HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		CT GROUP	20S
CENTRE NUMBER		INDEX NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

25 August 2021

2 hours

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.

For Examiner's Use		
1		/ 16
2		/ 18
3		/ 16
4		/ 25
Deductions	s.f.	
	units	
Total		/ 75

This document consists of **18** printed pages.

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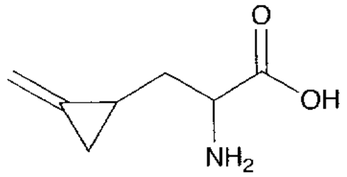
Answer **all** the questions in the spaces provided.

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; $C_7H_{11}O_2N$

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

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

....

....

....

....[2]

(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]

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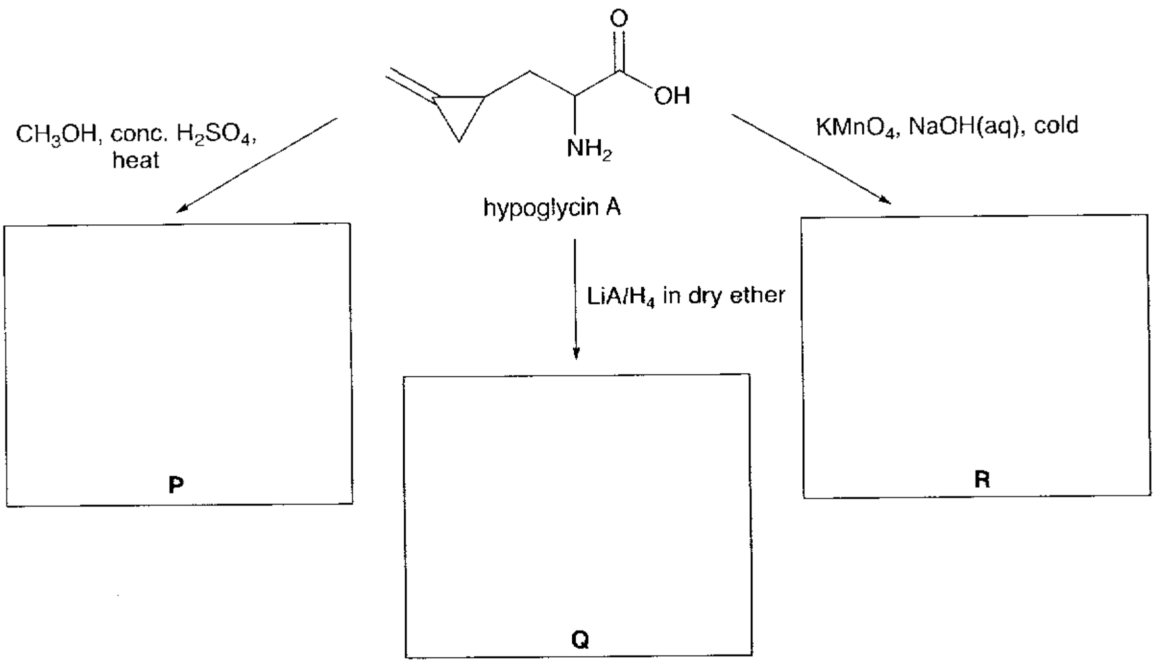
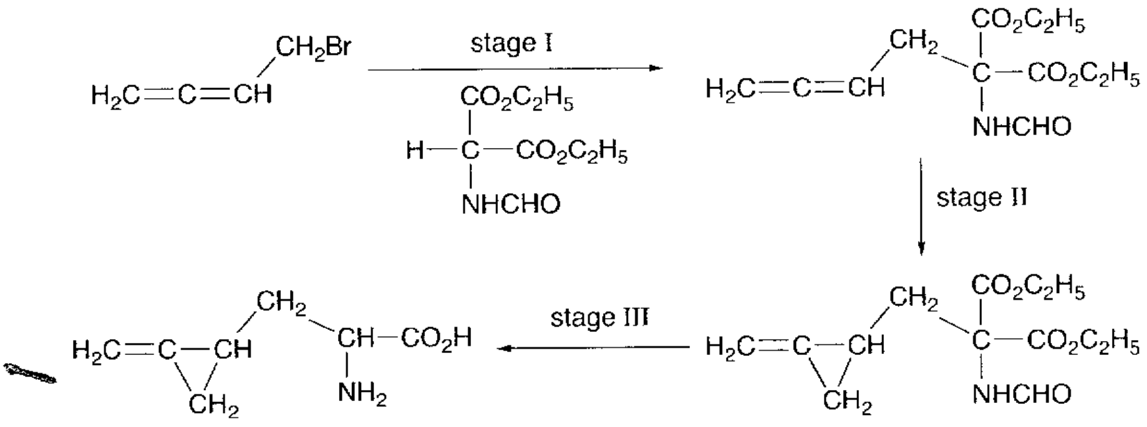
(b) Draw the structures of the major organic products, **P**, **Q** and **R**, when hypoglycin A reacts with each of the following reagents.



[3]

(c) Hypoglycin A can be synthesised from a 3-stage process.



hypoglycin A

(i) In the journal article where this synthesis was first published, stage I was described as a "condensation" reaction. Identify the small molecule that was produced.

....[1]

(ii) Suggest the *type of reaction* that occurs in stage II.

....[1]

(iii) In stage III, one of the two $-CO_2C_2H_5$ groups in the intermediate compound is lost. State the *type of reaction* the **other** $-CO_2C_2H_5$ group undergoes to obtain hypoglycin A.

....[1]

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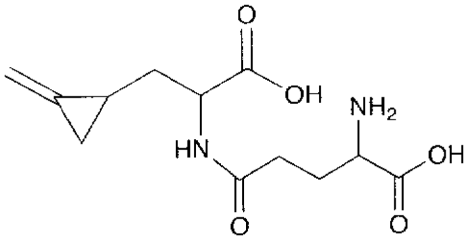
(iv) A by-product of stage III is methanoic acid, HCO_2H. Draw a dot-and-cross diagram of a molecule of methanoic acid.

[1]

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



hypoglycin B

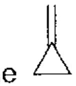
Suggest reagents and conditions to hydrolyse hypoglycin B in the laboratory and draw the organic products formed.

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  group and has a molecular formula of $C_6H_8O_2$.
- It has only one chiral centre and gives effervescence with $NaHCO_3(aq)$.
- No carbon atom in MCPA is bonded to four other carbon atoms.

Suggest a structure for MCPA.

[1]
[Total: 16]

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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.

element	C	Si	Ge	Sn	Pb
mp / °C	>3550	1410	937	232	327

Suggest, in terms of structure and bonding, why carbon has a higher melting point than tin.

....

....

....

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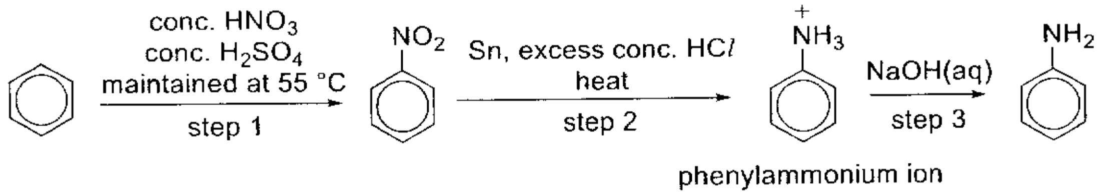
....

....[3]

Benzene can be converted into phenylamine in 3 steps.



(b) **(i)** State the role of H_2SO_4 in the formation of NO_2^+ during step 1.

....[1]

(ii) Identify the *type of mechanism* involved in step 1.

....[1]

As with most organic reactions, the yield of steps 1 and 2 is less than 100%, resulting in a 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]

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(c) Explain why nitrobenzene has a higher boiling point than water.

....

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....

....

....[2]

(d) $[SnCl_6]^{2-}$ ions are formed together with phenylammonium ions in step 2.

By considering the changes in the oxidation number of tin, construct a half-equation to illustrate the formation of $[SnCl_6]^{2-}$ in step 2.

....[1]

(e) **(i)** Explain, in terms of their structures, why phenylamine is a weaker base than ethylamine.

....

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....

....

....[2]

(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, $[SnCl_6]^{2-}$ 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.

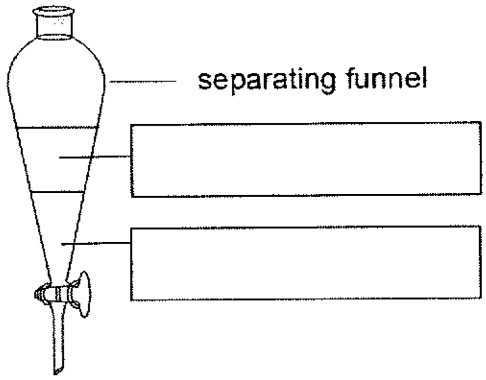
Phenylamine is more soluble in ethyl acetate than in water.

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

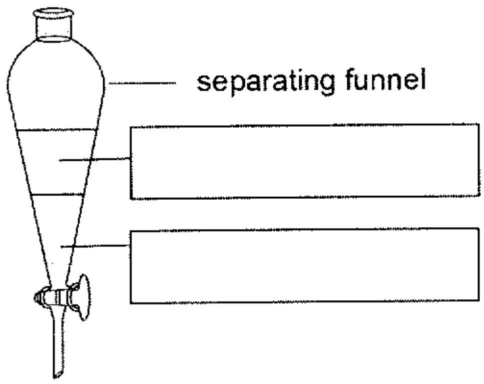
In the boxes below, indicate the locations of

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

After step 2:



After step 3:



[2]

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

....

....

....[2]

(g) Phenylamine reacts with acyl chlorides at a faster rate than with alkyl chlorides.

Give **two** reasons to explain the different reactivities of acyl chlorides and alkyl chlorides.

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....

