1 Planning (P)

In metal displacement reactions, a more reactive metal will displace a less reactive metal from a solution. Copper, silver and gold appear as elements in the earth due to their poor reactivity with the environment. These metals are easy to extract.

You are required to plan an experiment to determine the enthalpy change of a metal displacement reaction between zinc and copper(II) sulfate solution. Zinc reacts with aqueous copper(II) sulfate as shown by the equation below.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

The reaction is **exothermic** and spontaneous, requiring only a few minutes to go to completion.

You are provided with the following chemicals

- Zinc powder,
- 0.8 mol dm^{-3} copper(II) sulfate, $CuSO_4$

as well as apparatus commonly found in the laboratory.

(a) State the observations when the reaction goes to completion.

Blue $CuSO_4$ solution decolourises <u>and</u> pink copper solid is deposited at the bottom of the solution.

[1]

(b) Using the information above, write a plan to describe how you would determine the enthalpy change of the reaction between zinc and copper(II) sulfate.

Your plan must include

- a suitable mass of zinc to be used, and your justifications for choosing this mass,
- the volume of copper(II) sulfate solution to be used,
- detailed procedures of the experiment you would perform. Include details of the apparatus you would use, and
- the precautions you would take to minimise heat loss.

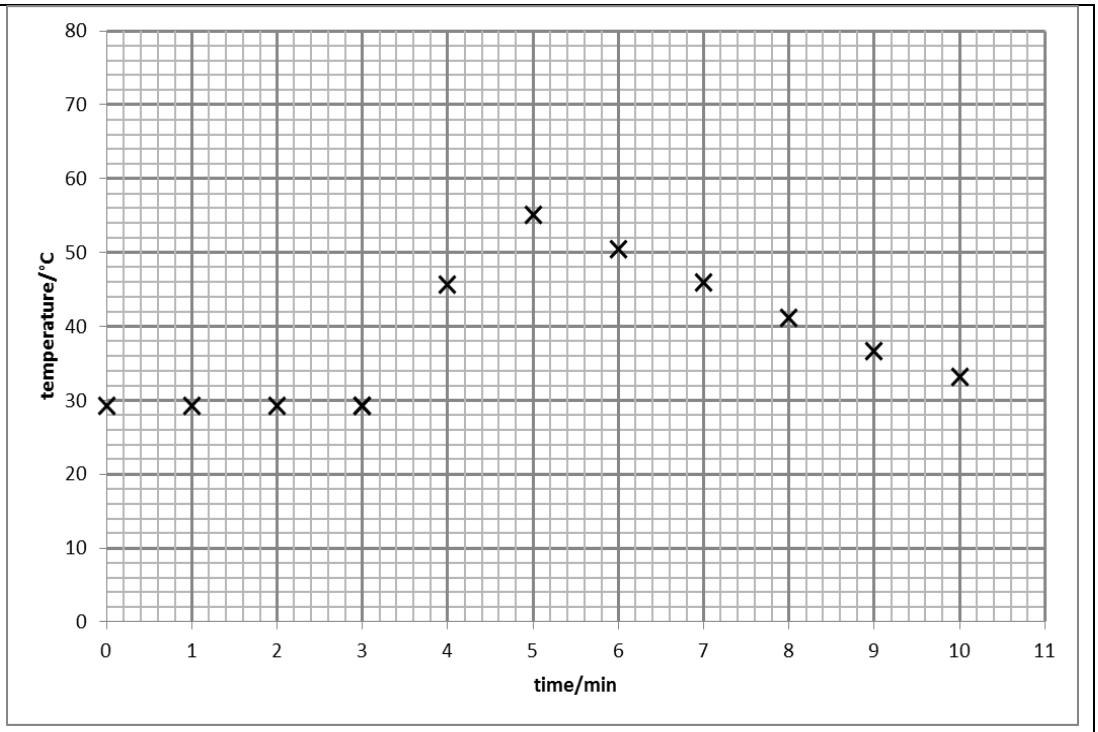
[4]

Assuming 25.0 cm^3 of $CuSO_4$ (aq) used,

Amount of $CuSO_4$ = (25/1000) x 0.8 = 0.0200 mol = amount of zinc required.

