

CANDIDATE NAME	CT GROUP	20S
CENTRE NUMBER	INDEX NUMBER	

CHEMISTRY

Paper 2 Structured Questions

Candidates answer on the Question Paper. Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **Centre number**, **index number** and **CT group** clearly in the spaces at the top of the page.

Write in dark blue or black pen.

You may use a 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.

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

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1	/ 16		
2	/ 18		
3	/ 16		
4		/ 25	
Deductions	s.f.		
	units		
Total		/ 75	

9729/02

2 hours

25 August 2021

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

1 Hypoglycin A occurs naturally in fruits such as lychees and longans. In 2017, scientists advised against over-consuming lychees on an empty stomach after discovering its role in a mysterious recurring outbreak of acute neurological illness since 1995 in Bihar, the largest lychee cultivation area in India.





hypoglycin A, C7H11O2N

(a) (i) Hypoglycin A contains a carboxylic acid functional group.

Explain the acidity of the carboxylic acid functional group in terms of its structure.

(ii) Identify as fully as you can the other functional groups present in hypoglycin A.
[2]
(iii) Explain whether hypoglycin A can show *cis-trans* isomerism.

.....[1]

(b) Draw the structures of the major organic products, P, Q and R, when hypoglycin A reacts with each of the following reagents.

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(iv) A by-product of stage III is methanoic acid, HCO₂H. Draw a dot-and-cross diagram of a molecule of methanoic acid.

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[1]

(d) The dipeptide, hypoglycin B, is also found in lychees and possesses the same toxic effects as hypoglycin A.



Suggest reagents and conditions to hydrolyse hypoglycin B in the laboratory and draw the organic products formed.

reagents and conditions:

organic products formed:

[3]

- (e) The toxicity of hypoglycin A and B arises when they metabolise in the body to form a compound, MCPA, which causes acute hypoglycemia leading to coma and fatality in the outbreaks.
 - MCPA retains the \bigtriangleup group and has a molecular formula of C₆H₈O₂.
 - It has only one chiral centre and gives effervescence with NaHCO₃(aq).
 - No carbon atom in MCPA is bonded to four other carbon atoms.

Suggest a structure for MCPA.

[1] [Total: 16] 2 (a) Among the elements of Group 14, those towards the top, carbon to germanium, have very different properties from those at the bottom, tin and lead. For example, the melting points show a marked change after germanium.

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mixture of reactants and products after each step. Purification is carried out to separate the products from the reactants before each subsequent step can be carried out.

Table 2.1 gives the melting and boiling points of benzene and nitrobenzene.

Table 2.1

compound	melting point / °C	boiling point / °C
benzene	5.5	80.1
nitrobenzene	5.7	211

(iii) Using the data in Table 2.1, state a physical method that can be used to separate nitrobenzene from benzene after step 1.

.....[1]

6

Exp	plain why nitrobenzene has a higher boiling point than water.
	[2]
[Sn	$Cl_6]^{2-}$ ions are formed together with phenylammonium ions in step 2.
By illus	considering the changes in the oxidation number of tin, construct a half-equation to strate the formation of $[SnCl_6]^{2-}$ in step 2.
	[1]
(i)	Explain, in terms of their structures, why phenylamine is a weaker base than ethylamine.
(ii)	Explain why the phenylammonium salt is soluble in water.
()	
	[1]

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- (iii) After step 2, the reaction mixture containing phenylammonium ion, [SnC*l*₆]²⁻ and nitrobenzene is shaken with water in a separating funnel and the two layers are allowed to separate.

The layer containing phenylammonium ion and $[SnCl_6]^{2-}$ is then transferred into another separating funnel and shaken with NaOH(aq) and organic solvent ethyl acetate, in step 3, to obtain phenylamine. The two layers are then allowed to separate.

Phenylamine is more soluble in ethyl acetate than in water.

compound	density / g cm ⁻³	solubility in water
nitrobenzene	1.20	insoluble
water	1.00	-
ethyl acetate	0.90	insoluble

After step 3:

In the boxes below, indicate the locations of

After step 2:

- phenylammonium ion and nitrobenzene after step 2,
- phenylamine and $[SnCl_6]^{2-}$ after step 3.