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....[2]

[Total: 18]

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3 (a) Chalcopyrite is a mineral from which copper is commonly extracted. Its formula is $CuFeS_2$ 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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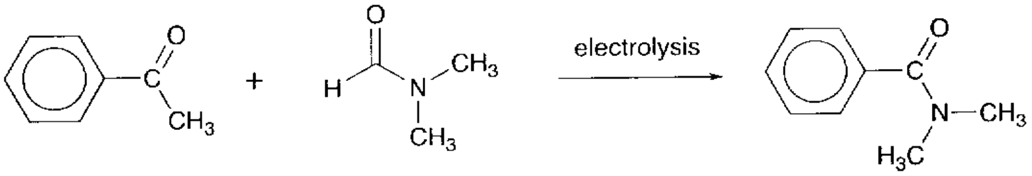
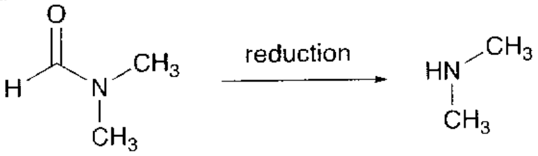
(b) Electrolysis can also be applied to organic synthesis due to its mild conditions and green potential. In 2013, chemists in Guangzhou, China, developed an electrosynthesis method to obtain amides from methyl ketones and formamides. A typical reaction is shown below.

reaction 1



a methyl ketone a formamide an amide product

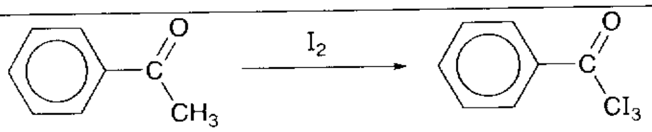
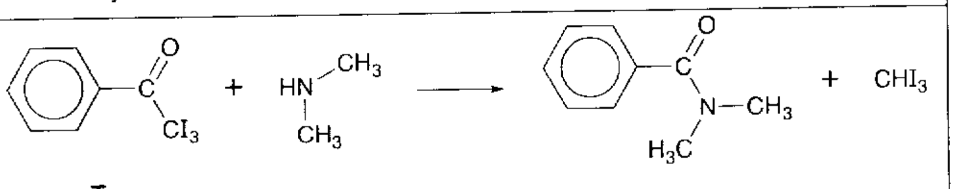
The synthesis occurs in a cell fitted with inert graphite and nickel electrodes. A solution of the reactants and sodium iodide dissolved in organic solvent is used as the electrolyte. The reactions occurring at the electrodes are:

graphite:	$2I^- \longrightarrow I_2$
nickel:	 the formamide amine

(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:

a	 the methyl ketone **T**
b	 **T**

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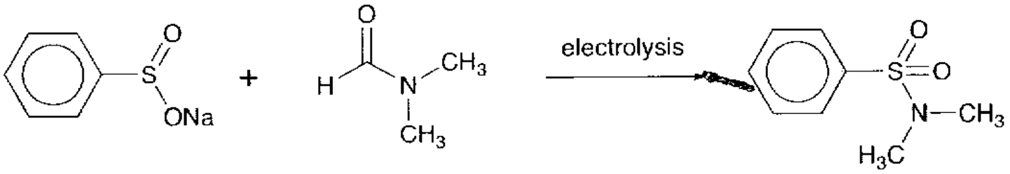
Conversion **b** occurs via a three-step mechanism.

- 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 CHI_3 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.

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....[1]

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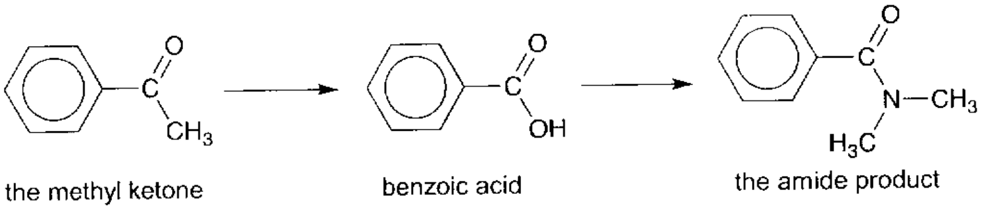
(iv) The amide product in *reaction 1* can also be synthesised using traditional organic synthesis methods from the same methyl ketone, via benzoic acid as an intermediate compound.



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:

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II:

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....[5]

[Total: 16]

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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 $E^\ominus$ values.

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....[2]

(b) Unlike the other halogens, the standard electrode potential for the reduction of $F_2(g)$ to $F^-(aq)$, $E^\ominus(F_2/F^-)$, cannot be determined by direct measurement in aqueous medium.

(i) Explain what is meant by the term *standard electrode potential*.

....

....

....

....[1]

(ii) Using relevant $E^\ominus$ values from the *Data Booklet*, suggest why $E^\ominus(F_2/F^-)$ cannot be measured directly in the aqueous medium.

....

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....

....

....

....[2]

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

reaction 2 $2Cl^-(aq) + F_2(g) \rightarrow Cl_2(g) + 2F^-(aq)$

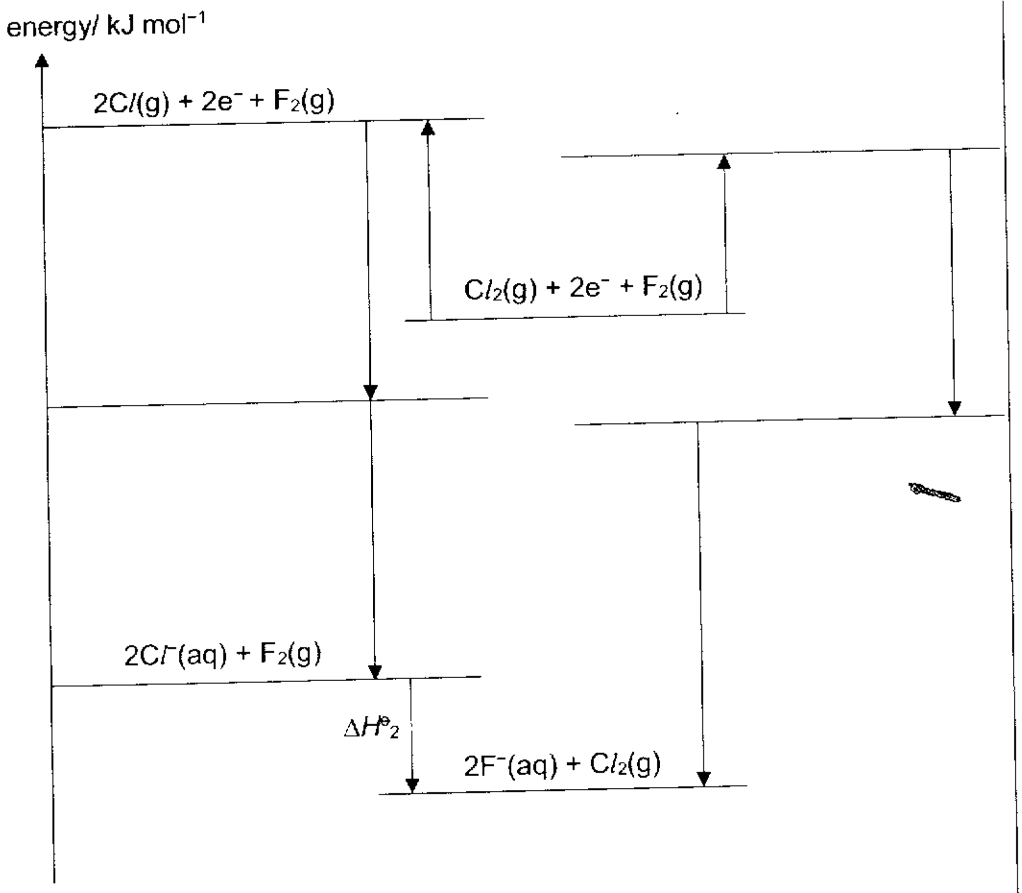
The standard Gibbs free energy change for *reaction 2*, $\Delta G^\ominus_2$, is first calculated. The standard cell potential for *reaction 2* can then be determined, and used to calculate a value for $E^\ominus(F_2/F^-)$.

(iii) Complete the energy level diagram below to calculate the standard enthalpy change of *reaction 2*, $\Delta H^\ominus_2$, 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.

Table 4.1

	fluorine	chlorine
first electron affinity of *X(g)/ kJ mol^{-1}	−328	−349
standard enthalpy change of hydration of X^-(g)/ kJ mol^{-1}	−504	−361

*X denotes the halogen fluorine or chlorine



$\Delta H^\ominus_2$ = ______________ kJ mol^{-1}

[4]

The entropy changes for the formation of the aqueous sodium halide salts from their constituent elements are shown below.

$Na(s) + \frac{1}{2}F_2(g) \rightarrow NaF(aq)$ $\Delta S^\ominus_r(NaF) = -108\ J\ K^{-1}\ mol^{-1}$

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(aq)$ $\Delta S^\ominus_r(NaCl) = -48\ J\ K^{-1}\ mol^{-1}$

(iv) Explain why the entropy change for both reactions above are negative.

....

....[1]

(v) Using an energy cycle or otherwise, determine the standard entropy change of *reaction 2*, $\Delta S^\ominus_2$, using the $\Delta S^\ominus_r$ values given above.

[2]

(vi) Hence determine the standard Gibbs free energy change, $\Delta G^\ominus_2$, for *reaction 2*.

[1]

(vii) Using your answer in **(b)(vi)**, calculate the standard cell potential, $E^\ominus_{cell}$, for the hypothetical *reaction 2*.

[1]

(viii) Hence, calculate the standard electrode potential, $E^\ominus(F_2/F^-)$, using an appropriate $E^\ominus$ value from the *Data Booklet*.

[1]

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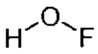
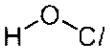
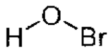
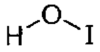
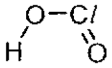
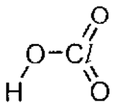
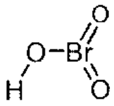
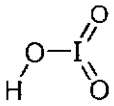
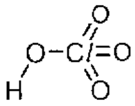
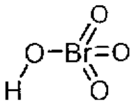
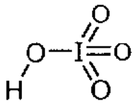
The halogens form oxoacids which have an OH group, accounting for their acidity. Table 4.2 lists some oxoacids of halogens and some of their pK_a values in brackets.

Table 4.2

oxoacids of F	oxoacids of C*l*	oxoacids of Br	oxoacids of I
 HFO	 HC*l*O (7.54)	 HBrO (8.55)	 HIO (10.5)
	 HC*l*O$_2$ (1.95)		
	 HC*l*O$_3$ (−1)	 HBrO$_3$	 HIO$_3$
	 HC*l*O$_4$ (−8)	 HBrO$_4$	 HIO$_4$

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

....

....[1]

(ii) Suggest a reason why

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

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

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....[3]

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(d) The relative stabilities of various chlorine-containing species with C*l* 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.

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

$$\underset{+7}{ClO_4^-} \xrightarrow{+1.20} \underset{+5}{ClO_3^-} \xrightarrow{+1.18} \underset{+3}{HClO_2} \xrightarrow{+1.65} \underset{+1}{HClO} \xrightarrow{+1.67} \underset{0}{Cl_2} \xrightarrow{+1.36} \underset{-1}{Cl^-}$$

The value on each arrow shows the standard electrode potential, $E^\ominus$ (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 $E^\ominus(ClO_4^-/ClO_3^-)$ is +1.20 V and $E^\ominus(ClO_3^-/HClO_2)$ 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 $HClO_3$ in acidic medium is given as $\mathbf{ClO_3^-} \rightarrow HClO_2$ rather than $\mathbf{HClO_3} \rightarrow HClO_2$.