Minimum mass of Zinc = 0.02 x 65.4 = <u>1.31 g</u>

		Procedure: 1. **Weigh an empty weighing bottle and record its mass.** 2. **Place between 1.40 g and 1.50 g of zinc powder into the weighing bottle (*excess zinc is used to ensure complete displacement*). Record all required weighings in an appropriate table.** 3. **Place a styrofoam cup in the 250 cm^3 beaker and measure, using a measuring cylinder, *25.0 cm^3* of $CuSO_4$ into the styrofoam cup.** 4. **Stir gently with the thermometer and record the initial temperature of the solution.** 5. **Add zinc from the weighing bottle to the plastic cup. Immediately stir with the thermometer and record the highest temperature reached.** 6. **Reweigh the weighing bottle with residual zinc powder, if any, and record the mass.** ***Accept any other suitable method.*** **To minimise heat loss, a lid should be added to the styrofoam cup to prevent heat from escaping to the surroundings. This would lead to a more reliable ΔT result.** ***1m for calculation of mass of zinc*** ***1m for steps 1,2,6*** ***1m for steps 3,4,5*** ***1m for method to minimise heat loss***
	(c)	A student carried out the reaction between zinc powder and copper sulfate solution using a data logger with a temperature probe. The zinc powder was added in at the third minute. He obtained a set of temperature readings at different time intervals. The student then plotted a graph of temperature against time, shown below.

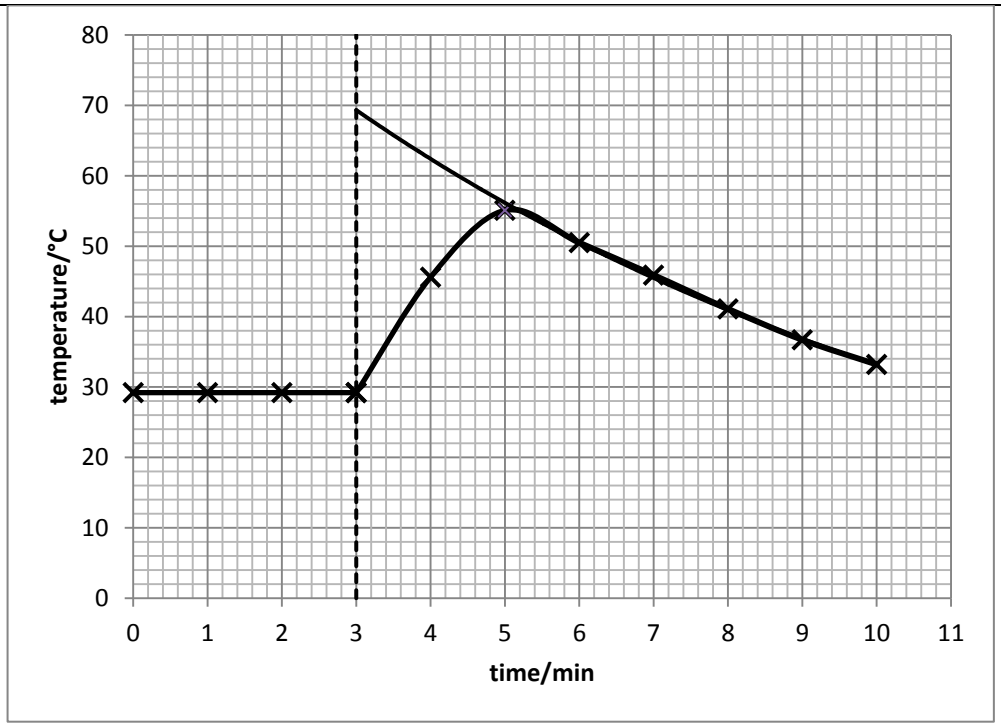


Using his graph, estimate a value for Δ**T** by extrapolating the curve to meet the vertical line representing the starting time of the experiment and hence determine the maximum temperature that could have been reached if heat loss to the surrounding were prevented.