(f) Describe a simple chemical test you could carry out to confirm the presence of phenylamine obtained. State what you would observe.

.....[2]

7

(g) Phenylamine reacts with acyl chlorides at a faster rate than with alkyl chlorides. Examiner's Give two reasons to explain the different reactivities of acyl chlorides and alkyl chlorides.

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.....[2]

[Total: 18]

3 (a) Chalcopyrite is a mineral from which copper is commonly extracted. Its formula is CuFeS₂ and it contains trace amounts of silver. After initial processing, the solid impure copper, containing iron and silver, is then purified by electrolysis.

Describe the electrode reactions that take place during this electrolysis, and explain in detail how each of the two impurity metals is removed from copper.

.....[4]

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(b) Electrolysis can also be applied to organic synthesis due to its mild conditions and green potential. In 2013, chemists in Guangzhou, China, developed an electrosynthesis method to obtain amides from methyl ketones and formamides. A typical reaction is shown below.

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reaction 1



The synthesis occurs in a cell fitted with inert graphite and nickel electrodes. A solution of the reactants and sodium iodide dissolved in organic solvent is used as the electrolyte. The reactions occurring at the electrodes are:



(i) Draw a labelled diagram of the electrolysis cell used above. Include details of the cathode, anode and electrolyte.

[2]

(ii) With the products formed at the electrodes, the following conversions are thought to occur in the electrolyte:



Conversion **b** occurs via a three-step mechanism.

- The amine acts as a nucleophile to react with the carbonyl group of **T** to form an alkoxide intermediate in the first step.
- The C=O bond is reformed, and the anion CI_3^- leaves in the second step.
- An acid-base reaction occurs in the third step to form CHI₃ and the amide product.

Suggest the mechanism for conversion **b**. Show any relevant lone pairs and charges, and indicate the movement of electron pairs with curly arrows.

[4]

(iii) The chemists in Guangzhou also conducted a control reaction, shown below, to determine whether the carbonyl group in the product of *reaction 1* originates from the methyl ketone or the formamide.



Use the result of this control reaction to deduce whether the carbonyl group in the product of *reaction 1* originates from the methyl ketone or the formamide, giving your reason.

 	 	 [1]

(iv) The amide product in *reaction 1* can also be synthesised using traditional organic synthesis methods from the same methyl ketone, via benzoic acid as an intermediate compound.

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the methyl ketone

benzoic acid

the amide product

Outline how you can convert

- I the methyl ketone to benzoic acid, and
- II benzoic acid to the amide product.

Include reagents and conditions for all reactions, and the structures of all other intermediate compounds, in your answer.

I:

 	 [5]
	[Total: 16]

- 4 This question is about Group 17 elements, the halogens, and their compounds.
 - (a) Use the *Data Booklet* to describe the relative reactivity of the halogens (chlorine, bromine and iodine) as oxidising agents, and relate this reactivity to relevant E° values.

.....[2] (b) Unlike the other halogens, the standard electrode potential for the reduction of $F_2(q)$ to $F^{-}(aq), E^{\circ}(F_2/F^{-})$, cannot be determined by direct measurement in aqueous medium. Explain what is meant by the term standard electrode potential. (i)[1] (ii) Using relevant E° values from the Data Booklet, suggest why $E^{\circ}(F_2/F^{-})$ cannot be measured directly in the aqueous medium.[2]

For

Examiner's use The standard electrode potential, $E^{\circ}(F_2/F^-)$, can be estimated however, by considering the hypothetical reaction between $Cl^-(aq)$ and $F_2(g)$ as shown in *reaction 2* below.

reaction 2 $2Cl^{-}(aq) + F_2(q) \rightarrow Cl_2(q) + 2F^{-}(aq)$

The standard Gibbs free energy change for *reaction 2*, ΔG°_{2} , is first calculated. The standard cell potential for *reaction 2* can then be determined, and used to calculate a value for $E^{\circ}(F_2/F^{-})$.

(iii) Complete the energy level diagram below to calculate the standard enthalpy change of *reaction 2*, ΔH^{o}_{2} , using relevant data from Table 4.1 and the *Data Booklet*. Label each level with the appropriate formulae and indicate the relevant enthalpy changes next to each arrow.