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.

$$\begin{array}{ccccccccccc} ClO_4^- & \xrightarrow{+0.37} & ClO_3^- & \xrightarrow{+0.30} & ClO_2^- & \xrightarrow{+0.68} & ClO^- & \xrightarrow{+0.42} & Cl_2 & \xrightarrow{+1.36} & Cl^- \\ +7 & & +5 & & +3 & & +1 & & 0 & & -1 \end{array}$$

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 $E^\ominus$ 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 Cl 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]

[Total: 25]

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2021 C2 H2 CHEMISTRY PRELIM PAPER 2
SUGGESTED SOLUTIONS

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1 (a) (i) The carboxylic acid functional group is acidic because the negative charge on its conjugate base anion is delocalized equally over two highly electronegative O atoms [1], stabilizing the conjugate base [1].

> This is a recall question. Refer to Section 4.1.1 of Carboxylic Acid & Derivatives lecture notes.
>
> Do read the question carefully. You were asked to explain the acidity of the carboxylic acid functional group. You should not be explaining the effect of the NH_2 group on the acidity of the carboxylic acid group Also, be very specific in the use of terms. You should explain why the conjugate base is stable by considering how well the negative charge is dispersed due to delocalization of negative charge of the conjugate base over 2 highly electronegative atoms. It is incorrect to say that the dispersion of the charge is through inductive effect.

(ii) alkene [1]
primary amine [1] *(note: [½] for "primary", [½] for "amine")*

> This question was well done but many students did not state the type of amine. Do note that N atom is only attached to one carbon chain which makes it a primary amine.

(iii) Hypoglycin A does not show *cis-trans* isomerism because one of the C=C carbon is attached to two identical groups / two hydrogen atoms. [1]

> You should apply the criteria for cis-trans isomerism and explain clearly the structural feature of hypoglycin A that makes it unable to exhibit cis-trans isomerism. In this case, there is a C=C that has restricted rotation but the molecule does not exhibit cis-trans isomerism as one of the carbon atoms is attached to two hydrogen atoms. Be direct in your answer and avoid stating what is missing. For instance, explanation such as "there is no two different groups on each side of C=C" is WRONG and confusing. You should be considering the two groups attached to each C of C=C, i.e. each end of C=C and not each side. It is also incorrect to say "hypoglycin A does not show cis-trans isomerism as there is no restricted rotation of bonds" because one of the criteria for cis-trans isomerism is in fact the presence of such bonds which is present in hypoglycin A (there is restricted rotation about C=C). Some students also recognize that there is restricted rotation about the 3-membered ring. However, one of the carbon atoms of this 3-membered ring has 2 H atoms attached to it and hence cis-trans isomerism is not possible.
>
> Do note that "the presence of chiral carbon" does not give rise to cis-trans isomerism. Instead, it may exhibit enantiomerism.

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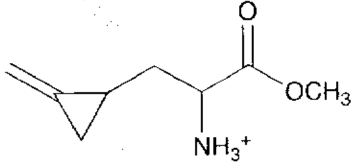
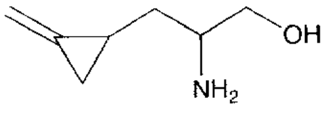
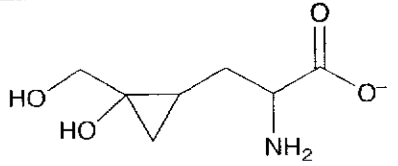
(b)

		
P [1]	**Q** [1]	**R** [1]

When hypoglycin A is heated with CH_3OH in the presence of conc. H_2SO_4 to form **P**, many students were able to recognize that esterification took place and used the carboxylic acid group in hypoglycin A to form an ester with CH_3OH. The presence of conc. H_2SO_4 means the basic NH_2 group in hypoglycin A will be protonated to form NH_3^+.

When hypoglycin A was reacted with $LiAlH_4$ in dry ether to form **Q**, reduction takes place. Only carboxylic acid in hypoglycin A is reduced to form a primary alcohol ($-CO_2H \rightarrow -CH_2OH$). Alkene is not reduced by $LiAlH_4$ in dry ether.

When hypoglycin A was reacted with cold $KMnO_4$ in NaOH(aq) to form **R**, this set of reagent and condition is for mild oxidation of alkene to form a diol. The alkaline medium will also cause the deprotonation of carboxylic acid to form carboxylate ($-CO_2^-$).

(c) **(i)** HBr [1]

By comparing the structures of the reactants and product in stage I, most students were able to see that the small molecule produced is HBr.

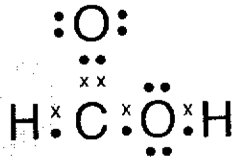
(ii) addition [1]

In stage II, the π bond of one of the C=C bonds was broken and two new σ bonds were formed. This type of reaction is addition.

(iii) hydrolysis [1]

In stage III, there are two $-CO_2C_2H_5$ groups in the reactant. You were told that one of the $-CO_2C_2H_5$ groups was lost and asked to state the type of reaction for the other $-CO_2C_2H_5$ group. From the product, you should be able to see that the other $-CO_2C_2H_5$ group was converted to $-CO_2H$. Hence the ester is hydrolysed to form carboxylic acid and the type of reaction is hydrolysis.

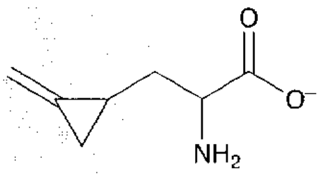
(iv)



[1]

Generally well done. You were told to draw the dot-and-cross diagram of molecular HCO_2H. Do remember to put in the lone pairs on the oxygen atoms.

(d) dilute NaOH, heat (with reflux)



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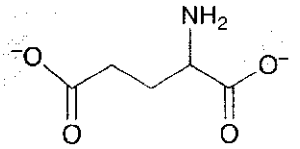
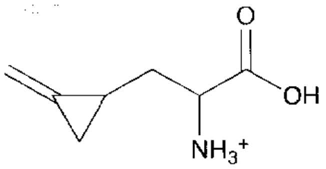
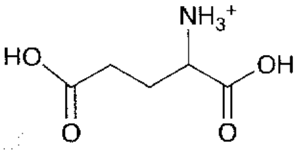


OR

dilute H_2SO_4, heat (with reflux)

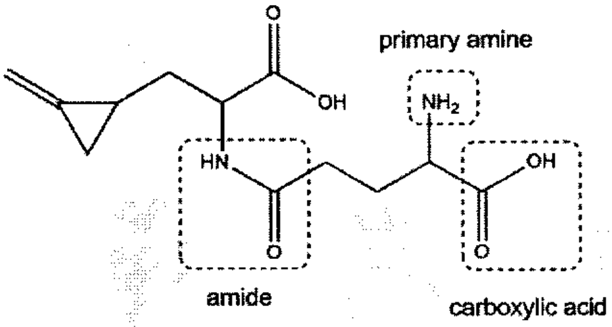


and



[1] for correct reagent and condition *(do not accept "enzyme")*
[1] for each correct product *(must be correctly protonated or deprotonated)*

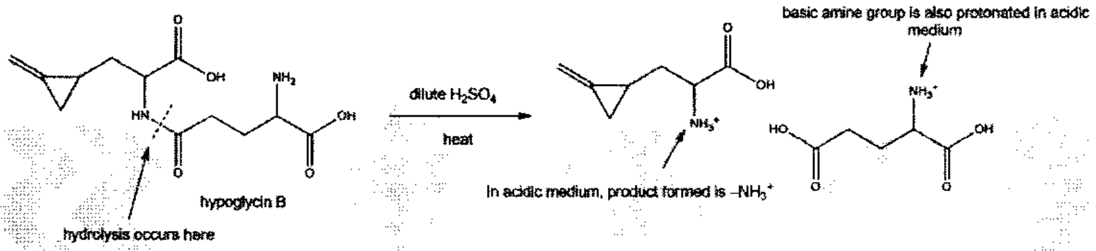
Hypoglycin B contains an amide functional group that can be hydrolysed. The other nitrogen atom on the right is not directly attached to C=O. This nitrogen-containing group is a primary amine and it is next to a carboxylic acid.



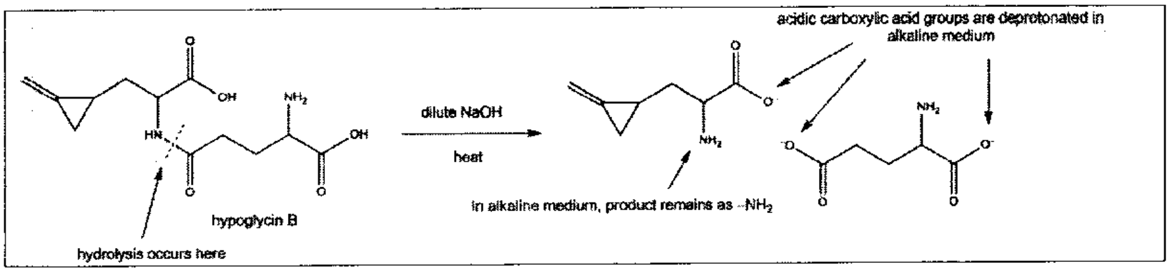
hypoglycin B

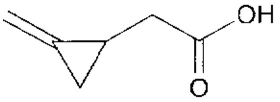
Hydrolysis of the amide should be conducted in an acidic or alkaline medium and with heating.

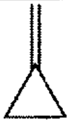
In acidic medium:



In alkaline medium:



(e)  [1]

You were told that the  group is retained. Hence there should not be any substituent attached to C=C in MCPA, just like hypoglycin A and hypoglycin B. This group accounts for 4 carbon atoms. Since MCPA gives effervescence with $NaHCO_3$, it contains $-CO_2H$ functional group which accounts for the 2 oxygen atoms. There is one last carbon atom to be accounted for and there can only be one chiral centre in the molecule. Hence MCPA has a $-CH_2CO_2H$ group attached to  as shown in the answer (the chiral centre is the carbon on the cyclopropane ring bonded to the $-CH_2CO_2H$ group.)

2 **(a)** More energy **[1]** **is** required to break covalent C–C bonds **[0.5]** in giant covalent **[0.5]** lattice of carbon than to break metallic bonding **[0.5]** between tin cations and sea of delocalised electrons in giant metallic **[0.5]** lattice of tin.