[2]

1m for correct extrapolation shown on graph plot

1m for calculation of ΔT = 69.0 – 29.5 = 39.5ºC (accept any value between 36 to 43, based on students' graph)



	(d)	Using your answers in **(b)** and **(c)**, determine the enthalpy change of the metal displacement reaction. [4.2 J of heat energy raises the temperature of 1 cm^3 of any solution by 1 ^oC]
		[1]
		$Q = mc\Delta T = (25.0)(4.2)(39.5) = 4147.5$ J **Limiting reagent is $CuSO_4$ as Zinc is added in excess.** **$\Delta H = - Q / n_{LR} = 3727.5 / 0.02 = - 207$ kJ mol^{-1} ;**
	(e)	Another student performed the same experiment but instead of using zinc powder, he used zinc metal strips. Identify one likely difference between this student's experiment and the one done in **(c)**. Explain your answer. [2]
		The rate of reaction will be slower. ; **This is due to the larger size of the zinc metal strips, giving rise to a smaller surface area of contact with the reactants. ;**
	(f)	Reactive metals such as aluminium are more difficult to extract. They are always found as compounds in nature. Suggest one method by which these reactive metals can be extracted from its compounds. [1]
		Electrolysis ;

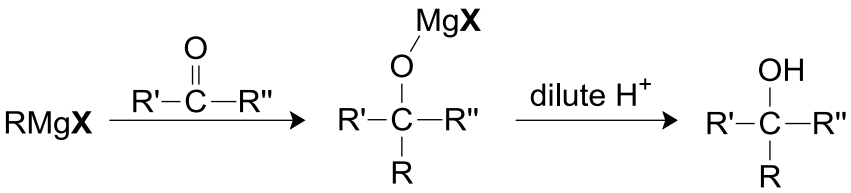
	(g)	Predict a probable enthalpy change value of the metal displacement reaction if the metal is now replaced with magnesium instead of zinc. Explain your answer.
		Student can state <u>any value</u> that is more exothermic than their answer obtained in (d). **Magnesium is higher up in the reactivity series, thus is it more reactive than Zinc (oxidises more readily than zinc), leading to a more vigorous reaction, enthalpy change is more exothermic. ;**
		[1]
		[Total:12]

2. This question concerns the conversion of a ketone to a tertiary alcohol using Grignard reagent.

Grignard reagent, RMgX, can be formed by reacting magnesium with a halogenoalkane, as shown in the equation below.

$$\mathbf{RX} + Mg \longrightarrow RMg\mathbf{X}$$

When Grignard reagent reacts with a ketone in the presence of dilute acid, the following reaction takes place.



The table below shows some physical properties of the reagents and the organic product of the reaction.

Substance	**Formula**	**Molar mass / g mol^{-1}**	**Density / g cm^{-3}**	**Solubility in water**	**Boiling point / °C**
1-Bromopropane	$CH_3CH_2CH_2Br$	122.9	1.35	Slightly soluble	71
Ethoxyethane	$C_2H_5OC_2H_5$	74.0	0.713	Slightly soluble	35
Magnesium	Mg	24.3	1.74	Insoluble	1110

Butanone	$CH_3COC_2H_5$	72.0	0.805	Soluble	80
Alcohol product			0.829	Slightly soluble	122

(a) In **Stage One** of the conversion, 1.335 g of magnesium is added to a flask containing an equimolar quantity of 1-bromopropane dissolved in 20 cm^3 of ethoxyethane. The mixture is then refluxed.

(i) Calculate the amount of magnesium used and hence the volume of 1-bromopropane used in **Stage One**.

Amount of Mg = 1.335 / 24.3 = 0.0549 mol ;

Amount of Mg = **0.0549 mol**

Mass of 1-bromopropane = 0.0549 × 122.9 = 6.747 g ;

Volume = 6.747 / 1.35 = 5.00 cm^3 ;

Volume of 1-bromopropane = **5.00 cm^3**

(ii) Explain why ethoxyethane can be used to dissolve 1-bromopropane.

Energy evolved from the formation of permanent dipole-permanent dipole between ethoxyethane and 1-bromopropane is sufficient to overcome the pd-pd between ethoxyethane and between 1-bromopropane.

identification of solute-solvent interaction and solute-solute and solvent solvent interactions;

energy requirement;

(iii) Suggest why prolonged heating at high temperature is required for reactions such as this.

