Name:	Mark Scheme	Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY 9647/03

Paper 3 **24 September 2013**

2 hours

Additional Materials: Data Booklet, Graph Paper & Writing Paper

INSTRUCTIONS TO CANDIDATES

1 Answer any **four** questions.

2 Begin each question on a fresh sheet of paper.

3 At the end of the examination:

- Staple or fasten all your work securely together with the Cover Sheet on top.
- Hand in the question paper separately.

INFORMATION FOR CANDIDATES

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

You are advised to show all workings and calculations.

You are reminded of the need for good English and clear presentation in your answers.

[Turn over

Answer any **four** questions.
Begin each question on **a fresh sheet of paper**.

1 Dinitrogen pentoxide, N_2O_5, can be produced by the following reaction sequence in the car engine:

I	$N_2(g) + O_2(g) \rightarrow 2NO(g)$	$\Delta H^{\ominus} = +180$ kJ mol^{-1}; $\Delta S^{\ominus} = +24.8$ J mol^{-1} K^{-1}
II	$NO(g) + {}^1/_2O_2(g) \rightarrow NO_2(g)$	$\Delta H^{\ominus} = -57.0$ kJ mol^{-1}
III	$2NO_2(g) + {}^1/_2O_2(g) \rightarrow N_2O_5(g)$	$\Delta H^{\ominus} = -110$ kJ mol^{-1}

(a) (i) Explain why reaction **I** does not take place at room temperature but occurs in car engine.

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$\Delta G^{\ominus}$ (+172.6 kJ mol^{-1}) is positive at 298 K, hence reaction **I** is not spontaneous at room temperature

The high temperature in the car engine causes the $T\Delta S^{\ominus}$ to become more positive (or $-T\Delta S^{\ominus}$ to become more negative). This will lead to a more negative $\Delta G^{\ominus}$ and hence reaction **I** becomes spontaneous.

(ii) Predict in reaction **II**, with reasons, the sign of $\Delta S^{\ominus}$.

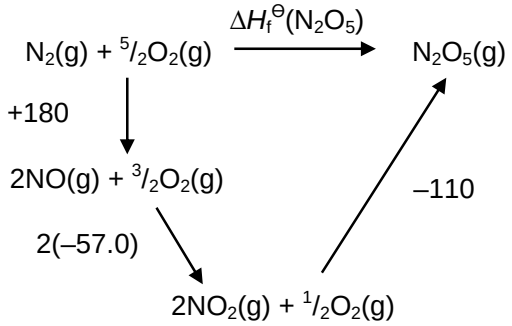
The amount of gases decreases from $1{}^1/_2$ mol to 1 mol, hence there are lesser number of ways to arrange the gaseous particles in the system. $\Delta S^{\ominus}$ is negative.

(iii) Nitrogen dioxide is a pollutant that is often produced in car engine. Suggest how the pollutant can be removed in the car engine.

$$2NO_2(g) \xrightarrow{Pt} N_2(g) + 2O_2(g)$$

The nitrogen dioxide is converted to nitrogen and oxygen gas in the catalytic convertor (with Pt as catalyst) in the car engine.

(iv) By drawing a suitable energy cycle and using the data above, calculate the standard enthalpy change of formation of dinitrogen pentoxide.



By Hess' law,
$\Delta H_f^{\ominus}(N_2O_5) = +180 + 2(-57.0) - 110 = \underline{-44.0 \text{ kJ mol}^{-1}}$

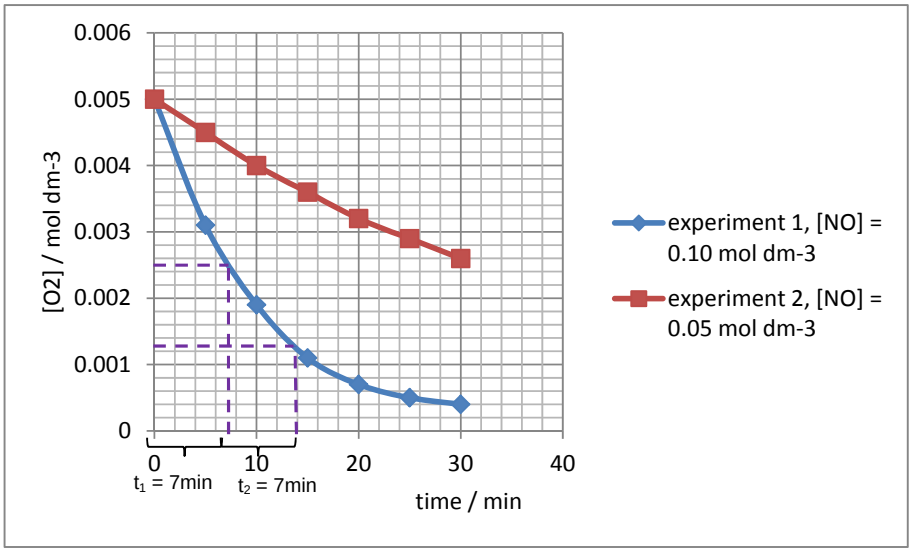
(b) The rate of reaction for reaction **II** was investigated and the following kinetics data was obtained.

Time/minutes	Experiment 1, with [NO] = 0.10 mol dm^{-3}	Experiment 2, with [NO] = 0.05 mol dm^{-3}
	$[O_2]$ / mol dm^{-3}	$[O_2]$ / mol dm^{-3}
0	0.0050	0.0050
5	0.0031	0.0045
10	0.0019	0.0040
15	0.0011	0.0036
20	0.0007	0.0032
25	0.0005	0.0029
30	0.0004	0.0026

(i) Explain why nitrogen monoxide is used in large excess.