It was indicated under Group 14 on page 52 of the *Data Booklet* that carbon is covalent whereas tin is metallic. As covalent compounds can be either giant covalent or simple covalent, candidates were expected to know that carbon has a **giant** covalent structure due to a relatively high melting point. The question did **not** specify carbon as graphite or diamond, candidates were expected to simply state the general structure and bonding of carbon: giant molecular and covalent C–C bonds.

The question asked for "structure and bonding", candidates should address the question. There should be two "structures" and two "bondings" for C and Sn, so in total four points should be mentioned, but some candidates missed out at least one out of the four.

A number of candidates did **not** show understanding of the definition of covalent bonding, **incorrectly** stating that covalent bonding occurs between the carbon "molecules". In fact, the covalent bonding occurs between the carbon **atoms**, which is the electrostatic forces of attraction between the positively charged nucleus of both the bonded atoms and their shared pair of electrons.

A number of candidates did **not** show understanding of the definition of intermolecular forces of attraction, which is the forces of attraction between simple covalent molecules. Melting or boiling involves breaking covalent bonding in substances with giant covalent structure. For simple covalent molecules, it involves overcoming intermolecular forces of attraction between the molecules.

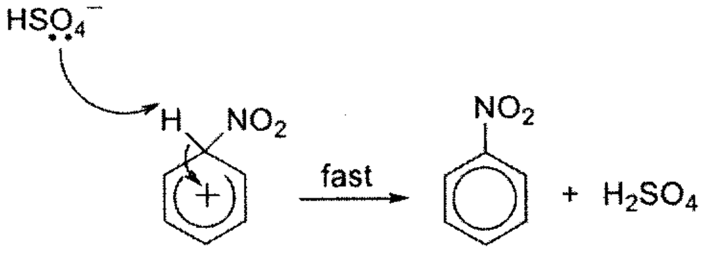
(b) **(i)** H_2SO_4 is a stronger Bronsted acid / proton donor **[1]** than HNO_3, hence the protonation of HNO_3 by H_2SO_4 eventually produces a strong electrophile NO_2^+.

As part of the learning outcomes under Topic 12 Arenes of the H2 Chemistry syllabus, candidates are required to recognise that concentrated sulfuric acid acts as a Bronsted-Lowry acid catalyst in the nitration of arenes with concentrated nitric acid.

In the following equation for the reaction between H_2SO_4 and HNO_3, as H_2SO_4 is a stronger Bronsted acid than HNO_3, H_2SO_4 protonates HNO_3 and the electrophile NO_2^+ is formed.

$$2H_2SO_4 + HNO_3 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

In part of the mechanism for electrophilic substitution as shown below, HSO_4^- deprotonates the intermediate and catalyst H_2SO_4 is regenerated.



Note that the question was specific in asking for the role of H_2SO_4 in the formation of NO_2^+, and **not** its role in the electrophilic substitution mechanism.

(ii) Electrophilic substitution **[1]**

As the delocalised π electron cloud in benzene is electron-rich, it attracts electrophiles (electron-deficient species) like NO_2^+. Although benzene is unsaturated, it does not undergo electrophilic addition like alkenes. As a result of the resonance stabilisation due to the delocalisation of the π electron cloud, benzene undergoes electrophilic substitution where one or more hydrogen atoms can be substituted by electrophiles. Electrophilic addition destroys the delocalised π electron cloud and this requires a significant amount of energy, which is highly unfavourable. Benzene preferentially undergoes electrophilic substitution reactions, which preserve its aromaticity.

(b) **(iii)** Distillation **[1]**

Using the data in Table 2.1, both benzene and nitrobenzene are liquids at room temperature and pressure and since the difference in boiling points of benzene and nitrobenzene is large, a simple distillation can be employed to separate them. Since benzene has a much lower boiling point than nitrobenzene, benzene will be distilled over first followed by nitrobenzene, thus the desired nitrobenzene product should be collected in a separate clean flask after benzene is completely distilled over. As the boiling point of nitrobenzene is above that of water, an oil bath should be employed. The following is the experimental setup for a simple distillation:

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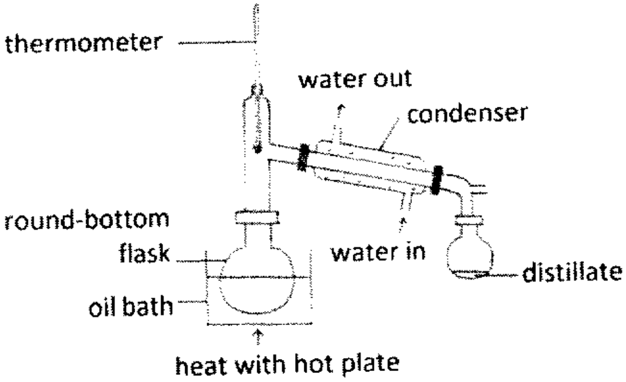


Although fractional distillation was accepted as an answer, it is unnecessary to employ a fractionating column as the difference in boiling points of benzene and nitrobenzene is greater than 10 °C. Note that fractional distillation is usually employed when the difference in boiling points of two liquids is less than 10 °C. You may wish to refer to Topic 8 Lecture Notes Section 6.2.2 on separation and purification techniques.

Furthermore, prior to carrying out the simple distillation, H_2SO_4 and HNO_3 must be separated from the benzene-nitrobenzene mixture using a separating funnel. This is possible because H_2SO_4 and HNO_3 are soluble in water whereas benzene and nitrobenzene are insoluble in water, thus giving rise to two immiscible layers that can be separated.

Some candidates suggested heating to boil off benzene and this is a bad idea. Firstly, most organic compounds are flammable, producing a flammable organic gas results in a potential fire hazard. Secondly, benzene is carcinogenic, converting and retaining it as a gas poses a potential health hazard.

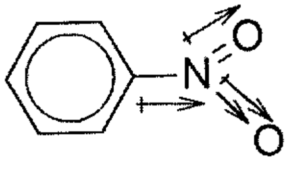
(c) Nitrobenzene has a larger electron cloud / more electrons than water. **[0.5]**

More energy **[0.5]** is required to break stronger dispersion forces **[0.5]** between nitrobenzene molecules than hydrogen bonding between water molecules.

[0.5] for mention of "intermolecular" or "between molecules" for nitrobenzene
Minus 0.5 if no comparison term used

As nitrobenzene has a simple covalent structure, boiling breaks intermolecular forces of attraction between nitrobenzene molecules. Note that boiling nitrobenzene does **not** result in breaking of its covalent bonds.

As the electronegativity of O>N>C and the electronegativity difference between C and H is relatively negligible, the dipole moments (represented by ⟼) in nitrobenzene are shown below:



Since the geometry about the central N atom is trigonal planar, nitrobenzene is polar as it has a net dipole moment. Polar nitrobenzene can form permanent dipole-permanent dipole interactions between its molecules. As nitrobenzene contains a large number of electrons, it can also form significant dispersion forces between its molecules.

Nitrobenzene does **not** have a H atom bonded to N/O/F and does **not** form hydrogen bonds. Water forms hydrogen bonds and as each hydrogen bond is formed between H atom (attached to N/O/F) and lone pair on highly electronegative atom (N/O/F), hydrogen bonding is generally stronger than permanent dipole-permanent dipole interactions due to a greater net dipole moment. Water is more polar than nitrobenzene, hence hydrogen bonding between water molecules is stronger than permanent dipole-permanent dipole interactions between nitrobenzene molecules. Therefore, permanent dipole-permanent dipole interactions between nitrobenzene molecules alone cannot be the reason to explain the higher boiling point of nitrobenzene as compared to water.

Each nitrobenzene molecule has 64 electrons whereas each water molecule has 10 electrons, hence the nitrobenzene molecule has a much larger electron cloud than the water molecule. Therefore, dispersion forces between nitrobenzene molecules is stronger than that between water molecules. Note that hydrogen bonding is the more significant intermolecular attraction between water molecules. Hence, stronger dispersion forces between nitrobenzene molecules is the main reason why nitrobenzene has a higher boiling point than water.

(d) $\text{Sn} + 6\text{C}l^- \rightarrow [\text{SnC}l_6]^{2-} + 4e^-$ **[1]**

With reference to the reactants provided in step 2, the oxidation number of Sn changes from 0 in Sn to +4 in $[\text{SnC}l_6]^{2-}$.

Since Sn is the element that is oxidised, the oxidation state of chlorine remains at −1. So to balance the half-equation from Sn to $[\text{SnC}l_6]^{2-}$, 4 electrons are lost and 6 $\text{C}l^-$ are required on the left to give:

$$\text{Sn} + 6\text{C}l^- \rightarrow [\text{SnC}l_6]^{2-} + 4e^-$$

What actually happened during the reaction is as follows:

From the *Data Booklet*,

$\text{Sn}^{2+} + 2e^- \rightleftharpoons \boxed{\text{Sn}}$ −0.14

$\text{Sn}^{4+} + 2e^- \rightleftharpoons \boxed{\text{Sn}^{2+}}$ +0.15

Nitrobenzene and Sn reacts to produce phenylammonium ion and Sn(IV) via two redox reactions. The redox reaction between nitrobenzene and Sn produces phenylammonium ion and Sn^{2+}. Subsequently, the redox reaction between nitrobenzene and Sn^{2+} produces phenylammonium ion and Sn^{4+}. However, the presence of excess $\text{C}l^-$ from the concentrated hydrochloric acid in the reaction mixture results in the formation of the complex ion $[\text{SnC}l_6]^{2-}$ where $\text{C}l^-$ serve as ligands and Sn^{4+} is the central metal ion.

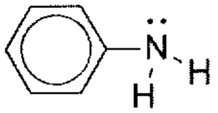
(e) **(i)** The lone pair of electrons on the N atom of phenylamine is delocalised into the benzene ring and hence it is less available for protonation. **[1]** This decreases the electron density on N. (or p orbital on N overlap with pi e cloud of benzene)

The lone pair of electrons on the N atom of ethylamine is made more available for protonation by the presence of the electron-donating ethyl group **[1]** which increases the electron density on N.

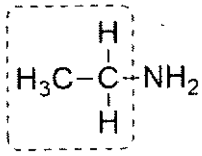
Candidates were expected to indicate what the lone pair on nitrogen was being made available for. In this case, the lone pair on nitrogen was made available for donation to proton.

It is **incorrect** to say that the lone pair on nitrogen of phenylamine is not available. Lone pair on nitrogen of phenylamine is less available than ethylamine but still available as it is still basic. This is in comparison to the lone pair on nitrogen of an *amide*, which is not available because an amide is **not** basic.

Based on the structure of phenylamine, there is only one lone pair on the nitrogen atom of a phenylamine molecule, so it is **incorrect** to say there are "lone pairs" on the nitrogen atom.



