction (1): $C(s) + O_2(g) \rightleftharpoons CO_2(g)$

reaction (2): $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$

reaction (3): $Ti(s) + O_2(g) \rightleftharpoons TiO_2(s)$

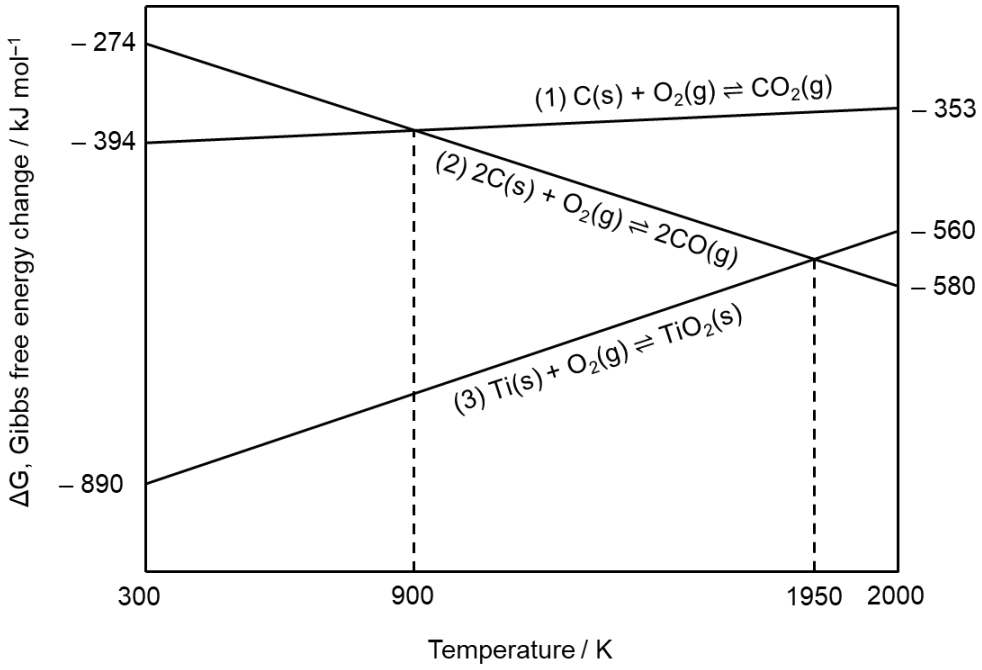

Fig. 4.1

Use Fig. 4.1 to answer parts **(a)** and **(b)**.

(a) **(i)** With reference to the ΔG equation, explain why the ΔG for reaction (1) is almost independent of temperature. [1]

(ii) Calculate the entropy change for reaction (3), in J mol^{-1} K^{-1}. [1]

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(b) Titanium can be obtained by the reduction of TiO_2 with carbon, via the reaction below.

reaction (4): $TiO_2(s) + 2C(s) \rightleftharpoons Ti(s) + 2CO(g)$

(i) Similar to enthalpy change of reaction, the Gibbs free energy change of a reaction can be calculated using an energy cycle.

Using ΔG values at 2000 K from Fig. 4.1 and with the aid of a suitable energy cycle, calculate ΔG for reaction (4) at 2000 K. [2]

(ii) State the temperature range for reaction (4) to be spontaneous. Explain your answer. [2]

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(c) **(i)** State two main assumptions of the kinetic theory as applied to an ideal gas. [2]

(ii) The Gibbs free energy change of any reversible reaction can be expressed as a function of K_p given by:

$$\Delta G = - RT \ln K_p$$

where K_p is the equilibrium constant expressed in terms of partial pressures of gases in bar. [1 bar = 10^5 Pa]

Using your answer to **(b)(i)**, determine the value of K_p for reaction (4) at 2000 K. [1]

If you were unable to calculate a value for the ΔG in **(b)(i)**, you should use –15 kJ mol^{-1}. This is **not** the correct answer for **(b)(i)**.

(iii) Write an expression for the equilibrium constant, K_p, for reaction (4). [1]

A typical reaction vessel for the reduction of TiO_2 with carbon has a volume of 100 dm^3.

(iv) Determine the equilibrium partial pressure of CO at 2000 K, in Pa. [1]

You may assume that carbon monoxide behaves as an ideal gas under such conditions.

(v) Hence, calculate the equilibrium mass of titanium produced at 2000 K. [2]

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(d) The chemistry of carboxylic acids involves a range of reactions from their formation via oxidation to their conversion into other useful derivatives.

