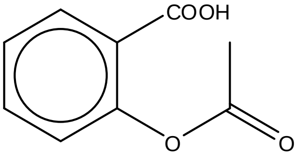
Planning

For Examiner's use

1 Distribution coefficient, K_D, is the ratio of equilibrium concentrations of a compound in a mixture of two immiscible solvents at a fixed temperature. Using two immiscible solvents, the distribution coefficient is a measure of the difference in solubility of a compound in these two solvents.

This experiment aims to find out the distribution coefficient of acetylsalicylic acid (ASA) in two immiscible mixtures, water and trichloromethane as well as water and methylbenzene. The values of the distribution coefficient can be used to determine Which is a better organic solvent for extracting ASA from water. It is predicted that each of these organic solvents will extract about 80-90% of ASA dissolved in water.

$$\text{Distribution coefficient, } \mathbf{K_D}_{\ \textbf{(organic solvent / water)}} = [\text{ASA}]_{\text{in organic solvent}} / [\text{ASA}]_{\text{in water}}$$



Acetylsalicylic acid

To find $\mathbf{K_D}_{\textbf{ (organic solvent /water)}}$ of ASA, a certain volume of the organic solvent is added to a measured volume of 0.01 mol dm^{-3} ASA (aq). Vigorous shaking of the mixture enables ASA to dissolve in the mixture of solvents. The mixture will reach equilibrium when it is left to stand for an hour at a suitable temperature.

The concentration of ASA in each solvent is determined by extracting 10.0 cm^3 of the solution from the aqueous layer and titrating the aliquots against NaOH (aq). By assuming that the remaining amount of ASA is dissolved in the organic solvent, the concentration of ASA in organic solvent can be calculated.

You are provided with

- 80 cm^3 of 0.01 mol dm^{-3} ASA (aq)
- 80 cm^3 trichloromethane
- 80 cm^3 methylbenzene
- 100 cm^3 separating funnel for mixing and separating the two solutions
- 0.010 mol dm^{-3} stock solution of NaOH (aq)

(a) In an experiment, the **independent variable** is a parameter that can be manipulated independently, whereas the **dependent variable** is the data to be collected that varies with the parameters that are manipulated.
State the independent variable and dependent variable in this experiment. **[2]**

		Independent variable – Organic solvent **Dependent variable – Concentration of ASA in water and the organic solvent**		
	(b)	A student who was conducting the experiment discovered that the NaOH stock solution should be diluted to 0.001 mol dm^{-3} before it is suitable for titrating the aqueous sample. In light of the extraction efficiency of the organic solvents, suggest why the 0.010 mol dm^{-3} NaOH stock solution is too concentrated for titrating the aqueous sample.	**[1]**	
		After extracting about 80-90% of ASA from the aqueous solution, the concentration of ASA (aq) is around 0.001 mol dm^{-3}. The volume of 0.010 mol dm^{-3} NaOH used in the titration would be too small resulting in a large percentage error.		
	(c)	**Procedures** Describe the procedure to determine K$_{\textbf{D (trichloromethane/water)}}$ of ASA. Your plan should include • necessary steps to set up the equilibrium of ASA in water and trichloromethane • appropriate apparatus used • suitable volumes of solutions and solvents • details for titration of aqueous ASA solution, including the indicator and the end point colour. You should note that the same procedure should be suitable for repeating with a mixture of methylbenzene and ASA (aq).	**[5]**	
		1. Using a measuring cylinder, measure 40 cm^3 of 0.01 mol dm^{-3} ASA (aq) and transfer it into the separating funnel. Measure 40 cm^3 of trichloromethane and transfer it into the separating funnel. **2. Shake the mixture vigorously. Leave the separating funnel to stand for one hour at constant room temperature.** **3. Using a 10 cm^3 pipette, measure out 10.0 cm^3 of the aqueous ASA solution. Transfer this solution into a conical flask.** **4. Titrate the solution against the diluted NaOH (aq) using phenolphthalein as the indicator. Titrate until permanent pink colour is seen.** **5. Repeat the titration to obtain consistent results.**		
	(d)	**Evaluation and analysis** A student used 40 cm^3 of 0.01 mol dm^{-3} ASA (aq) and 40 cm^3 of trichloromethane in the experiment. From the titration, it was found that 10.0 cm^3 of ASA (aq) required ***n*** cm^3 of 0.0010 mol dm^{-3} of NaOH (aq) for neutralisation.		