It has high activation energy / reaction is slow ;

It involves breaking of a strong covalent bond or C-Br bond ;

		(iv)	Give the structural formula of the Grignard reagent formed.
			$CH_3CH_2CH_2MgBr$;
			[8]
	(b)	In **Stage Two** of the conversion, the mixture from **Stage One** is allowed to cool and 4.0 cm^3 of butanone is added dropwise. The mixture is then gently heated under reflux.	
		(i)	Assuming that the reaction between magnesium and 1-bromopropane in **Stage One** had 100% yield, show with calculations that the Grignard reagent is in excess.
			Amount of butanone used = 4.0 × 0.805 / 72.0 = 0.04472 mol ; **Amount of butanone required = Amount of Grignard reagent** **= Amount of Mg = 0.0549 mol** **Since amount of butanone used is less than the amount required, it is a limiting reagent, hence Grignard reagent is in excess. ;**
		(ii)	State the type of reaction undergone in **Stage Two**.
			Nucleophilic addition ;
			[3]
	(c)	In **Stage Three** of the conversion, the mixture from **Stage Two** is cooled using an ice bath, and then 25 cm^3 of 4 mol dm^{-3} dilute hydrochloric acid is slowly added.	
		(i)	Draw the structure of the tertiary alcohol produced from the reaction.
			$CH_3CH_2C(CH_3)(OH)CH_2CH_2CH_3$;
		(ii)	Suggest why the mixture is cooled before adding the dilute hydrochloric acid.

To slow down the vigorous reaction / The hydrolysis reaction is highly exothermic ;

[2]

(d) After the formation of the tertiary alcohol, the mixture from **Stage Three** is added to a separating funnel. The lower aqueous layer is separated and shaken successively with two 10 cm^3 portions of ethoxyethane, retaining the ethoxyethane extracts and combining them with the original ethoxyethane layer.

(i) Using the data given in the table, explain why the ethoxyethane forms a layer above the aqueous layer.

It is only slightly soluble in water ;

It has a smaller density than water ;

(ii) Suggest why the aqueous layer is shaken with ethoxyethane.

To extract the product alcohol formed as it is more soluble in ethoxyethane ;

[3]

(e) The combined ethoxyethane layer is then washed successively with 20 cm^3 of each of the following:

- Saturated sodium carbonate solution
- Anhydrous calcium chloride

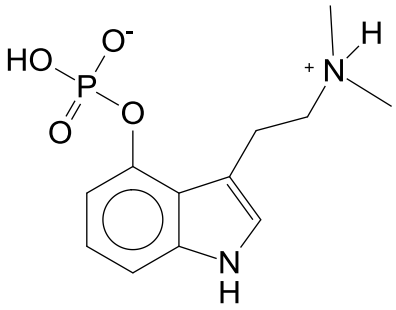
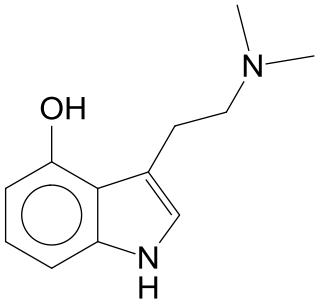
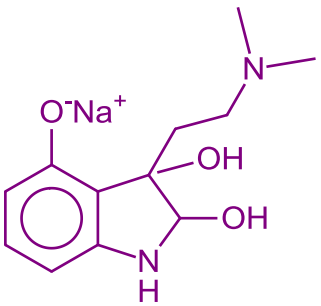
The solutions used to wash the ethoxyethane layer are each intended to remove a particular impurity.

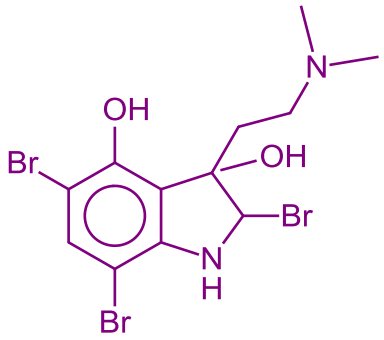
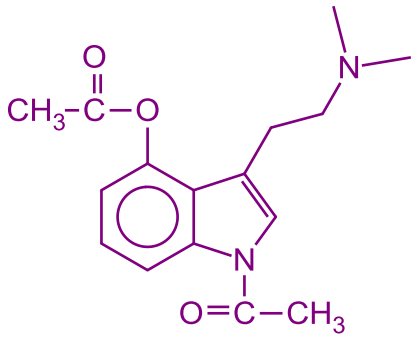
Suggest the impurity removed in each step.