This is to ensure that the concentration of nitrogen monoxide remains approximately constant so that the rate of reaction will be independent of the concentration of nitrogen monoxide.

(ii) Using the same axes, plot graphs of $[O_2]$ against time for the two experiments.



(iii) Use your graphs to determine the order of reaction with respect to O_2 and NO, showing your workings clearly.

Using the curve for experiment 1, $t_1 \approx t_2 \approx 7$ min. The half-lives of O_2 are approximately constant at 7 min, hence the reaction is first order with respect to O_2.

When [NO] = 0.1 mol dm^{-3}, initial rate = 4 x 10^{-4} mol dm^{-3} min^{-1}
When [NO] = 0.05 mol dm^{-3}, initial rate = 1 x 10^{-4} mol dm^{-3} min^{-1}
When [NO] is doubled, the initial rate is quadrupled. Hence, the reaction is second order with respect to NO.

(iv) State the rate equation of reaction **II** and hence calculate the rate constant,

including its units.

rate = $k[O_2][NO]^2$

Using initial rate method:
$4 \times 10^{-4} = k(0.005)(0.1)^2$
$k = 8.00\ mol^{-2}\ dm^6\ min^{-1}$

or using half-life method:
rate = $k'[O_2]$ where $k' = k[NO]^2$
$k' = \ln 2 / 7 = 0.09902\ min^{-1}$
$k = 0.09902 / (0.1)^2 = 9.90\ mol^{-2}\ dm^6\ min^{-1}$

(v) Explain how the half-life of oxygen will be affected when the concentration of nitrogen monoxide is doubled.

rate = $k[O_2][NO]^2$
rate = $k'[O_2]$ where $k' = k[NO]^2$
$t_{1/2} = \ln 2 / k'$
$= \ln 2 / k[NO]^2$

When [NO] is doubled, the half-life of O_2 will be <u>reduced by 4 times</u>.

(c) The nitrogen dioxide produced in reaction **II** is able to form dinitrogen tetraoxide as shown below:

$2NO_2(g) \rightleftharpoons N_2O_4(g)$
brown colourless

Explain whether the enthalpy change of dimerisation is endothermic or exothermic. Hence, predict the colour change of the reaction mixture when the temperature is increased.

The forward reaction is exothermic as N-N bond is formed during dimerisation. By Le Chatelier's principle, an increase in temperature favours the backward reaction and the position of equlibrium shifts to the left. Hence, the colour of the reaction mixture becomes darker brown.

[Total: 20]

2 Transition elements, such as cobalt, copper and chromium, have different properties that can distinguish themselves from the main group element such as magnesium. With their unique properties, transition elements are capable of having variable oxidation states and forming coloured complexes.

(a) What do you understand by the term *transition element*?

A transition element is a d-block element that is capable of forming at least one ion with a partially-filled d-subshell.

(b) When air is bubbled through an aqueous solution containing $CoCl_2$, NH_4Cl and NH_3, and the resulting solution evaporated, crystals of a salt **X** can be isolated. **X** has the following composition by mass:

Co, 25.2 %; N, 24.0 %; H, 5.1 %; Cl, 45.7 %

On adding an excess of aqueous silver nitrate to an aqueous solution containing 0.01 mol of **X**, 1.43 g of silver chloride is precipitated.

Determine the formula of the octahedral cation in **X**. Hence, calculate the oxidation number of the cobalt atom in **X**.

	Co	N	H	C*l*
% mass	25.2	24.0	5.1	45.7
% mole	0.428	1.714	5.1	1.287
Mole ratio	1	4	12	3

n(AgC*l*) = 1.43 / 143.5 ≈ 0.01 mol

1 mol of complex contains 1 mol of free chloride ions. Hence, the formula of the octahedral cation is $\underline{[Co(NH_3)_4Cl_2]^+}$

Oxidation number of cobalt = $\underline{+3}$

(c) Haemocyanin is a copper containing oxygen transport molecule in horseshoe crabs. Both oxygenated and deoxygenated forms of haemocyanin contain copper ions. Haemocyanin is colourless when deoxygenated and blue when it is exposed to oxygen.

Suggest the oxidation states of copper in the oxygenated and deoxygenated forms of haemocyanin. Hence explain the difference in colour observed.

Oxidation state of Cu in oxygenated state = +2
Oxidation state of Cu in deoxygenated state = +1

In the oxygenated state, as the higher energy d-orbital is empty and d-electron in the lower energy d-orbital can be promoted to a higher energy level in Cu^{2+} (d^9), the colour of haemocyanin is blue.

In the deoxygenated state, all d orbitals are fully filled in Cu^+ (d^{10}), hence d-d transition is not possible which results in colourless haemocyanin.

(d) Reagents containing transition elements are commonly used in organic syntheses. A common reagent used is potassium dichromate(VI).
In the organic synthesis below, observations are made when an optically active organic halogen derivative **A**, $C_5H_{11}ClO$ is reacted with several reagents to yield the final organic product **E**, $C_{10}H_{16}O_4$.

Compound **A**, $C_5H_{11}ClO$ is an organic halogen derivative that fumes with thionyl chloride in pyridine. When **A** reacts with aqueous sodium hydroxide, it yields equimolar of **B** and **C** with the same molecular formulae, $C_5H_{12}O_2$.