Based on the structure of ethylamine, there is only one electron-donating ethyl group on the nitrogen atom of an ethylamine molecule, so it is **incorrect** to say there are "electron donating alkyl groups" on the nitrogen atom.



$$H_3C-\overset{H}{\underset{H}{C}}-NH_2$$

one alkyl group

(ii) Favourable ion-dipole interactions formed between phenylammonium ions and water molecules. **[1]**

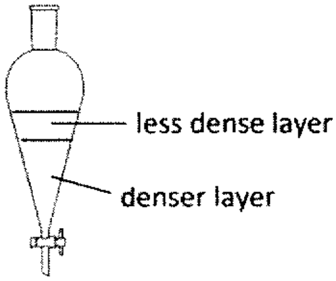
Salt is a general term for a chemical compound consisting of cations and anions. An example of a phenylammonium salt is phenylammonium chloride, $C_6H_5NH_3Cl$, which is an ionic compound with strong electrostatic forces of attractions between oppositely charged $C_6H_5NH_3^+$ and Cl^- ions. Solid phenylammonium chloride dissolves in water because $C_6H_5NH_3^+$ and Cl^- ions form strong ion-dipole interactions with water molecules. While based on the definition of hydrogen bonding, candidates may expect the H bonded to N in $C_6H_5NH_3^+$ to form hydrogen bonds with O of H_2O, the solubility of the salt is due to interaction between **both** cation and anion with water and hence hydrogen bonding was not accepted as the anion (Cl^-) can only form ion-dipole interaction with water.

The energy released from the ion-dipole interactions between $C_6H_5NH_3^+$ ions and water molecules as well as between Cl^- ions and water molecules is able to overcome ionic bonding between solid $C_6H_5NH_3^+$ and Cl^- ions and hydrogen bonding between water molecules.

(iii) After step 2,
Top layer: phenylammonium ion
Bottom layer: nitrobenzene
[1]

After step 3,
Top layer: phenylamine
Bottom layer: $[SnCl_6]^{2-}$
[1]

Using the data in Table 2.1, nitrobenzene is a liquid at room temperature and pressure.
Given nitrobenzene is insoluble in water from the table provided whereas phenylammonium ion is soluble in water from 2(e)(ii), nitrobenzene and water containing dissolved phenylammonium ion will form two immiscible layers in a separating funnel. As the density of water is less than nitrobenzene, water containing the dissolved phenylammonium ion will form an immiscible layer above the nitrobenzene layer. For your information, a filtration to remove solid Sn is necessary before the use of the separating funnel.



Step 3 involves the deprotonation of phenylammonium ion (the conjugate acid of phenylamine) by a strong base NaOH(aq) to give phenylamine via an acid-base reaction. After the addition of NaOH(aq), the phenylammonium ion is converted to phenylamine.

Phenylamine is more soluble in ethyl acetate than in water and hence phenylamine formed dissolved in ethyl acetate while the ionic $[SnCl_6]^{2-}$ remains dissolved in water. Since ethyl acetate in insoluble in water, two immiscible layers are obtained with the less dense ethyl acetate layer on top and water with higher density at the bottom. Hence the top layer contains phenylamine and the bottom layer contains $[SnCl_6]^{2-}$.

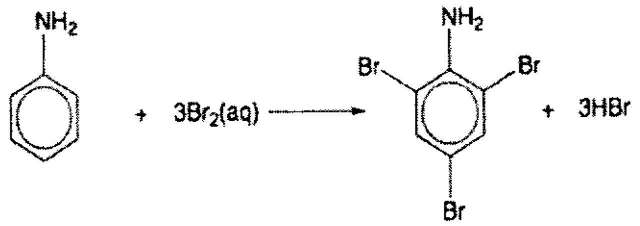
For your information, subsequent removal of the solvent ethyl acetate (usually using a rotary evaporator) from the ethyl acetate-phenylamine mixture will give the pure phenylamine. You may wish to refer to Topic 8 Lecture Notes Section 6.2.2 on separation and purification techniques.

(f) Add Br_2(aq). **[1]**

Yellow-orange Br_2(aq) solution will decolourise **[0.5]**
and white ppt of 2,4,6-tribromophenylamine will form. **[0.5]**

As part of the learning outcomes under Topic 19 Nitrogen compounds of the H2 Chemistry syllabus, candidates are required to describe the reaction of phenylamine with **aqueous** bromine.

In phenylamine, the lone pair of electrons on the nitrogen atom is delocalised into the benzene ring, the electron density in the ring is greatly increased, making phenylamine much more susceptible to electrophilic attack than benzene. Hence, the presence of the $-NH_2$ group highly activates the benzene ring towards electrophilic substitution.



NH_2 group on benzene is 2,4-directing and strongly activating. Hence tri-substitution takes place to form 2,4,6-tribromophenylamine which is insoluble in water and hence a white precipitate will be observed.

White fumes of HBr(g) may **not** be observed as HBr(g) dissolves in aqueous solution.

Some candidates realised phenol will give the same observations with aqueous bromine producing the white ppt 2,4,6-tribromophenol instead, and thus suggested using neutral $FeCl_3$(aq), on top of Br_2(aq), in a separate test to show that the absence of violet colouration with neutral $FeCl_3$(aq) but decolourisation of yellow-orange Br_2(aq) and white ppt formation would confirm the presence of phenylamine. While this answer was accepted, do note that the question asked for "a simple chemical test", hence the suggestion of using neutral $FeCl_3$(aq), on top of Br_2(aq), would meant two chemical tests that may be a basis for the rejection of the answer.

Although **not** written in the learning outcomes under Topic 19 Nitrogen compounds of the H2 Chemistry syllabus, some candidates suggested the decolourisation of reddish brown liquid bromine and the formation of white fumes of HBr(g) as a suitable chemical test. Similar to phenol, phenylamine may react with liquid bromine to give 2-bromophenylamine and 4-bromophenylamine as major products. However, the use of aqueous bromine is a better answer than the use of liquid bromine due to multiple aspects. Firstly, the reaction of phenylamine with aqueous bromine is part of the learning outcomes under Topic 19 but not for liquid bromine. Secondly, decolourisation of liquid bromine occurs with alkenes as well, while the two obvious observations (decolourisation and white ppt) with the use of aqueous bromine will make it unique for the confirmation of phenylamine (and phenol). Thirdly, liquid bromine is a fuming liquid producing toxic brown bromine gas, making it difficult to handle as compared to aqueous bromine.

(g) The acyl chloride is more reactive towards nucleophile (phenylamine) than chloroalkane (alkyl chloride).

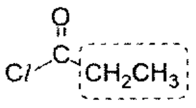
This is because the acyl carbon is more electron-deficient due to two electronegative atoms O and Cl but chloro-substituted carbon in chloroalkane is less electron-deficient due to only one electronegative Cl atom. **[1]**

The trigonal planar geometry around the acyl carbon also makes it less hindered for the nucleophile to attack but the tetrahedral geometry around the chloro-substituted carbon in chloroalkane makes it relatively more hindered towards nucleophilic attack. **[1]**

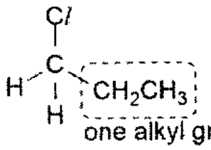
As the common reactant is phenylamine, the different reactivities refers to acyl chloride being more susceptible to nucleophilic attack than chloroalkane. Acyl chloride, being more reactive than chloroalkane, reacts with phenylamine (nucleophile) via nucleophilic acyl substitution (condensation). Chloroalkane reacts with phenylamine (nucleophile) via nucleophilic substitution. Although nucleophilic acyl substitution and nucleophilic substitution are different reaction mechanisms, they both involve a nucleophilic attack on the acyl chloride/chloroalkane. (Refer to Topic 18 Lecture Notes Section 4.2 for nucleophilic acyl substitution, Topic 13 Lecture Notes Section 3.1.1 for bimolecular nucleophilic substitution and unimolecular nucleophilic substitution.) It is **incorrect** to compare the rate of "hydrolysis" as the nucleophile is phenylamine, neither water nor $OH^-(aq)$.

Since the common nucleophile is phenylamine, you should compare the electron-deficient carbon in the acyl chloride and chloroalkane. The two reasons require the consideration of both the electronic effect (electron deficiency of the reacting carbon in attracting electron-rich nucleophile) and the steric effect (the geometry about the reacting carbon for the ease of the approach by the nucleophile).

The most common misconception is stating that chloro-substituted carbon in chloroalkane is less electron-deficient due to electron-donating alkyl group, without considering the presence of an electron-donating alkyl group on the acyl carbon as well. For example, the acyl chloride and chloroalkane below each has an alkyl group attached to the electron-deficient carbon. Note that the primary chloroalkane on the right will undergo bimolecular nucleophilic substitution.

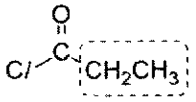


one alkyl group

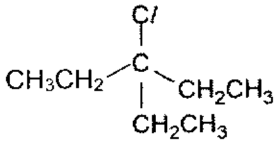


one alkyl group

In the following example, while it is correct that two additional electron-donating alkyl groups will make the electron-deficient carbon in chloroalkane less electron-deficient, the question generally compares acyl chloride with chloroalkane without the mention of whether to compare with a primary, secondary or tertiary chloroalkane or even CH_3Cl. Therefore the obvious difference would be the electron-withdrawing C=O group or electronegative O atom in acyl chloride which is absent in chloroalkane.



one alkyl group



three alkyl groups

3 (a) $Cu^{2+} + 2e \rightleftharpoons Cu$ $E^\ominus = +0.34$ V
$Fe^{2+} + 2e \rightleftharpoons Fe$ $E^\ominus = -0.44$ V
$Ag^+ + e \rightleftharpoons Ag$ $E^\ominus = +0.80$ V

At the anode,

Cu metal is oxidized to form $Cu^{2+}(aq)$ ions and dissolves into the electrolyte:
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e$

As $E^\ominus(Fe^{2+}/Fe)$ is more negative than $E^\ominus(Cu^{2+}/Cu)$, Fe is more readily oxidized than Cu and will also dissolve at the anode into the electrolyte:

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$Fe(s) \rightarrow Fe^{2+}(aq) + 2e$

$E^{\ominus}(Ag^+/Ag)$ is more positive than $E^{\ominus}(Cu^{2+}/Cu)$, Ag is less readily oxidized than Cu and will not dissolve. It falls to the bottom of the cell as anode sludge.

At the cathode,

Cu^{2+} is preferentially reduced and deposited onto the pure Cu cathode:
$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

As $E^{\ominus}(Fe^{2+}/Fe)$ is more negative than $E^{\ominus}(Cu^{2+}/Cu)$, Fe^{2+} is less readily reduced than Cu^{2+} and will remain in the electrolyte as aqueous ions.