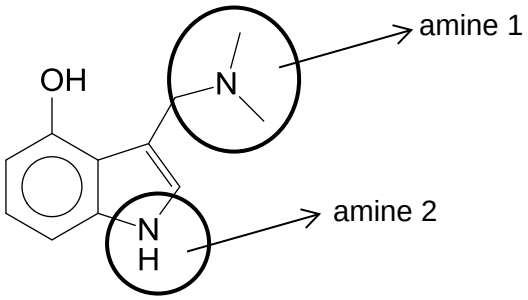
Solution	Impurity
Saturated sodium carbonate solution	**HC*l* ;**
Anhydrous calcium chloride	**Water ;**

[2]

[Total: 18]

3.	Psilocybin is a naturally occurring psychedelic compound produced by more than 200 species of mushrooms, collectively known as psilocybin mushrooms. As a prodrug, psilocybin is quickly converted by the body to psilocin, which has mind-altering effects such as euphoria, hallucinations, and changes in perceptions. Recent studies done at Imperial College London and Johns Hopkins School of Medicine conclude, when used properly, psilocybin acts as an antidepressant. The structures of psilocybin and psilocin are shown below.  psilocybin  psilocin		
	(a)	A prodrug is a precursor chemical compound to a drug to improve how the drug is absorbed, distributed, metabolised, and excreted. Explain why psilocybin can be better absorbed by the body compared to psilocin.	
		Psilocybin is more soluble in water ; **It can form ion dipole interactions with water ;**	
			[2]
	(b)	Draw the structure of the major organic product formed when psilocin reacts with	
		(i)	cold dilute $KMnO_4$ in aqueous NaOH
			

			Diol ; **Sodium phenoxide salt ;**
		(ii)	$Br_2(aq)$
			 **Disubstitution on benzene ;** **EA at alkene observing Markokvnikov's rule ;**
		(iii)	CH_3COCl
			 **Formation of ester ;** **Formation of amide ;**
			[6]

	(c)	Amines are weakly alkaline. There are two amine groups in psilocin with different basicity. State which amine group behaves as the weaker base. Explain your answer.  	
		Amine 2 is the weaker base. ; **The lone pair of electrons on amine 2 is delocalised into the benzene ring (or the sp^2 hybridised carbon in C=C);** **This decreases the availability of the lone pair to accept proton. ;** **(Do not accept amine 1 is connected to 3 electron-donating groups)**	
			[3]
			[Total: 11]

4.	**(a)**	The major buffer system that is used to control the pH of blood is the carbonic acid – hydrogen carbonate buffer system. H_2CO_3 (aq) ⇌ HCO_3^- (aq) + H^+ (aq)	
		(i)	Give two equations to show how the buffer system in blood helps to control pH.
			When small amount of acid is added: **HCO_3^- + H^+ → H_2CO_3 ;** When small amount of base is added: **H_2CO_3 + OH^- → HCO_3^- + H_2O ;**
		(ii)	The pH of human blood plasma is usually maintained at about 7.4. The

ratio of $[H_2CO_3]$: $[HCO_3^-]$ in blood plasma is 20 : 1.

Calculate the K_a of H_2CO_3.

$pH = pK_a + lg([salt]/[acid])$

$7.4 = pK_a + lg([HCO_3^-] / [H_2CO_3])$

$7.4 = pK_a + lg(1/20)$;

$pK_a = 8.701$

$K_a = 10^{-8.701} = 1.99 \times 10^{-9}$ mol dm^{-3} ;

K_a of H_2CO_3 = **1.99×10^{-9} mol dm^{-3}**

[4]

(b) The temperature of a sample of gas **X** is measured at various pressures, keeping the volume of the system constant. The following results were obtained.

Pressure /kPa	Temperature /°C
6.0	27.0
8.0	127.0
10.0	227.0

(i) Deduce whether the sample of gas **X** is behaving ideally.

Show calculation that P/T is constant (20.0 Pa K^{-1} or 0.0200 kPa K^{-1}) ;

Conclude gas X behaves ideally ;

(ii) Hence suggest a reason for the behaviour of gas **X** in this sample.

There is negligible intermolecular forces of attraction between the molecules / the volume of molecules is insignificant as compared to the volume of the gas. ;

[3]

(c) Electrosynthesis is the synthesis of chemical compounds using electrochemical cells. In one such reaction, a concentrated aqueous solution of sodium

propanoate, $CH_3CH_2COO^-Na^+$, is electrolysed in an alkaline medium using platinum electrodes. At the anode, a mixture of carbon dioxide and butane is formed. At the cathode, hydrogen gas is evolved.