When **B** and **C** are separated, each compound is found to rotate plane-polarised light in opposite directions with equal magnitude. **C** is then heated under reflux with acidified potassium dichromate(VI) to yield **D** which produces effervescence with sodium carbonate. When **D** is further refluxed in the presence of concentrated sulfuric acid, a neutral organic product **E**, $C_{10}H_{16}O_4$ is obtained.

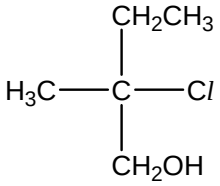
(i) Suggest, with explanations, the structures for compounds **A**, **B**, **C**, **D** and **E**.

- **A**, an optically active compound, contains a chiral centre with optical

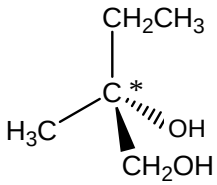
isomers which can rotate plane-polarised light.

- **A** undergoes substitution reaction with thionyl chloride to produce fumes of HC*l*. **A** is an alcohol.
- **A** undergoes nucleophilic substitution (or S_N1) with NaOH(aq) to produce a racemic mixture containing **B** and **C**. **A** is a chloroalkane or **B**/**C** are alcohols.
- **B** and **C** are able to rotate plane-polarised light. Hence, they are optical isomers (enantiomers), each containing a chiral centre. **B** and **C** form a racemic mixture.
- **C** is oxidised by $K_2Cr_2O_7/H^+$ to give **D**, a carboxylic acid. **C** contains a primary alcohol.
- **D** undergoes neutralisation (acid-base reaction) with Na_2CO_3 effervescence of CO_2. **D** contains a carboxylic acid group.
- Two **D** molecules undergo condensation reaction (esterification) to produce the ester, **E**.

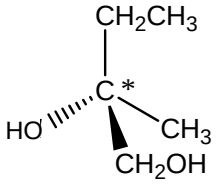
Structures



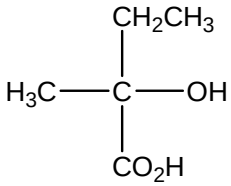
A



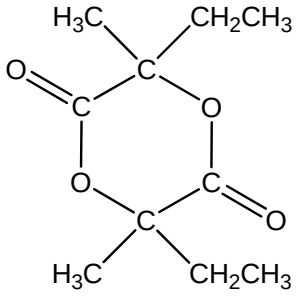
B



C

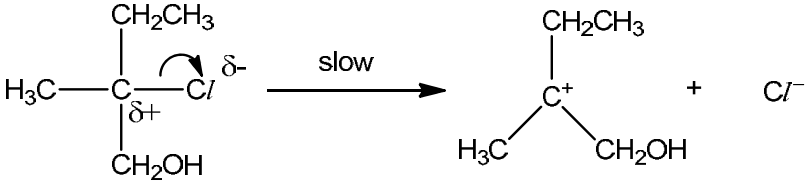


D

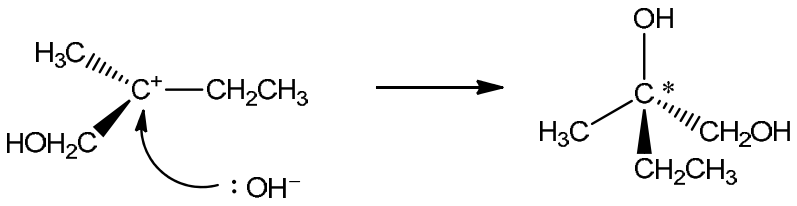


E

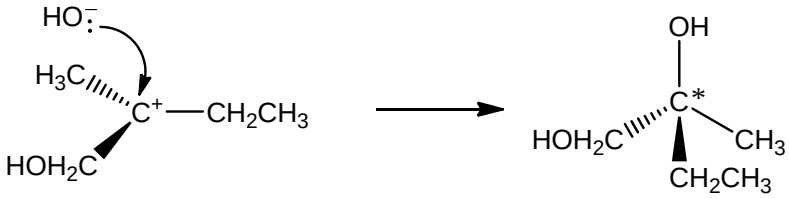
(ii) Describe the mechanism of the reaction of **A** with aqueous sodium hydroxide to produce **B** and **C**. Indicate clearly in your mechanism how equimolar of **B** and **C** is obtained.



Attack of nucleophile **below** trigonal planar carbocation:



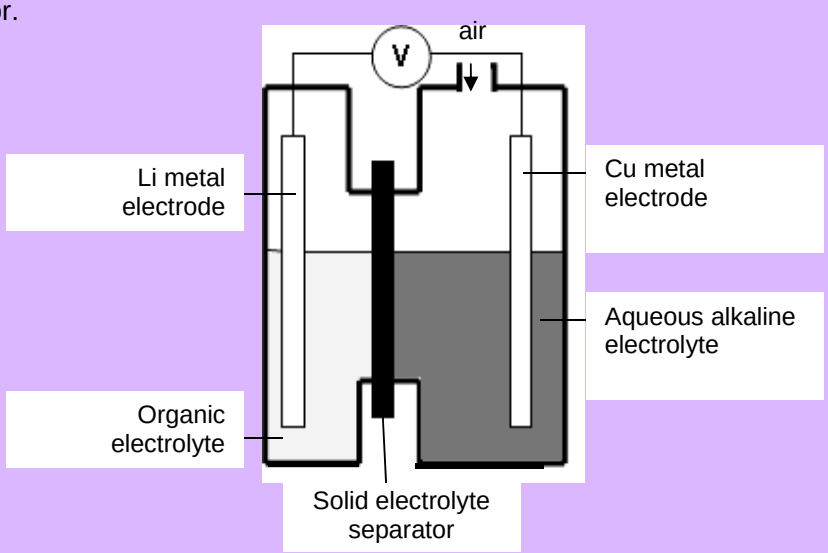
Attack of nucleophile **above** trigonal planar carbocation:



Formation of equimolar of **B** and **C** is due to the attack of the nucleophile, OH-, on either side (top or bottom) of the trigonal planar carbocation intermediate with <u>equal probability</u>.