[1] correct explanation for Ag
[2] correct reactions and explanations for Cu and Fe
[1] relevant $E^{\ominus}$ values quoted and correct state symbols for all species

This question comes directly from the syllabus learning outcome, testing your understanding of the process of electrolytic purification of copper. Refer to the lecture notes for the explanation and try to understand this process if you did not do well for this question.

How to quote E° values: Write either "$E^{\ominus}(Cu^{2+}/Cu) = +0.34$ V" or write the half-*equilibrium* with the value on the right, as shown above. Do **not** use the "→" arrow unless the reaction *actually* occurs at the electrodes. Several answers contradicted themselves when writing "$Ag^+ + e \rightarrow Ag$" while explaining Ag does not oxidise.

Bear in mind the $E^{\ominus}$ values given in your data booklet are *solely* for the half-equilibria *as they are written in the data booklet*. Do **not** switch the equilibrium around or change the sign of $E^{\ominus}$.

Use "$Cu^{2+} + e^- \rightleftharpoons Cu$ $\quad E^{\ominus} = +0.34$ V"
Avoid "$Cu \rightleftharpoons Cu^{2+} + e^-$ $\quad E^{\ominus} = +0.34$ V"

Which $E^{\ominus}$ values to quote: Credit is given for *relevant* $E^{\ominus}$ values quoted. $E^{\ominus}(Fe^{2+}/Fe)$ should be the one used in this answer since Fe has a greater tendency to oxidise to Fe^{2+} than to Fe^{3+} as $E^{\ominus}(Fe^{2+}/Fe)$ is more negative than $E^{\ominus}(Fe^{3+}/Fe)$. Some answers quoted $E^{\ominus}$ values related to water, oxygen or hydrogen, which are not relevant in this explanation, as the focus is on why the two impurity metals can be removed. The voltage applied in this process is such that it is sufficient to drive the oxidation of Cu at the anode and the reduction of Cu^{2+} at the cathode. Our task is to explain how such a design will elegantly remove metals that are either more or less reactive than Cu.

The question first asks to "describe the electrode reactions that take place". The best way to describe the reaction is to write the half equations (with the "→" arrow) and its state symbols. If you describe in words, make sure all the details from the half-equation and state symbols are included. Statements like "Cu is oxidized" are incomplete as the product is unknown and there are no state symbols. Also, both reactions of Cu and Fe at the anode must be described.

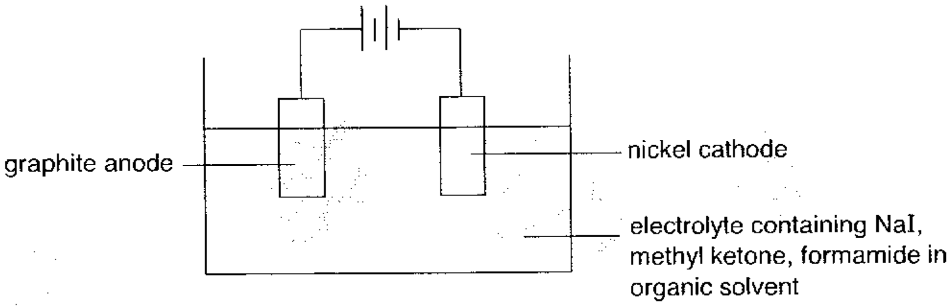
Some candidates seem to consider Fe removed just because it dissolves at the anode. This is **incorrect** because, now that Fe^{2+} is in the electrolyte, Fe^{2+} may reduce at the cathode to become Fe and hence be mixed with the pure Cu! The considerations at the cathode must be taken into account for this purification to work.

How to compare $E^\ominus$ values: It is essential to use "more negative/positive" or "less negative/positive" like in the answer above. Writing "higher/larger/smaller/lower" instead only makes your answer ambiguous as $E^\ominus$ values can be negative or positive. This is the same for terms like ΔH, ΔS and ΔG.

The meaning behind a more/less negative $E^\ominus$ value: if $E^\ominus(Fe^{2+}/Fe)$ is more negative than $E^\ominus(Cu^{2+}/Cu)$, it means **Fe is more readily oxidized** to Fe^{2+} compared to Cu (oxidising to Cu^{2+}). It *also* means **Fe^{2+} is less readily reduced** back to Fe than Cu^{2+} (reducing to Cu). You should include this in your explanation. Be clear which species (metal or the metal ion) is oxidized or reduced. Using "it" at every juncture or simply "copper" or "iron" makes your answer ambiguous. Confusion between the species is penalized.

Diagram of the set-up is not required in this question. Common errors for those who drew the diagram include incorrect electrolyte and cathode. The electrolyte is $CuSO_4(aq)$ (**not** H_2SO_4 or $Cu(NO_3)_2$) and the cathode is pure Cu (**not** platinum).

(b) (i)



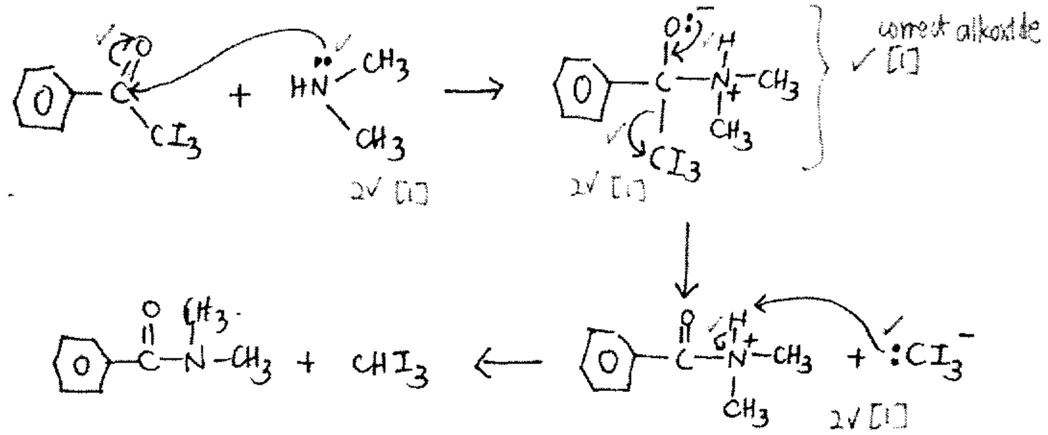
[1] correct labels of cathode, anode and electrolyte. cathode and anode must be placed at correct poles of the battery.
[1] graphite is the anode, nickel is the cathode

Diagrams with separate half-cells, voltmeter instead of battery, gas tubes of iodine and/or salt bridge indicates confusion between a galvanic cell and an electrolytic cell. Review the respective diagrams in the lecture notes to differentiate between the two set-ups and their purpose if you did not do well for this part.

You must label all 3 components in your diagram as stated in the question. For the electrolyte, you must include the species mentioned in the question. There should **not** be products in the electrolyte at the start. Including "amine" and "iodine" in the electrolyte suggests some confusion between a galvanic cell or electrolytic cell as well. The concentrations need not be 1 mol dm^{-3} as well.

It is fine to write "organic solvent" as given. Many answers gave specific solvents e.g. CCl_4, hexane, ethanol, and are not penalized though they might react in other ways. However, "aqueous" electrolyte is clearly incorrect.

(ii)



[½] for each correct arrow, must start from correct lone pair/bond and end at correct atom/bond
[1] for correct alkoxide intermediate

The amine does **not** dissociate to give free H^+ ions at the start since it is a very weak acid. Start with the amine itself in the first step, as stated in the question. After the amine donated its lone pair to form the new C–N bond in step 1, there should be a "+" charge on N. Many answers missed out this "+" charge on N after step 1.

When drawing curly arrows: be *very precise* where each arrow starts and ends. For example:
- Step 2, the arrow must start from the lone pair on O (not the negative charge or the C–O bond!) and end on the C–O bond (not C atom!).
- Step 3, CI_3^- acts as the base and its lone pair is from C (not I). So the arrow starts from the lone pair on C in CI_3^- and ends at the H atom attached to N in the intermediate.

If your arrows are drawn in the wrong direction, bear in mind that the curly arrow represents the movement of *electrons*, and **not** the species or atoms. For e.g. it is incorrect to draw the arrow from the H^+ to the CI_3^- ion.

(iii) The carbonyl group comes from the methyl ketone because:
in the control, S=O from the reactant similar to methyl ketone remains in the product / C=O group from formamide is lost. [1]
OR
if the carbonyl group comes from formamide, the product would have a C=O group and not the S=O group.

The key observation is that of the *sulfur* atom in the *product* of the control reaction. When the carbonyl group in the methyl ketone is replaced with a S=O group in the control reaction, the S=O group is the one that is retained in the product, despite the use of the same formamide molecule. Answers which showed this logic clearly are awarded credit.

Avoid vague answers e.g. "when the reactant is changed, the product is changed" (in what way is it changed and how does this lead to your conclusion?) or "since there is a S=O group, the carbonyl group comes from the methyl ketone" (where is this S=O group and how does its presence in the reactant or the product of the control reaction help you conclude?)

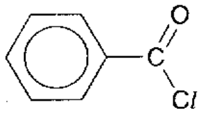
Some incorrect answers focused on the number of S=O/C=O bonds instead. Having two doubly bonded O atoms in the product could suggest both O come from the sulfur-containing reactant OR one O comes from the sulfur-containing reactant and the other comes from the formamide. Hence it is inconclusive to only count the number of "=O" in the product. The key is the sulfur atom.

The term "carbonyl" is used incorrectly e.g. S=O is not a "carbonyl". Answers which state "carbonyl is attached to S atom" will mean "–S-C=O", and **not** S=O.

(iv) **I**:
1) I_2, NaOH(aq), heat **[1]**
2) HC*l*(aq) **[1]**
OR
$KMnO_4$, dil H_2SO_4, heat **[2]**

II:
1) PC*l*$_5$ **[1]**
2) $HN(CH_3)_2$ **[1]**

intermediate compound:



[1]

I: The conversion of methyl ketone to benzoic acid is best done through the iodoform reaction followed by acidification. Note that there should be "heat" for iodoform but no need "heat" for just acidification.

The alternative $KMnO_4$ oxidation answer is accepted only for this specific molecule. Bear in mind most ketones are resistant to oxidation according to the syllabus.

"Acidified" or "alkaline" is **not** accepted, please give the specific reagent.

An alternative conversion which first reduce the methyl ketone using LiA*l*H_4 in dry ether to obtain the 2° alcohol, which then undergoes iodoform reaction or oxidation by $KMnO_4$ is accepted, though the reduction step is unnecessary.