		Outline how you would use her results to determine $K_{D\ (\text{trichloromethane/water})}$ of ASA.	[3]	
		Amount of ASA in aqueous solution = 4*n* / 1000 x 0.0010 **= $4n \times 10^{-6}$ mol** **Concentration of ASA in aq solution = $(4n \times 10^{-6}) / 0.040$** **= $\underline{n \times 10^{-4}\ \text{mol dm}^{-3}}$** **Concentration of ASA in trichloromethane** **= $[(\frac{40}{1000} \times 0.01) - (4n \times 10^{-6})] / \frac{40}{1000}$** **= $\underline{0.01 - 0.0001n\ \text{mol dm}^{-3}}$** $K_{D\ (\text{trichloromethane /water})}$ **of ASA** **= $(0.01 - 0.0001n) / (n \times 10^{-4})$** **$=(100-n)/n$**		
	(e)	The procedure and calculations above is repeated using methylbenzene and ASA (aq). Suggest how the values of the distribution coefficient for the two solvent mixtures can be used to identify which is the better organic solvent for extracting ASA from water.	**[1]**	
		The larger the value of distribution coefficient the better the organic solvent will be at extracting ASA from water.		
				[Total: 12 marks]

2	Photographic films are coated with fine particles of silver halides, mainly silver bromide. Exposing the film to light promotes reduction of Ag^+ so that some Ag^+ ions are converted into fine granules of silver. During the film development process, the silver granules will be converted to form the photographic image captured on film. Any excess silver bromide on the film darkens when it is exposed to light and causes the photo to turn black over time. This can be prevented by 'fixing' the film to dissolve the excess silver bromide and washing the solution away. The fixer solution contains aqueous sodium thiosulfate, $Na_2S_2O_3$.				*For Examiner's use*
	(a)	**(i)**	Thiosulfate ions act as monodentate ligands and bind to silver ions to form a complex. The silver(I) dithiosulfate ion has a linear shape about the silver ion. Write the formula of silver(I) dithiosulfate ion. **$[Ag(S_2O_3)_2]^{3-}$**	**[1]**	

(ii) When the film is immersed in the aqueous solution, silver bromide granules dissolve to a small extent, according to Equation 1.

$$AgBr\ (s) \rightleftharpoons Ag^{+}\ (aq) + Br^{-}\ (aq) \text{ ------- Equation 1}$$

With the help of another equation, explain why silver bromide is soluble in aqueous sodium thiosulfate solution. **[3]**

$Ag^{+}\ (aq) + 2S_2O_3^{2-}\ (aq) \rightarrow [Ag(S_2O_3)_2]^{3-}\ (aq)$

When the film is exposed to thiosulfate ions in the fixer solution, aqueous silver ions form $[Ag(S_2O_3)_2]^{3-}$ (aq) which lowers the concentration of Ag^{+}. This causes the position of equilibrium 1 to shift to the right so that AgBr dissolves.

(b) A student suggests that a 5.0 mol dm^{-3} solution of aqueous ammonia can also be used as a fixer solution for photographic films. She suggests that the following reaction will occur.

$$AgBr\ (s) + 2NH_3\ (aq) \rightleftharpoons [Ag(NH_3)_2]^{+}\ (aq) + Br^{-}\ (aq) \text{ ------ Equation 2}$$

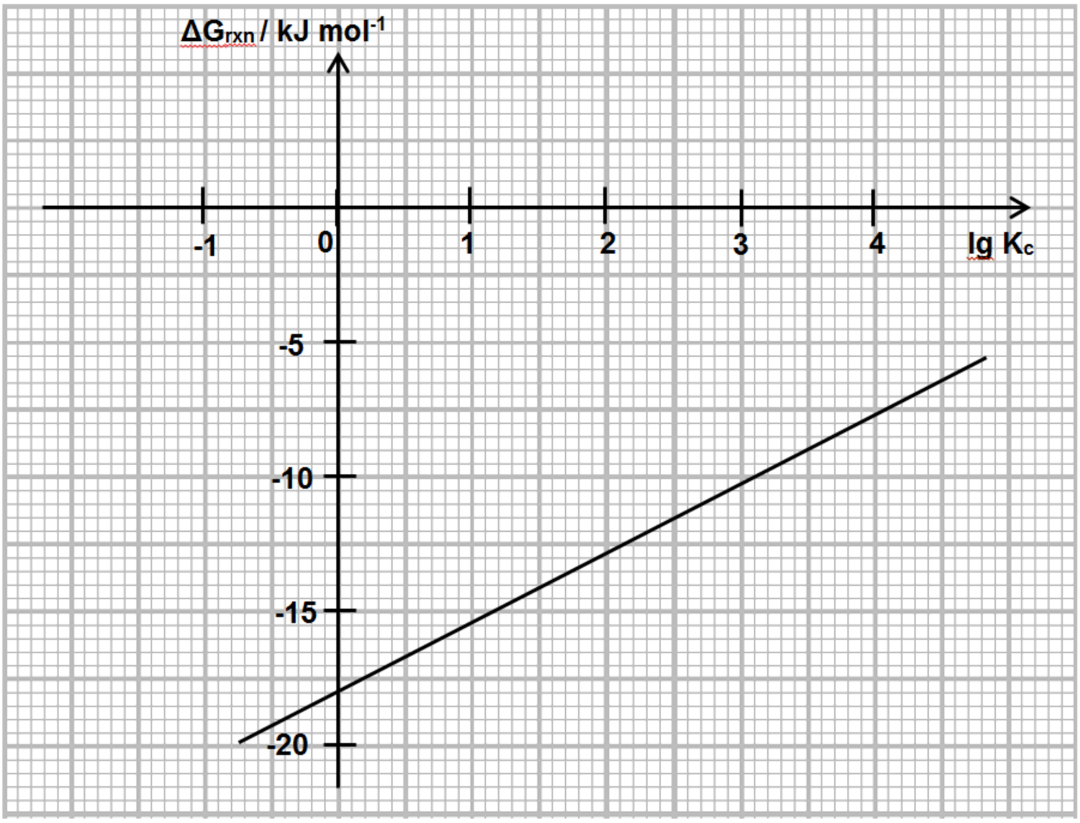
The student decides to calculate the equilibrium constant of Equation 2, K_{c2}, so as to justify her suggestion.