[Total: 20]

3 (a) A low–cost lithium–copper air fuel cell consisting of a copper electrode immersed in an aqueous alkaline electrolyte and a lithium electrode immersed in an organic electrolyte has recently been developed. Mixing of the two electrolyte solutions is prevented by using a solid electrolyte separator where only lithium ions can pass through the separator.



The copper electrode is oxidised by oxygen in the air to copper (I) oxide. During discharge, copper(I) oxide will be reduced to copper solid at the electrode. Similarly, during discharge, lithium will be oxidised to give lithium ions and pass through the separator into the aqueous alkaline electrolyte.

(i) State the direction of the flow of electron during discharge in the lithium–copper air fuel cell.

From Li to Cu

(ii) Write ionic half–equations for the reaction that occur at each electrode during discharging.

Anode: $Li \rightarrow Li^+ + e$

Cathode: $Cu_2O + H_2O + 2e \rightarrow 2Cu + 2OH^-$

(iii) It is discovered that the voltage of this fuel cell is +2.30V. Using relevant data from the *Data Booklet*, predict the electrode potential for the cathode reaction. State an assumption that you have made.

$E^\theta_{cell} = E^\theta_{red} – E^\theta_{oxd}$

$+2.30 = E^\theta_{red} – (–3.04)$

$E^\theta_{red} = –0.74V$

It is assumed that voltage of the fuel cell is measured at standard conditions of 298 K and 1 atm with the electrolyte concentration at 1 mol $dm^{–3}$.

(iv) Explain why lithium ions are allowed to pass through the separator.

An increase in $[OH^-]$ at cathode compartment builds up negative charges and an increase in [Li+] at anode compartment builds up positive charges. Hence Li^+ ions flow from anode compartment to cathode compartment to maintain a balance in charges (or maintain electrical neutrality) in the fuel cell.

(v) Two different electrolytes are used in this lithium–copper air fuel cell. Suggest a reason why an aqueous alkaline electrolyte cannot be used solely in this fuel cell.

The lithium metal electrode will react violently with water (forming lithium hydroxide and hydrogen gas) hence an aqueous alkaline electrolyte cannot be used at the anode compartment.

[8]

(b) The copper(I) oxide is reddish–brown in colour. When concentrated hydrochloric acid is added to it and the mixture warmed, it is observed that the precipitate dissolved to give a colourless solution. The copper complex formed is linear in shape.

Suggest an identity for the copper complex and give an equation for the reaction.

[2]

A colourless water soluble $CuCl_2^-$ complex ion is formed when hydrochloric acid is added.

$Cu_2O(s) + 4HCl(aq) \rightarrow 2\ CuCl_2^-(aq) + H_2O(l) + 2H^+(aq)$

(c) An experiment is conducted to determine the formula of complex formed between copper(II) and ammonia.

100 cm^3 of 0.100 mol $dm^{–3}$ of copper(II) sulfate is mixed with 100 cm^3 of aqueous ammonia. The resulting solution, which contains an excess of ammonia is then shaken with trichloromethane and allowed to stand for equilibrium to be established.

25.0 cm^3 of trichloromethane layer is found to neutralise 26.00 cm^3 of 0.025 mol $dm^{–3}$ hydrochloric acid while 25.0 cm^3 of aqueous layer required 21.00 cm^3 of 1.00 mol $dm^{–3}$ hydrochloric acid for neutralisation.

The equilibrium constant of ammonia between the aqueous layer and the

trichloromethane layer is 25.0.

$$NH_3\,(aq) \rightleftharpoons NH_3\,(CHCl_3)$$

$$K = \frac{[\text{ammonia}]_{\text{aqueous}}}{[\text{ammonia}]_{CHCl_3}}$$

Calculate the following:

(i) the concentration of ammonia in the trichloromethane layer.

$[NH_3] = 26.00/25.0 \times 0.025 = 0.026$ mol dm^{-3}

(ii) the concentration of free ammonia in the aqueous layer, using the equilibrium constant.

$$K = \frac{[\text{ammonia}]_{\text{aqueous}}}{[\text{ammonia}]_{CHCl_3}} = 25.0$$

$[\text{ammonia}]_{\text{aqueous}} = 0.026 \times 25.0 = 0.65$ mol dm^{-3}

(iii) the total concentration of ammonia (free and complexed) in the aqueous layer.

Total [ammonia] = $21.00/25.0 \times 1.00 = 0.84$ mol dm^{-3}

(iv) the value of *n* in the formula of the complex ion $[Cu(NH_3)_n]^{2+}$, stating one assumption made in the calculation.