A longer alternative is to reduce the methyl ketone first to the alcohol, then dehydrate the alcohol (using excess conc. H_2SO_4, heat) to obtain the alkene, followed by oxidative cleavage using $KMnO_4$. This is accepted provided all reagents, conditions and intermediate products are correct, but has too many unnecessary steps and room for error.

II: The common error for this conversion is to react the amine directly with benzoic acid, without realizing that an acid-base reaction will occur instead of the intended "condensation". The amine is basic and benzoic acid is acidic ☹

Therefore, you must convert benzoic acid to the acid chloride first. The reaction of **acid chloride** with amine also does **not** require conc. H_2SO_4 and heat (unlike for carboxylic acids). In fact, adding any acid or "aqueous" reagent or solvent (e.g. ethanol) will cause the reaction to fail, since the acid chloride will readily react with water (to form carboxylic acid), ethanol (to form ester), and any acid will protonate the amine causing it to **not** act as a nucleophile.

The correct name for the amine is N,N-dimethylamine (**not** "ethylamine" or "secondary amine"). "Dimethylamine" is accepted though *not entirely accurate.* Condensed formulae $HN(CH_3)_2$ or CH_3NHCH_3 are fine, but "$NHCH_3CH_3$" is **not** entirely correct. It is best to draw out the structure.

4 **(a)** Their reactivity as oxidising agents decreases down the group. **[1]**

	$E^\ominus$/ V
$Cl_2 + 2e^- = 2Cl^-$	+1.36
$Br_2 + 2e^- = 2Br^-$	+1.07
$I_2 + 2e^- = 2I^-$	+0.54

This is shown by the decreasing values of $E^\ominus$: **[1]**

This question only required students to **describe** the relative reactivity of the halogens as oxidising agents (which means the ease at which they are reduced) and **relate** it to relevant $E^\ominus$ values. As the question did not ask for "why" there is a decreasing reactivity down the group, you should **not** be using size of atoms, bond energies etc. which are all irrelevant and sometimes even incorrect, in your answers.

(b) **(i)** The standard electrode potential of a half-cell is the **potential difference/emf** between the **half-cell** and a **standard hydrogen electrode** at **standard conditions of 298 K, 1 bar for gases and 1 mol dm^{-3} for solutions**. **[1]**

Learn your definitions well.
The term *potential difference* is different from the term *potential.*
There are 3 conditions that should be stated in your definition.

(ii)

	$E^\ominus$/ V
$F_2 + 2e^- = 2F^-$	+2.87
$O_2 + 4H^+ + 4e^- = 2H_2O$	+1.23

[1] for quoting the values or showing the values in their calculations

$E^\ominus(F_2/F^-)$ is very much more positive then $E^\ominus(O_2/H_2O)$

OR

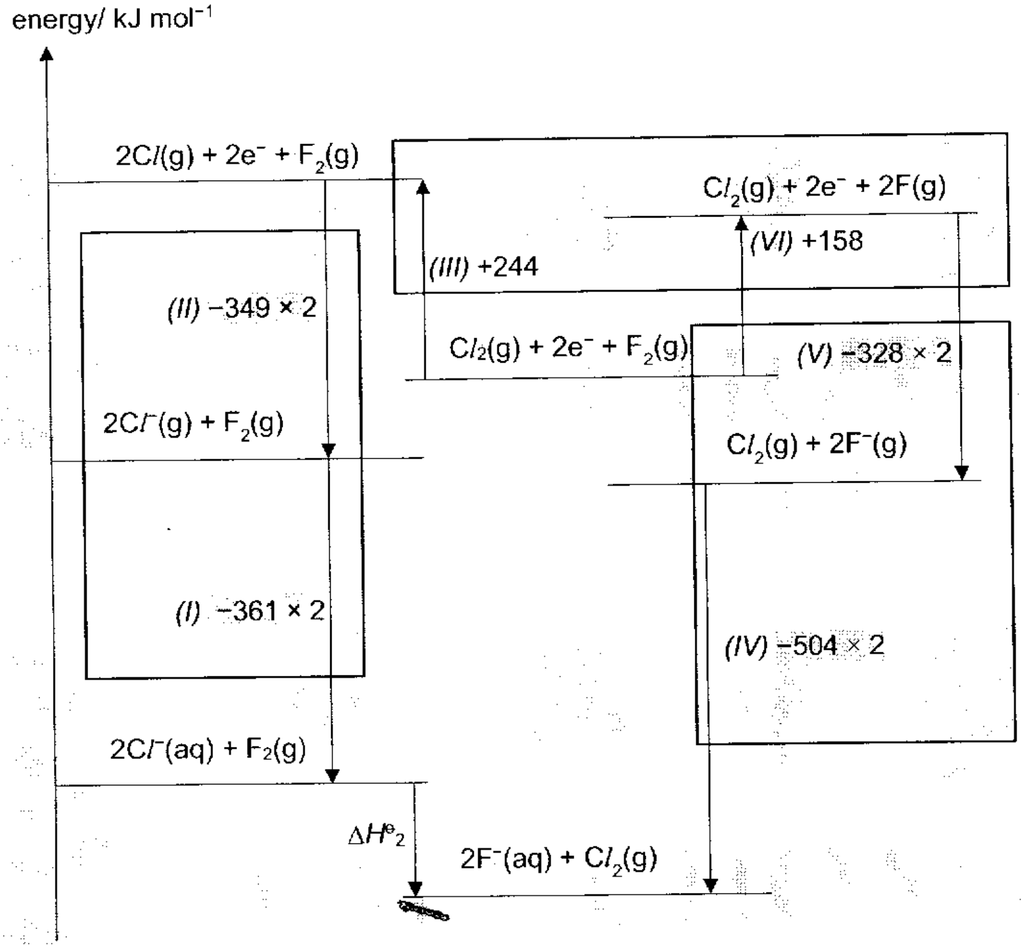
$E^\ominus_{cell} = 2.87 - 1.23 = +1.64\ V > 0\ V$, **[1]**

therefore F_2 will oxidise H_2O and we cannot bubble in F_2 into water.

Just stating that "the $E^\ominus(F_2/F^-)$ is high" is insufficient as it is unclear how high is high without comparison to the reducing agent. In the aqueous medium, aside from F^-, the only other reducing agent is water, so you should compare $E^\ominus(F_2/F^-)$ to $E^\ominus(O_2/H_2O)$ and note that fluorine will oxidise water to O_2. Some students considered the oxidation of H_2O to H_2O_2 instead which is **incorrect**. This has much less tendency to happen than the oxidation of H_2O to O_2, as $E^\ominus(H_2O_2/H_2O) = +1.77$ V is less negative than $E^\ominus(O_2/H_2O) = +1.23$ V.

Note: In reality, a mixture of O_2 and O_3 will be produced.

(iii)



By Hess' Law,
$\Delta H^\ominus_2 + 244 + (-349 \times 2) + (-361 \times 2) = +158 + (-328 \times 2) + (-504 \times 2)$
$\Delta H^\ominus_2 = -330$ kJ mol^{-1} **[1]** ecf based on the cycle (3, 4 s.f. accepted)
3 × [1] for getting the 3 parts correct in each box.

The left hand side of the cycle is very similar to the right hand side as all the enthalpy changes are essentially the same, except that those on the left involve chlorine while those on the right involve fluorine.

(I) Two moles of $Cl^-(g)$ are hydrated and are converted into $Cl^-(aq)$.
So for this step, the value of $\Delta H = 2 \times \Delta H_{hyd}(Cl^-(g)) = -361 \times 2$

(II) It can be observed that $Cl(g)$ gained an electron to give $Cl^-(g)$, so this step describes the first electron affinity of chlorine. Since there are two moles of $Cl(g)$, please remember to multiply by 2.

The value of $\Delta H = 2 \times \text{EA}(Cl) = -349 \times 2$

(III) In this step, the $Cl_2(g)$ molecule dissociated into $2Cl(g)$ atoms. This is achieved by breaking the $Cl-Cl$ single bond.
The value of $\Delta H = \text{BE}(Cl-Cl) = +244$

(IV) Two moles of $F^-(g)$ are hydrated and are converted into $F^-(aq)$.
So for this step, the value of $\Delta H = 2 \times \Delta H_{hyd}(F^-(g)) = -504 \times 2$

(V) It can be observed that $F(g)$ gained an electron to give $F^-(g)$, so this step describes the first electron affinity of fluorine. Again, remember to multiply by 2.
The value of $\Delta H = 2 \times \text{EA}(F) = -328 \times 2$

(VI) In this step, the $F_2(g)$ molecule dissociated into 2 $F(g)$ atoms. This is achieved by breaking the F–F single bond.
The value of $\Delta H = \text{BE}(F-F) = +158$

(iv) There is <u>a decrease in the number</u> of moles <u>of gas</u> particles (from ½ mole of gas to none), so there are fewer ways in which the particles and their energies can be distributed and entropy decreases, therefore ΔS°_r is negative. **[1]**

For both equations, there is ½ mol of gaseous reactant and 0 mol of gaseous product, so this should be the main reason for the decrease in entropy since gases have high entropy and the reduction in the number of moles of gases will definitely cause a drop in entropy. The decrease in number of gas particles <u>must</u> be explicitly stated in your answer. Note also that this is **not** a phase change.

Please read Topic 05 Energetics Section 9.2.1 (3) for more examples.

(v)

$$\begin{tikzcd}
2Na(s) + 2Cl^-(aq) + F_2(g) \arrow[rr, "\Delta S^{\circ}_2"] \arrow[dr, "2 \times -108"'] & & Cl_2(g) + 2F^-(aq) + 2Na(s) \arrow[dl, "2 \times -48"] \\
& 2Na^+(aq) + 2F^-(aq) + 2Cl^-(aq) &
\end{tikzcd}$$

$\Delta S^{\circ}_2 = 2 \times -108 + 2 \times 48 = -120 \text{ J mol}^{-1} \text{ K}^{-1}$ (2, 3, 4 s.f. accepted with units)
[1] for correct use of Hess' Law
[1] for final answer Note: No cycle needed.

The entropy changes given (ΔS°_r) are defined for ½ mol of $X_2(g)$. To calculate ΔS°_2, for the reaction 2: $2Cl^-(aq) + F_2(g) \rightarrow Cl_2(g) + 2F^-(aq)$, there is 1 mol of each halogen $X_2(g)$, hence we should multiply each ΔS°_r by 2.