Write half equations for the reactions which occur at the anode and cathode respectively.

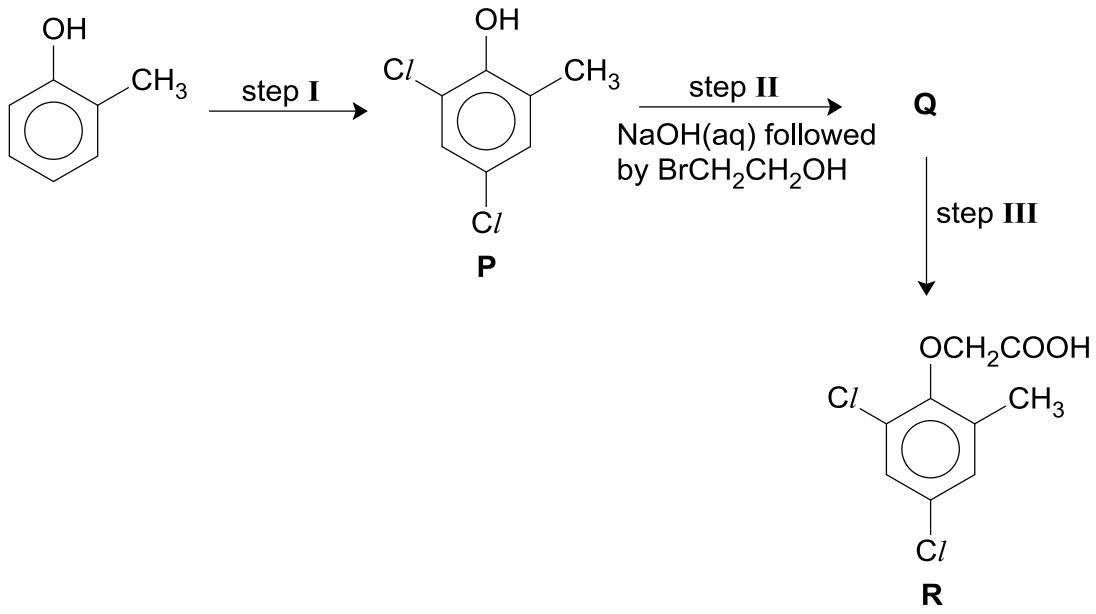
Anode: **$2\ CH_3CH_2COO^- \rightarrow 2\ CO_2 + CH_3CH_2CH_2CH_3 + 2e$;**

Cathode: **$2\ H_2O + 2e \rightarrow H_2 + 2\ OH^-$;**

[2]

[Total: 9]

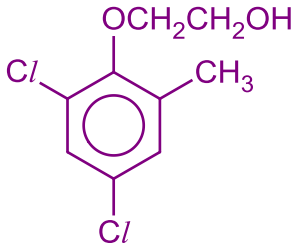
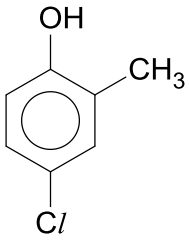
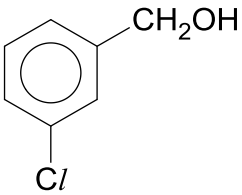
5. The reaction scheme below shows a three-step synthesis of compound **R** from 2-methylphenol.