[8]

[ammonia] (complexed) = $0.84 - 0.65 = 0.19$ mol dm^{-3}

$n_{Cu2+} = 0.100 \times 0.100 = 0.0100$ mol

$n_{\text{ammonia (complexed)}} = 0.19 \times 200/1000 = 0.038$ mol

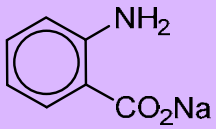
$n = 0.038/0.01 = 3.8$

$\approx \underline{4}$

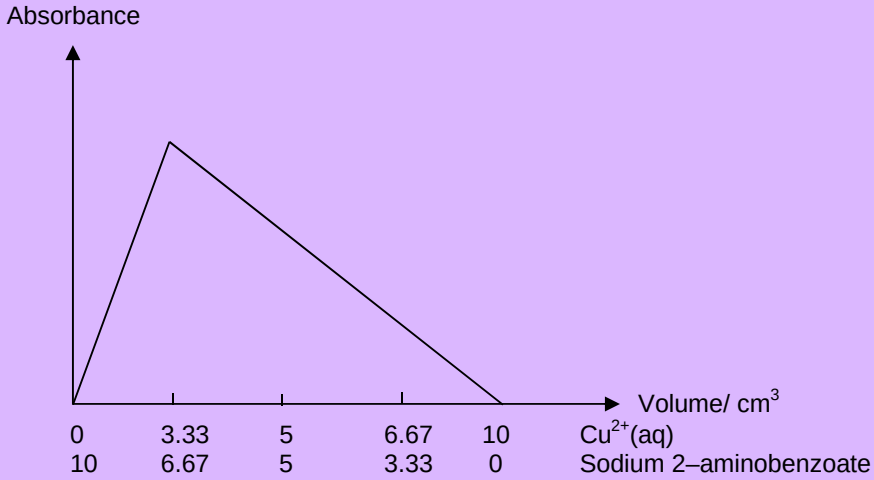
Assumption: (Any one)

1. All the ammonia ligands (complexed) reacted with hydrochloric acid.
2. None of the copper complex ion is partitioned/ migrated to the organic layer.

(d) Sodium 2–aminobenzoate is a bidentate ligand that can form a complex with $Cu^{2+}(aq)$. Different volumes of 0.05 mol dm^{-3} $Cu^{2+}(aq)$ and 0.025 mol dm^{-3} sodium 2–aminobenzoate are mixed to form a few mixtures.



These mixtures show light absorbancy as shown in the graph below. The absorbance is proportional to the concentration of the complex.



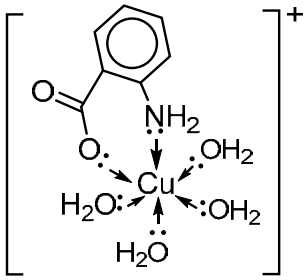
Determine the mole ratio of the copper ion to the 2–aminobenzoate ligand in the octahedral complex formed, with the maximum light absorbance, and draw its structure.

[2]

no. of moles of $Cu^{2+} = 3.33/1000 \times 0.05 = 1.665 \times 10^{-4}$ mol

no. of moles of 2–aminobenzoate $= 6.67/1000 \times 0.025 = 1.665 \times 10^{-4}$ mol

$Cu^{2+} \equiv$ 2–aminobenzoate ligand



[Total: 20]

4 A tooth is made up of two parts: the crown and the root. Dental crown is the visible part of the teeth which is made of enamel and dentine.

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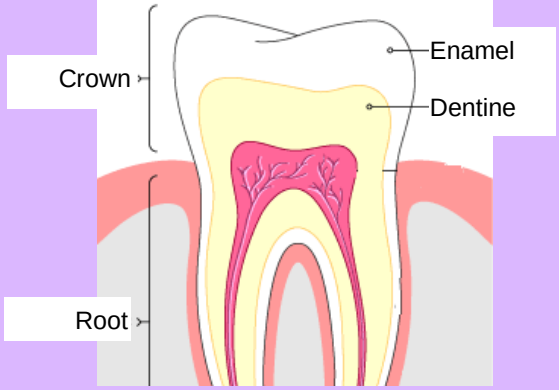


The enamel is made of hydroxyapatite, $Ca_5(PO_4)_3OH$. In the mouth, mineral substances such as calcium ions and phosphate ions that are present in saliva contribute to the formation and decomposition of the hydroxyapatite. These two processes occur simultaneously until an equilibrium is reached. The formation process is called mineralisation of the enamel, whereas the decomposition process is called demineralisation.

$$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

Presence of dental plaque is a major cause for demineralisation of tooth. The pH of dental plaque can be significantly reduced by presence of acetic and lactic acids. If it goes below the critical pH for a long period of time, demineralisation process can occur and dental cavities will appear.

(a) Explain how an acidic medium can affect the demineralisation of teeth.

[2]

$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$ --- (1)
In an acidic medium, the H^+ ions can react with OH^- or PO_4^{3-} ions produced during demineralisation of hydroxyapatite in eqm (1). By Le Chatelier's Principle, this shifts the equilibrium (1) forward (or to the right), encouraging/ accelerating the demineralisation process which resulted in tooth decalcification.

(b) It is known that fluoride ions ensure a better protection for teeth. One of the proposed mechanisms to explain this phenomenon suggests that fluoride ions can substitute the hydroxide ions of hydroxyapatite during the mineralisation process to form fluoropaptite, $Ca_5(PO_4)_3F$, which has a lower solubility. (K_{sp} value of fluoroapatite = 1.0×10^{-60})

(i) Write the balanced equation for the reaction describing the demineralisation of fluoroapatite in water. Hence write a Ksp expression of fluoroapatite.

$Ca_5(PO_4)_3F(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + F^-(aq)$

K_{sp} of fluoroapatite = $[Ca^{2+}]^5[PO_4^{3-}]^3[F^-]$

(ii) Calculate the solubility of fluoroapatite in water and hence the concentration of phosphate ions.