Two electrode reactions are shown in Table 4.1.

Table 4.1

electrode reaction	$E^{\ominus}$ / V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$CH_3COOH + 2H^+ + 2e^- \rightleftharpoons CH_3CHO + H_2O$	**U**

(i) Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential, $E^{\ominus}$, of the $Cr_2O_7^{2-}(aq) / Cr^{3+}(aq)$ electrode. Include all necessary chemicals and show the direction of electron flow in the circuit. [3]

(ii) Construct the ionic equation for the reaction between ethanal and acidified potassium dichromate. [1]

(iii) The $E^{\ominus}_{cell}$ of an electrochemical cell consisting of a standard CH_3COOH / CH_3CHO electrode and a standard $Cr_2O_7^{2-}(aq) / Cr^{3+}(aq)$ electrode is +2.27 V.

Calculate the value of the standard electrode potential, **U**, in Table 4.1. [1]

(iv) Explain how the voltage of this cell would change when aqueous sodium hydroxide is added to the CH_3COOH / CH_3CHO half-cell. [2]

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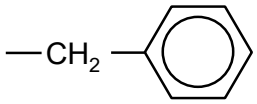
5 Amino acids play central roles both as building blocks of proteins and as intermediates in metabolism.

Some amino acids found in proteins are shown in Table 5.1.

Table 5.1

amino acid	abbreviation	formula of side chain
aspartic acid	asp	$-CH_2CO_2H$
glutamine	gln	$-CH_2CH_2CONH_2$
phenylalanine	phe	

(a) Blood plasma contains 90 % water. Suggest and explain which amino acids in Table 5.1 are likely to be found on the outer surface of proteins molecules in blood plasma at pH 7.4.

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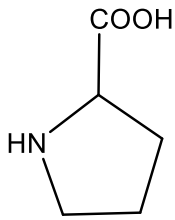
(b) **(i)** The structure of another amino acid, proline (pro), is 

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Draw the structural formula of the tripeptide, asp–pro–phe. [1]

(ii) The enzyme, chymotrypsin, selectively hydrolyses at the carboxyl end of phenylalanine (phe) and tyrosine (tyr) residues.

The enzyme, trypsin, selectively hydrolyses at the carboxyl end of arginine (arg) residues.

An octapeptide **J** was analysed and the results were as follows.

- **J** contains the partial sequence tyr–ala–pro.
- Complete hydroylsis of **J** gave the following eight amino acids:

  ala, arg, asp, gln, pro, tyr, 2 × phe
- On reaction with chymotrypsin, **J** gave tyr, gln and two different tripeptides.
- On reaction with trypsin, **J** gave arg and a heptapeptide only.

Determine the amino acid sequence of **J**. [2]

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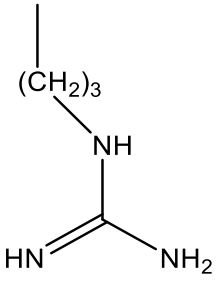
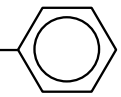
(c) Electrophoresis is a technique used to separate mixtures of amino acids based on the mobility of ions in an electric field.

A mixture of arginine, aspartic acid and phenylalanine was placed at the center of the electrophoresis plate in a buffer solution of pH 6.0. A potential difference was then applied across the plate.

The pK_a values of the acidic groups of each amino acid are shown in Table 5.2.

Table 5.2

amino acid	formula of side chain	pK_a of α–carboxyl group	pK_a of α–amino group	pK_a of side chain
arginine		2.03	9.00	12.10
aspartic acid	—CH_2CO_2H	1.95	9.66	3.71
phenylalanine	—CH_2 	2.18	9.09	–

(i) Draw the structure of the major species in a phenylalanine solution at pH 6.0. [1]

(ii) On Fig. 5.1, use a 'x' to indicate the relative positions of each of the amino acid after the electrophoresis at pH 6.0. Label the amino acids clearly. [2]

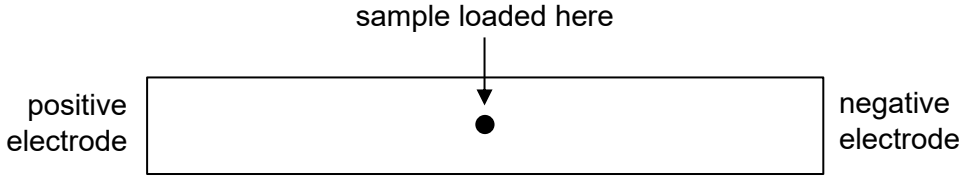
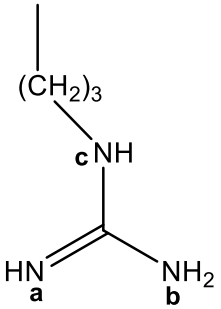


Fig. 5.1

(iii) The side chain of arginine is shown.