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The cons	entropy changes for the formation of the stituent elements are shown below.	ne aqueous sodium halide salts from their
1	$Aa(s) + \frac{1}{2}F_2(g) \rightarrow NaF(aq)$	ΔS^{Θ}_{r} (NaF) = -108 J K ⁻¹ mol ⁻¹
١	$Aa(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(aq)$	$\Delta S^{\Theta}_{r}(NaCl) = -48 \text{ J K}^{-1} \text{ mol}^{-1}$
(iv)	Explain why the entropy change for bo	th reactions above are negative.
		[1]
(v)	Using an energy cycle or otherwise, or reaction 2, ΔS°_{2} , using the ΔS°_{r} values	Jetermine the standard entropy change of given above.
		[2]
(vi)	Hence determine the standard Gibbs fr	ee energy change, ΔG^{e_2} , for <i>reaction</i> 2.
		[1]
(vii)	Using your answer in (b)(vi) , calculate hypothetical <i>reaction 2</i> .	e the standard cell potential, E^{e}_{cell} , for the
		[1]
viii)	Hence, calculate the standard electrod E° value from the <i>Data Booklet</i> .	e potential, <i>E</i> ^e (F₂/F⁻), using an appropriate
		[1]

The halogens form oxoacids which have an OH group, accounting for their acidity. Table 4.2 lists some oxoacids of halogens and some of their pK_a values in brackets.

oxoacids of F	oxoacids of Cl	oxoacids of Br	oxoacids of I
H ^O F	H ^O Cl	H ^O Br	H∕ ^O ∕I
HFO	HC/O (7.54)	HBrO (8.55)	HIO (10.5)
	0−C <i>l</i> H O HC <i>l</i> O ₂ (1.95)		
	О-С/ НО НС/О₃ (−1)	O−Br H O HBrO₃	O−I HO3
	,0 ,0−C/=0 H 0 HC/04 (=8)	O−Br=O H O HBrO₄	

Table 4.2

(c) (i) Suggest why oxoacids of fluorine with more than one oxygen do not exist.

.....

(ii) Suggest a reason why

I pK_a decreases down the second column of Table 4.2 for the oxoacids of C*l*.

.....[1]

II pK_a increases across the first row of Table 4.2 for HC/O, HBrO and HIO.

(d) The relative stabilities of various chlorine-containing species with *Cl* in different oxidation states can be summarised in a Latimer diagram. The chlorine-containing species in the diagram include oxoacids and their conjugate bases, the oxoanions.

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The Latimer diagram for chlorine in acidic medium is shown below.

The value on each arrow shows the standard electrode potential, E° (in V), of the two connected species, and the number below each species is the oxidation state of C*l* in the species.

For example, the diagram shows that $E^{\oplus}(C/O_4^-/C/O_3^-)$ is +1.20 V and $E^{\oplus}(C/O_3^-/HC/O_2)$ is +1.18 V.

(i) What is the pH of acidic solutions when measuring **standard** electrode potentials?

.....[1]

(ii) In the diagram above, the reduction of chloric acid HC/O₃ in acidic medium is given as C/O₃⁻ → HC/O₂ rather than HC/O₃ → HC/O₂.

Suggest why this is so by calculating the ratio of $[ClO_3^-]$ to $[HClO_3]$ at the pH found in **(d)(i)**, using appropriate data from Table 4.2.

[1]

(iii) The Latimer diagram for chlorine in basic medium is shown below.

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A disproportionation reaction is one whereby a single species is both oxidised and reduced.

Calculate relevant standard cell potentials to determine whether Cl_2 disproportionates to its two neighbours in the Latimer diagram more readily in the acidic medium or in the basic medium.

- [2]
- (iv) Hence comment on how the E° values on the right and left of a species in the Latimer diagram shows its tendency to disproportionate into its two neighbours.

.....[1]

(v) Based on the two Latimer diagrams given, chlorine-containing species with C*l* in **one** particular oxidation state can disproportionate spontaneously in **both** acidic and basic mediums.

Use your answer in (d)(iv) to predict this oxidation state of Cl.

[1].....[1] [Total: 25]