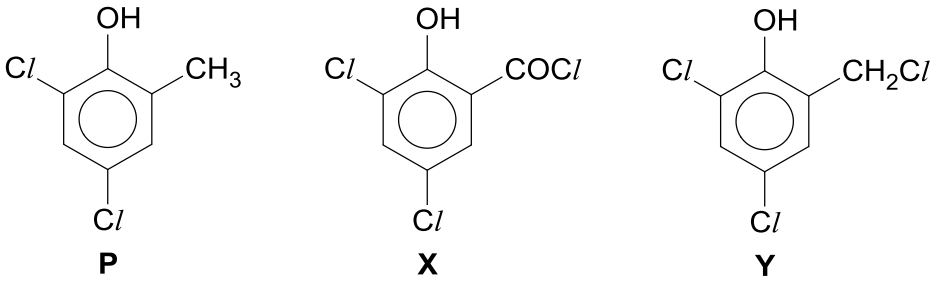


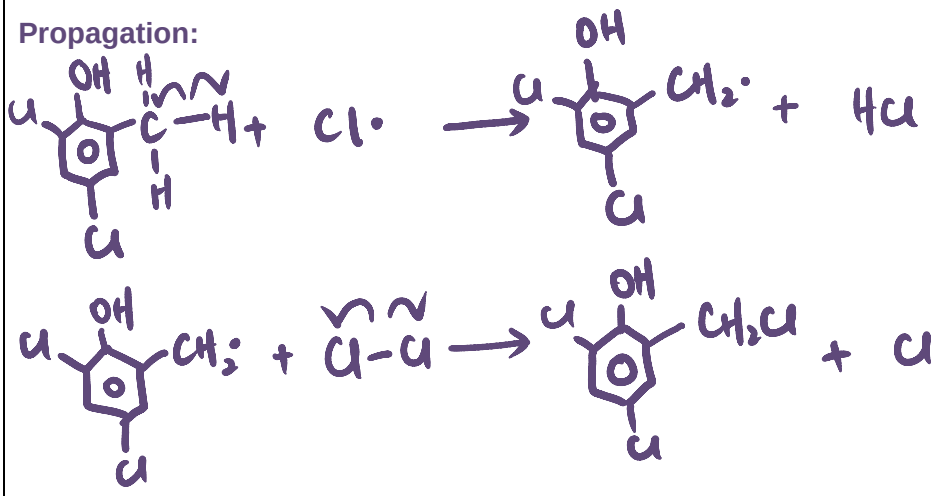
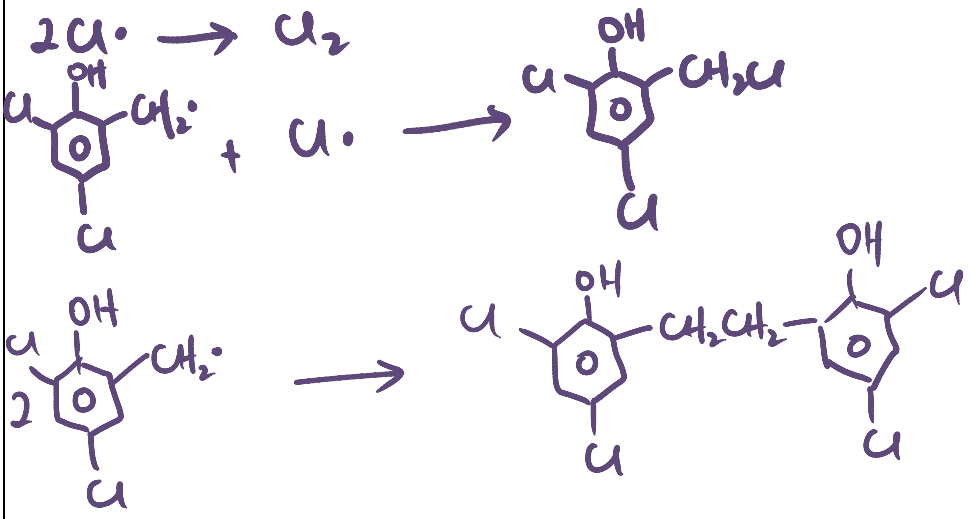
(a) (i) State the reagents and conditions for steps **I** and **III**.

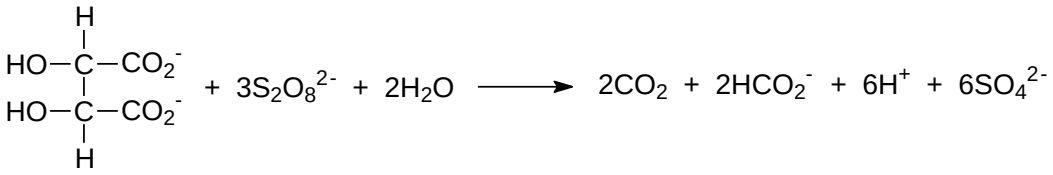
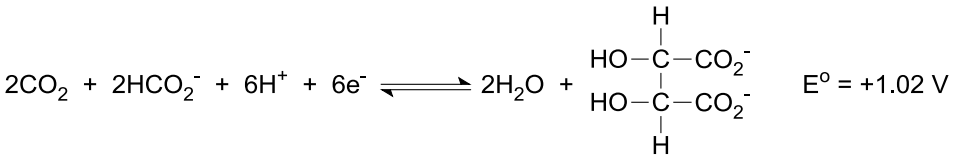
Step	Reagents and conditions
I	**Cl_2(aq) ;**
III	**$K_2Cr_2O_7$, dil H_2SO_4, heat ;**

(ii) Draw the structure of **Q**.