Let the solubility of fluoroapatite be x.
K_{sp} of fluoroapatite = $[Ca^{2+}]^5[PO_4^{3-}]^3[F^-] = 1.0 \times 10^{-60}$

$1.0 \times 10^{-60} = (5x)^5(3x)^3(x)$
$x = 6.11 \times 10^{-8}$ mol dm^{-3}
Solubility of fluoroapatite in water is 6.11×10^{-8} mol dm^{-3}

$[PO_4^{3-}] = 3x = 1.83 \times 10^{-7}$ mol dm^{-3}

(iii) In the presence of a weak acid, HF, the concentration of fluoride ions from demineralisation of fluoroapatite is less than expected. Explain why this is so.

[7]

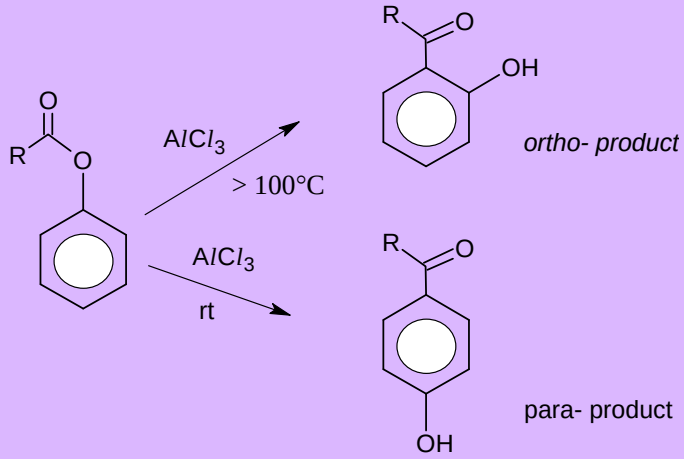
$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

$Ca_5(PO_4)_3F(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + F^-(aq)$ --- (2)

The common ion, $F^-(aq)$, from the dissociation of weak acid HF will cause equilibrium (2) to shift backwards (or left) by Le Chatelier's Principle. Thus, the solubility of fluoroapatite decreases and hence concentration of fluoride ions is lesser than expected.

(c) A phenyl ester can be converted to a hydroxyl phenyl ketone via a rearrangement reaction known as the Fries rearrangement.

It involves migration of an acyl group of phenyl ester to the benzene ring. The reaction is ortho, para–selective and the position of acylation can be regulated by the choice of temperature. A Lewis acid catalyst like A*l*C*l*$_3$ is required.



Using the Fries rearrangement in step **II** of the reaction scheme below, give the reagents and conditions for steps **I** – **IV** and deduce the structures for intermediates **A** – **C**.

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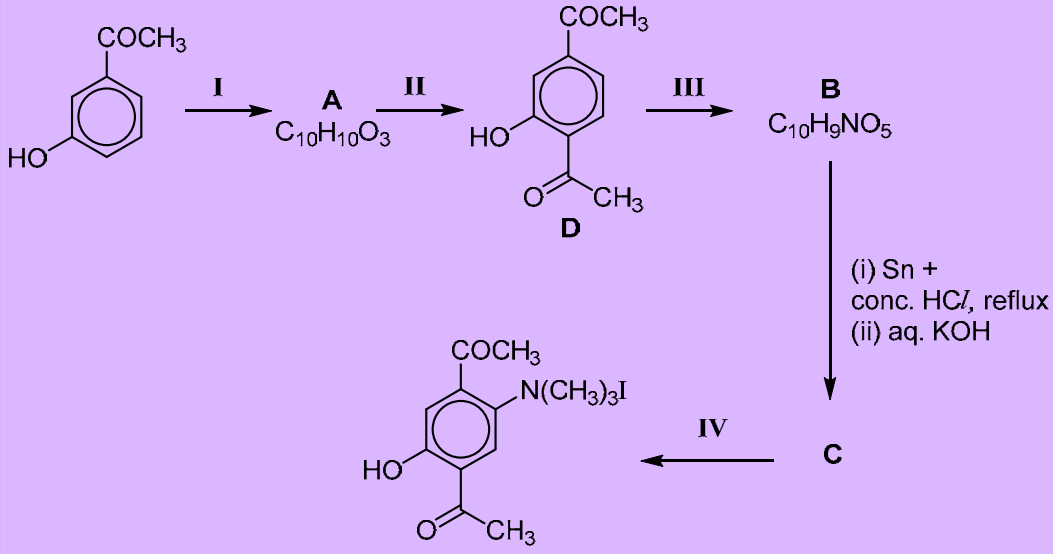
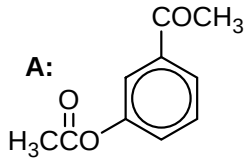


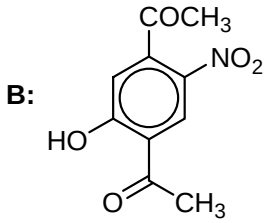
[7]

I: CH_3COCl (OR NaOH followed by CH_3COCl), r.t.
II (Fries rearrangement): $AlCl_3$, heat at > 100°C
III: dilute HNO_3, r.t. OR conc. HNO_3 & conc. H_2SO_4, reflux
IV: excess CH_3I, heat

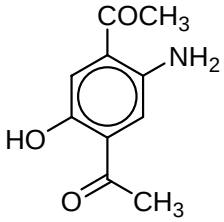
A:



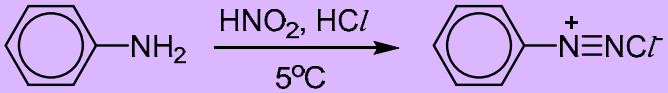
B:



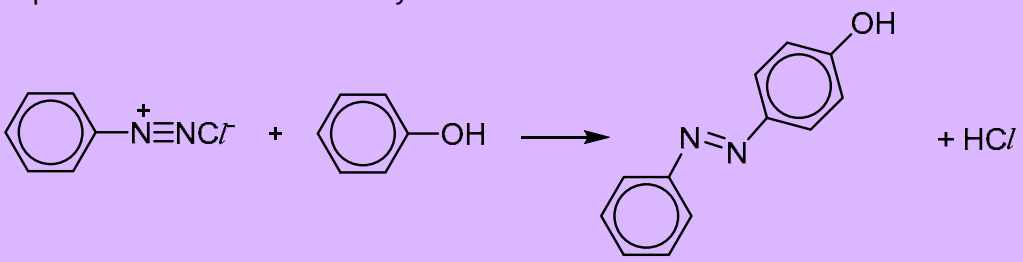
C:



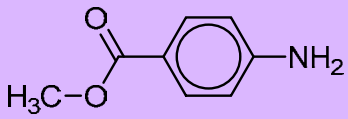
(d) Aromatic amines can react with cold nitrous acid and hydrochloric acid to form diazonium salts.



These salts undergo azo coupling reactions with arenes such as phenol to form azo compounds that can be used as dyes.

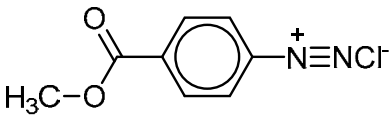


A student attempts to synthesise an azo compound from the following aromatic amine, **E**, using the azo coupling reaction.



(**E**)

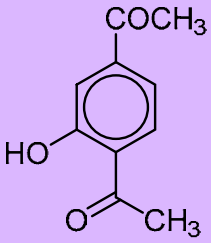
(i) Give the structure of the diazonium salt formed when **E** reacts with cold nitrous acid and hydrochloric acid.



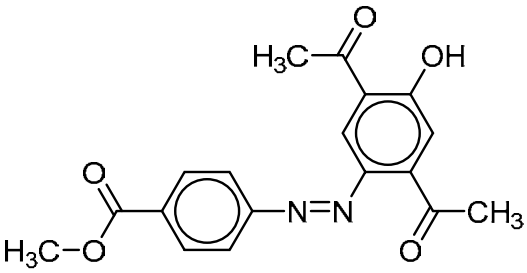
(ii) State the type of mechanism that azo coupling reaction undergoes.

Electrophilic substitution

(iii) Draw the structure of the possible azo compound formed between the diazonium salt in (**i**) and **D**.



D



(iv) Suggest a reason why the azo compound may not be obtained during the synthesis.

Any one:

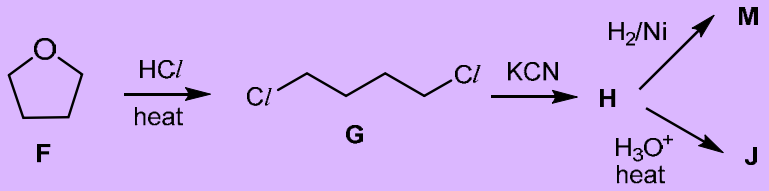
- **D** has two electron–withdrawing acyl group (CH_3CO–) attached to the aryl ring of phenol which will decrease its electron density and hence the reactivity of **D** towards coupling reaction with the diazonium salt.
- The bulky substituents on the aryl ring of D cause steric hindrance and it is more difficult for the dizaonium salt (electrophile) to approach the aryl ring.

[4]
[Total: 20]

5 Nylon is a generic designation for a family of polyamides. They are condensation copolymers formed by reacting equal parts of a diamine and a dicarboxylic acid.

Two useful precursors (**M** and **J**) for the synthesis of a type of Nylon are prepared from tetrahydrofuran (**F**).

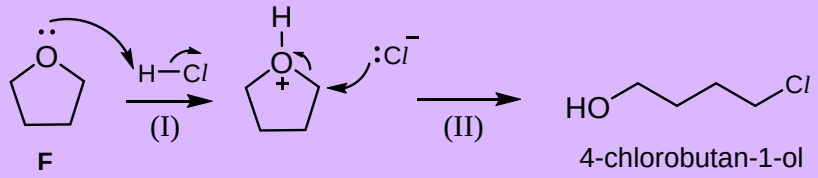
15



The mechanism of the reaction between **F** and HC*l* to form **G** involves four steps (I) – (IV).

(I) The first step involves the protonation of tetrahydrofuran (**F**).

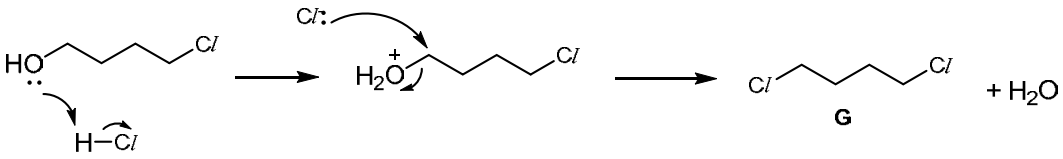
(II) This is followed by the attack of a chloride ion on the cyclic intermediate to open up the cyclic ring with the breaking of a C–O bond. This gives 4–chlorobutan–1–ol.