Nitrogen atoms, **a**, **b** and **c**, are all sp^2 hybridised. Only one of the nitrogen atoms will be protonated in an acidic medium. Identify which nitrogen atom would be protonated. Explain your answer. [1]

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(d) The Strecker method is a series of chemical reactions which synthesises an amino acid from an aldehyde as a starting material.

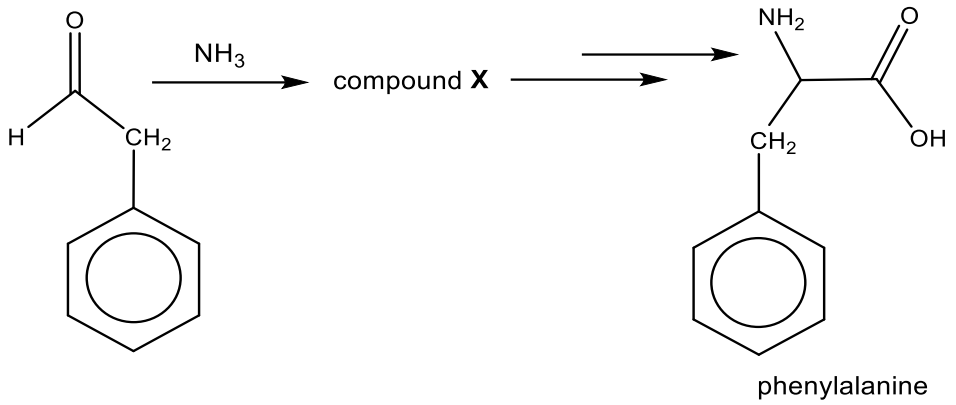

Fig. 5.2

(i) In Fig. 5.2, the first stage involves ammonia acting as a nucleophile, followed by the elimination of a water molecule to form compound **X**. Suggest a structure for **X**. [1]

(ii) A starting material, compound **Y**, can be used to prepare aspartic acid via the Strecker method.

Suggest the structure of **Y**. [1]

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(e) Group 2 carbonates decompose when heated.

Describe and explain the trend in the thermal stability of the Group 2 carbonates. [2]

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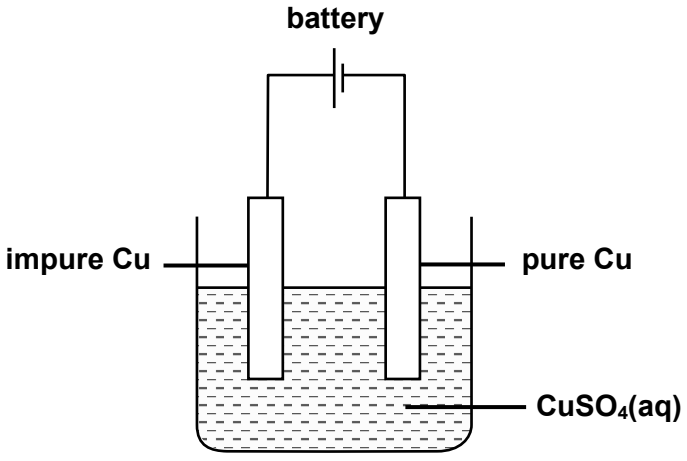
(f) An impure copper bar containing impurities of cobalt and metal **M** was purified using electrolysis.



A current of 0.850 A was passed through the cell above. After 40.0 minutes, the mass of one electrode increased by 0.680 g and the mass of the other electrode decreased by 0.714 g. The electrolyte was further analysed and it was found that the amount of Cu^{2+} ions decreased by 4.62×10^{-4} mol.

M was found underneath one of the electrodes.

(i) Explain, in terms of electrode reactions, how each of the two impurity metals was removed from copper, using relevant data from the *Data Booklet*. [3]

(ii) Use the information in part **(f)** to calculate a value for the Faraday's constant obtained from this experiment. [1]

(iii) Use your answer to **(f)(ii)** and the *Data Booklet* to calculate a value for the Avogadro's constant obtained from this experiment. [1]

(iv) Calculate the masses of copper, cobalt and **M** removed from the copper bar. [2]

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[Total: 20]

Additional answer space

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