			 ;
		(iii)	Step **II** involves two types of reactions. State the two types of reactions and suggest the role of NaOH(aq) in this step.
			acid-base neutralisation ; nucleophilic substitution ; **To produce a stronger nucleophile ;**
			[6]
	(b)	Compound **S** can also be formed from 2-methylphenol  **S**	
		(i)	State the reagent and condition required for the conversion.
			Cl_2 in CCl_4, room temperature, absence of UV ;
		(ii)	Give a simple chemical test that can be used to distinguish **S** from its isomer, **T**. State the reagent and condition used and the observation for both compounds.  **T**
			$K_2Cr_2O_7$, dil H_2SO_4, heat ; **T will turn the orange solution green, forming a white ppt. Solution**

			remains orange for S ; **or** **Br_2(aq) ;** **S will decolourise orange Br_2, forming a white ppt. T will not decolourise orange Br_2. ;** **or** **PCl_5 or $SOCl_2$** **T will give white fumes. S will not give white fumes. ;**
			[3]
	(c)	Compound **P** and two other compounds, **X** and **Y**, are shown below  **P** **X** **Y**	
		(i)	The three compounds are reacted with hot ethanolic silver nitrate. Compare and explain the relative rate of formation of white precipitate for the three compounds.
			Slowest to fastest : P < Y < X ; **C-Cl bond in P is the strongest because the p orbital of Cl overlaps with the pi-electron cloud of the benzene, making it stronger than an alkyl C-Cl bond ;** **For X, the electronegative O atom causes the carbonyl carbon to be very electron deficient ;** **hence most susceptible to nucleophilic attack ;**

		(ii)	**P** can be converted to **Y**. Describe the mechanism for the conversion of **P** to **Y**.
			Free radical substitution **Initiation:**  **Propagation:**  **Termination:**  **Name of mechanism + initiation ;** **Propagation ;** **Termination (any 2 equations) ;**
		(iii)	The white precipitate formed in **(c)(i)** is accidentally mixed with a sample of cream precipitate of AgBr(s). Explain how pure AgBr(s) can be recovered

			from the mixture, writing equation where appropriate.
			Add dilute aqueous ammonia to the sample of solids. ; **The white ppt will dissolve while AgBr(s) remains.** **AgC*l* + $2NH_3$ → $[Ag(NH_3)_2]^+$ + C*l*$^-$;** **Filter the mixture and wash the residue with distilled water and dry the solid AgBr. ;**
			[10]
	(d)	Peroxodisulfate(VI) ion, $S_2O_8^{2-}$, is capable of oxidising the tartrate ion, $[CH(OH)(CO_2^-)]_2$, to carbon dioxide and methanoate ion.  The reaction is very slow, even at elevated temperature. The rate of reaction can be increased by adding in a suitable catalyst such as manganese(III) ions.
		(i)	State the property of transition metals which make them good homogeneous catalysts.
			Their ability to exhibit variable oxidation states ;
		(ii)	Using data from the *Data Booklet* and the reduction potential given below, propose a mechanism to show how manganese(III) ion can work as a catalyst for this reaction. 
			Step 1: **$6Mn^{3+}$ + $[CH(OH)CO_2^-]^2$ + $2H_2O$ → $6Mn^{2+}$ + $2CO_2$ + $2HCO_2^-$ + $6H^+$** **$E°_{cell}$ = +1.49 + (-1.02) = +0.47 V** **Step 2:** **$2Mn^{2+}$ + $S_2O_8^{2-}$ → $2Mn^{3+}$ + $2SO_4^{2-}$**

			$E°_{cell}$ = +2.01 + (-1.49) = +0.52 V **Equation + $E°_{cell}$ for step 1 ;** **Equation + $E°_{cell}$ for step 2 ;**
			[3]
			[Total: 22]