(III) The third step involves the protonation of 4–chlorobutan–1–ol.

(IV) The last step is the attack of another chloride ion on the intermediate, with the removal of a H_2O molecule, forming **G**.

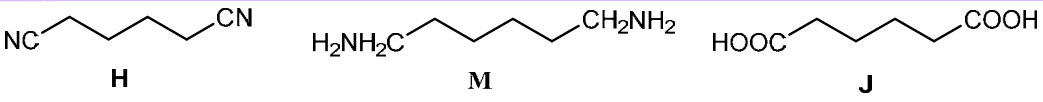
(a) (i) Using the information, propose a mechanism for the formation of **G** from 4–chlorobutan–1–ol, showing clearly the movement of electrons using curly arrows.



(ii) What type of reaction takes place in step (II)?

Nucleophilic substitution.

(iii) Suggest the structures for **H**, **M** and **J**.



[7]

(b) The elements of Group VII, especially chlorine, play an important role in the development of chemistry. The following are reactions that involve element of chlorine and its compounds.

(i) Identify the element **K** below and explain the observations as far as you can. Equation is not required.

Element **K** forms a colourless gaseous hydride which dissolves readily in water to form a strongly acidic solution. When this solution is shaken with aqueous chlorine in the presence of hexane, two layers of liquid are obtained and a violet colour is seen at one of the layers.

Element K is iodine.

Gaseous HI dissociates in water to form H^+ and I^- giving a strongly acidic

solution as H–I bond is weak and easily broken. I^- ions in the solution will be oxidised by aqueous Cl_2 to I_2 which readily dissolves in organic solvent (hexane) to give a violet colouration.

(ii) When a sample of interhalogen compound **L**, I_xCl_y was dissolved in an excess of aqueous potassium iodide, a brown solution was obtained. The brown solution required 34.0 cm^3 of 0.50 mol dm^{-3} sodium thiosulfate for reaction.

When the experiment was repeated with another sample of **L** of the same mass with excess potassium iodide, a yellow precipitate was first obtained with careful addition of aqueous silver nitrate. When the yellow precipitate was filtered off, a white precipitate of mass 1.83 g was obtained when more aqueous silver nitrate was added.

Determine the formula of compound **L** and hence construct a balanced equation between compound **L** and potassium iodide.

$I_xCl_y + yI^- \rightarrow [(x + y)/2]\ I_2 + yCl^-$

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

n(I_2) produced when reacted with KI
= [0.50 x (34.0/1000)] / 2 = 8.50 x 10^{-3} mol

n(Cl) in **L** = 1.83 / 143.5 = 0.0128 mol

⇨ y = 0.0128, x = 4.20 x 10^{-3}
simplest mole ratio, x:y = 1:3
Hence formula of **L** is ICl_3.
$ICl_3 + 3I^- \rightarrow 2I_2 + 3Cl^-$

(iii) Anhydrous iron(III) chloride is a dark brown solid which exist as a dimer, Fe_2Cl_6 in the solid state. It is a moisture sensitive solid which forms an acidic solution in water. In the gaseous state, the dimer increasingly dissociates into its monomer completely at 400 ^oC.

0.450 g of Fe_2Cl_6 and 1.069 g of $FeCl_3$ were placed in a 0.500 dm^3 evacuated flask and heated to 350 ^oC. The pressure of the mixture at equilibrium was found to be 8.01 x 10^4 Pa.

- Explain, with equation, how iron(III) chloride, $FeCl_3$ forms an acidic solution in water.
- Calculate the equilibrium constant, K_c (including its units) for the dissociation of Fe_2Cl_6 at 350 ^oC.

The high charge density of hydrated Fe^{3+} ion enables it to attract electrons away from one of its surrounding water molecules, thereby polarising and weakening the O–H bond which results in the release of a proton.

$FeCl_3$ (s) + $6H_2O$ (l) $\rightarrow [Fe(H_2O)_6]^{3+}$ (aq) + $3Cl^-$ (aq)

$[Fe(H_2O)_6]^{3+}$ (aq) $\rightleftharpoons$ $[Fe(H_2O)_5(OH)]^{2+}$(aq) + H^+(aq)

Assuming ideal behaviour,

$$pV = n_{total}\ RT$$

$$8.01 \times 10^4 \times 0.500 \times 10^{-3} = n_{total} \times 8.31 \times (273+350)$$

$$n_{total} = 0.007735 \text{ mol}$$

Initial amount of Fe_2Cl_6 = $\frac{0.450}{55.8x2 + 35.5x6} = 0.001386$ mol

Initial amount of $FeCl_3$ = 1.069 / 162.3 = 0.006587 mol

Let amount of Fe_2Cl_6 dissociated at equilibrium be x mol

	$Fe_2Cl_6(g)$	$\rightleftharpoons$	$2FeCl_3(g)$
Initial amount / mol	0.001386		0.006587
Change in amount / mol	$-x$		$+2x$
Equilibrium amount / mol	$0.001386 - x$		$0.006587 + 2x$

Hence, $0.001386 - x + 0.006587 + 2x = 0.007735$

$$0.007973 + x = 0.007735$$

$$x = -2.38 \times 10^{-4}$$

Equilibrium constant, K_c for the dissociation of Fe_2Cl_6

$=[(6.111 \times 10^{-3})^2/0.500] / (1.624 \times 10^{-3})$

$= \underline{0.0460 \text{ mol dm}^{-3}}$

[Total: 20]