(vi) $\Delta G^{\circ}_2 = \Delta H^{\circ}_2 - T\Delta S^{\circ}_2$
$= -330 - (298 \times -0.120)$
$= -294.2 \text{ kJ mol}^{-1}$ **[1]** (accept 3, 4 s.f. + units) ecf

If units of $\Delta G^\ominus_2$ and $\Delta H^\ominus_2$ used are kJ mol^{-1}, then units of $\Delta S^\ominus_2$ should be in kJ mol^{-1} K^{-1}.
If units of $\Delta G^\ominus_2$ and $\Delta H^\ominus_2$ used are J mol^{-1}, then units of $\Delta S^\ominus_2$ should be in J mol^{-1} K^{-1}.

The temperature under standard conditions is <u>298 K</u>. This is **different** from the <u>temperature at s.t.p. of 273 K and r.t.p. of 293 K.</u>

(vii) $\Delta G^\ominus_2 = -294.2 \times 1000 = -nFE^\ominus_{cell} = -2 \times 96500 \times E^\ominus_{cell}$
$E^\ominus_{cell} = +1.52$V **[1]** ecf (2 d.p. + units)

In this reaction: $2Cl^-(aq) + F_2(g) \rightarrow Cl_2(g) + 2F^-(aq)$
2 moles of electrons were transferred from chloride ions to fluorine molecules. This can be seen from the total change in oxidation state of each species:

$2Cl^-$ ($-1 \times 2 = \mathbf{-2}$) to Cl_2 ($0 \times 2 = \mathbf{0}$) —— total change in O.S. of +2
F_2 ($0 \times 2 = \mathbf{0}$) to $2F^-$ ($-1 \times 2 = \mathbf{-2}$) —— total change in O.S. of −2

So n = 2 in this case.

Units of $\Delta G^\ominus_2$ should be in J mol^{-1}. If you get an $E^\ominus_{cell}$ that is very close to 0 V, it might be an indication that something is wrong. You might have forgotten to convert the units for $\Delta G^\ominus_2$ to J mol^{-1}.

(viii) $E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$
$1.52 = E^\ominus(F_2/F^-) - E^\ominus(Cl_2/Cl^-)$
<u>$E^\ominus(F_2/F^-) = 1.52 + 1.36 = +2.88$ V **[1]** ecf (2 d.p. + units)</u>

In this reaction: $2Cl^-(aq) + F_2(g) \rightarrow Cl_2(g) + 2F^-(aq)$

So F_2 is reduced and the F_2/F^- half-cell is the half-cell where reduction takes place; Cl^- is oxidized and the Cl_2/Cl^- half-cell is the half-cell where oxidation takes place.

Therefore the $E^\ominus_{red} = E^\ominus(F_2/F^-)$; and $E^\ominus_{ox} = E^\ominus(Cl_2/Cl^-) = +1.36$ V from the *Data Booklet.*

Also note that since $E^\ominus(F_2/F^-) = +2.87$ V from the *Data Booklet*, if you notice that **your** answer is very different from this value, you might want to check your working from previous parts.

(c) **(i)** Fluorine cannot form more than one covalent bond as it <u>cannot expand its octet</u>
OR
Fluorine <u>does not have energetically accessible d orbitals</u>. **[1]**

Fluorine is in period 2, so its next accessible orbitals that can be used are in the 3rd quantum shell, which is too high in energy.

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Fluorine has an atomic radius of F = 0.072 nm which is approximately the same as that of O (0.073 nm) which can form 2 bonds and N (0.074 nm) which can form 3 bonds. So it is **incorrect** to argue that fluorine cannot be bonded to more than 1 atom due to its small size.

Fluorine is the most electronegative element, but that does **not** explain why it cannot form more than one covalent bond. Any answers referencing this is irrelevant.

(ii) I

As the number of electronegative/electron-withdrawing oxygen increases, **[1]** the negative charge is dispersed more by the electron-withdrawing O and conjugate base becomes more stable, hence the acid becomes stronger and the pK_a decreases.

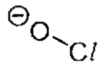
Other accepted answers: with more Cl=O bonds, the conjugate base can be stabilized more as there are more resonance structures or negative charge can be delocalised over more Cl=O bonds in the conjugate base.

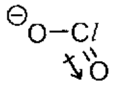
II

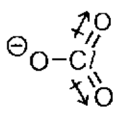
The electronegativity of the halogens and hence the electron-withdrawing effect decreases in the order $Cl > Br > I$ or electronegativity of Cl highest and I lowest **[1]** hence negative charge is dispersed the most in ClO^- and stability of the conjugate base decrease in the order $ClO^- > BrO^- > IO^-$ and the pK_a increases from $HClO$ to HIO.

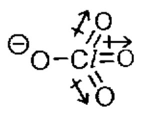
[1] for either mentioning correctly about the negative charge in conjugate base being dispersed / stability of conjugate bases /explicit links to acidity such as the extent of polarization/weakening of the O-H bond.

It is **not** sufficient to just mention that there are more O atoms going down the second row. There must be some interpretation of how O atoms will affect the stability of the conjugate base, such as its electron-withdrawing property being able to help disperse the negative charge in the conjugate base. As can be seen below, the more O atoms there are, the more electron-withdrawing groups there are that can help to disperse the negative charge on the conjugate base.









The conjugate base here is the oxoanion, please do **not** name it as alkoxide, it is obviously not the conjugate base of an alcohol. When in doubt, you can just call it the *conjugate base* of the acid.

Going across the first row, the electronegativity of the halogens decreases and hence their electron-withdrawing effect decreases and the negative charge is dispersed to a lesser extent. There is **no** need to write essays to explain *why* the electronegativity decreases, that just isn't the point of the question.

(d) **(i)** pH = −lg1 = 0 **[1]**

$[H^+]$ = 1 mol dm^{-3} under standard conditions for acidic solutions. Common **misconception** is that pH = 1 if $[H^+]$ = 1 mol dm^{-3}. Please key into the calculator if you are uncertain.

(ii) $[H^+]$ = 1 mol dm^{-3}.

$$K_a = \frac{[H^+][ClO_3^-]}{[HClO_3]}$$

$$\frac{[1][ClO_3^-]}{[HClO_3]} = 10$$

$[ClO_3^-] : [HClO_3] = 10 : 1$, therefore the major species at pH = 0 is ClO_3^-. **[1]**

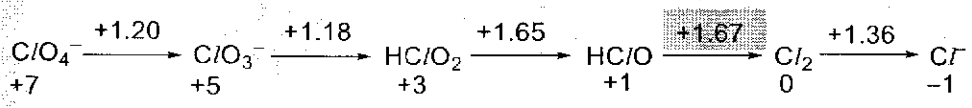
pK_a of $HClO_3$ = −1, therefore $-\lg K_a = -1$ and $K_a = 10$.

(iii) In acid, $E^\ominus_{cell}$ for disproportionation = 1.36 – 1.67 = $\underline{-0.31\text{ V} < 0}$. Therefore it is not spontaneous. **[0.5]**

In base, $E^\ominus_{cell}$ for disproportionation = 1.36 – 0.42 = $\underline{+0.94\text{ V} > 0}$. Therefore it is spontaneous. **[0.5]**

Therefore reaction is spontaneous and disproportionation takes place more readily in basic medium **[1]** (Answer to 2 d.p.)

If Cl_2 were to disproportionate to its neighbours, it means that it will be oxidized and reduced at the same time. Based on the Latimer diagram in acidic conditions, it would mean that Cl_2 was reduced to Cl^- (the relevant $E^\ominus$ value is the one on the right of Cl_2 in yellow) and oxidized to HClO (the relevant $E^\ominus$ value is the one on the left of Cl_2 in green).



$$\underset{+7}{ClO_4^-} \xrightarrow{+1.20} \underset{+5}{ClO_3^-} \xrightarrow{+1.18} \underset{+3}{HClO_2} \xrightarrow{+1.65} \underset{+1}{HClO} \xrightarrow{+1.67} \underset{0}{Cl_2} \xrightarrow{+1.36} \underset{-1}{Cl^-}$$

For this reaction, we need to look at the two relevant equations:

$E^\ominus(Cl_2/Cl^-)$ = +1.36 V (This is for the reduction of Cl_2 to Cl^-)
$E^\ominus(HClO/Cl_2)$ = +1.67 V (This is for the oxidation of Cl_2 to HClO)

We then calculate $E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} = E^\ominus(Cl_2/Cl^-) - E^\ominus(HClO/Cl_2) < 0$ and conclude that such a disproportionation is not spontaneous.

Similarly, in alkaline conditions:

$E^\ominus(Cl_2/Cl^-)$ = +1.36 V (This is for the reduction of Cl_2 to Cl^-)
$E^\ominus(ClO^-/Cl_2)$ = +0.42 V (This is for the oxidation of Cl_2 to ClO^-)

We then calculate $E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} = E^\ominus(Cl_2/Cl^-) - E^\ominus(ClO^-/Cl_2) > 0$ and conclude that such a disproportionation is spontaneous.

(iv) If the $E^\ominus$ on the right of the species is more positive than the $E^\ominus$ on the left of the species, the species will have the tendency to disproportionate. **[1]**

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From **(iii)**, you would have concluded that $E^\ominus_{cell} = E^\ominus_{right} - E^\ominus_{left}$. The species will only tend to disproportionate when $E^\ominus_{cell} > 0$, conversely, the species will **not** disproportionate if $E^\ominus_{cell} < 0$. It is **insufficient** to state that "the more positive the $E^\ominus$ on the right is and the less positive the $E^\ominus$ on the left is, then the disproportionation has higher tendency to occur", as the $E^\ominus_{cell}$ might still be negative if the $E^\ominus$ on the right is less positive than that on the left based on this conclusion.

(v) +3 **[1]**

$$\underset{+7}{ClO_4^-} \xrightarrow{+1.20} \underset{+5}{ClO_3^-} \xrightarrow{+1.18} \underset{+3}{HClO_2} \xrightarrow{+1.65} \underset{+1}{HClO} \xrightarrow{+1.67} \underset{0}{Cl_2} \xrightarrow{+1.36} \underset{-1}{Cl^-}$$

$$\underset{+7}{ClO_4^-} \xrightarrow{+0.37} \underset{+5}{ClO_3^-} \xrightarrow{+0.30} \underset{+3}{ClO_2^-} \xrightarrow{+0.68} \underset{+1}{ClO^-} \xrightarrow{+0.42} \underset{0}{Cl_2} \xrightarrow{+1.36} \underset{-1}{Cl^-}$$

The Latimer diagrams for both acidic (top) and basic (bottom) medium are shown above. There is only one oxidation state in which the $E^\ominus$ on the right of the species is more positive than the $E^\ominus$ on the left in both acidic (+1.65 V > +1.18 V) and basic (+0.68 V > +0.30 V) medium, which is the +3 oxidation state. Species with this oxidation state should be predicted to disproportionate in both medium.