In order to calculate K_{c2}, the student considers another equilibrium as shown by Equation 3.

$$Ag^{+}\ (aq) + 2NH_3\ (aq) \rightleftharpoons [Ag(NH_3)_2]^{+}\ (aq) \text{ ------- Equation 3}$$

The graph of **ΔG_{rxn}** against **lg K_{c3}** is given for the reaction of excess 5.0 mol dm^{-3} NH_3 (aq) and Ag^{+} (aq) where K_{c3} is the equilibrium constant of Equation 3.

The graph shows the relationship $\Delta G_{rxn} = \Delta G° + RT \lg K_{c3}$ for Equation 3.



(i) State the value of ΔG_{rxn} when the reaction is at dynamic equilibrium. **[1]**

$\Delta G_{rxn} = 0$

(ii) Hence calculate the value of K_{c3} for the reaction between excess 5.0 mol dm^{-3} NH_3 (aq) and Ag^+ (aq) using $\Delta G_{rxn} = \Delta G° + RT \lg K_{c3}$, where R is the molar gas constant. **[2]**

From the graph, when $\Delta G_{rxn} = 0$,
$\Delta G°$ = (accept -17500 to -18500 J mol^{-1})

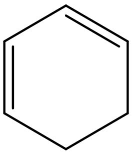
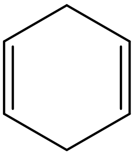
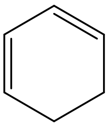
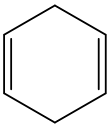
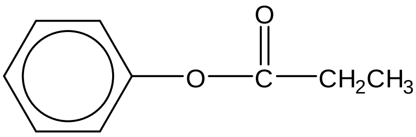
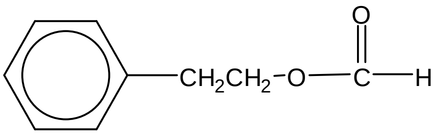
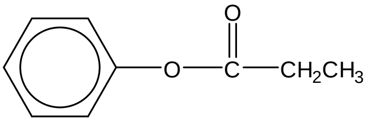
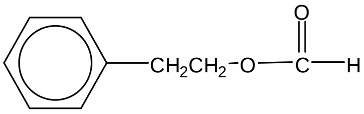
$\Delta G_{rxn} = \Delta G° + RT \lg K_{c3}$
$0 = -18000 + 8.31 \times 298 \lg K_{c3}$
$K_{c3} = \underline{1.82 \times 10^{7}}$ mol^{-2} dm^{6}

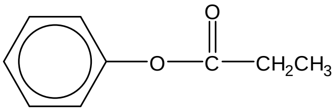
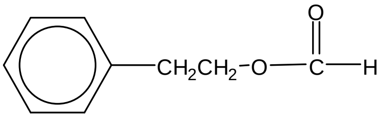
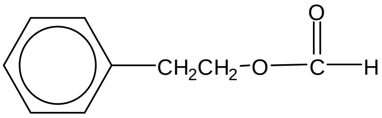
(iii) The K_{sp} value of AgBr is 5.35×10^{-13}.

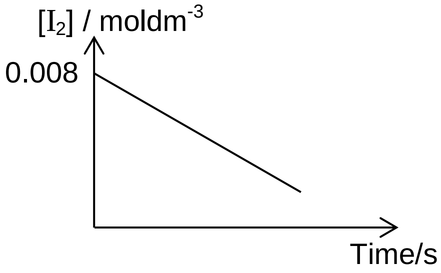
Write an equation to show the relationship between K_{c2}, K_{c3} and K_{sp} of AgBr (s). **[1]**

$K_{c2} = K_{sp} \times K_{c3}$

(iv) Using your answers in **(b)(ii)** and **(b)(iii)**, calculate the value of K_{c2}.
[You may use $K_{c3} = 2.00 \times 10^{7}$ for this calculation if you did not get an answer for **(b)(ii)**.] **[1]**

			K_{c2} = 5.35 x 10^{-13} x 1.82 x 10^{7} **= 9.74 x 10^{-6} mol dm^{-3}** **Or K_{c2} = 5.35 x 10^{-13} x 2.00 x 10^{7}** **= 1.07 x 10^{-5} mol dm^{-3}**		
		(v)	Use your calculated value from **(b)(iv)** to explain whether 5.0 mol dm^{-3} NH_3 (aq) can be used as fixer solution. **5.0 mol dm^{-3} NH_3 (aq) cannot be used as a fixer solution since the small value of K_{c2} shows that equilibrium 2 lies to the left and does not favour dissolving of AgBr (s).**	**[1]**	
	(c)	Suggest methods by which the following compounds could be distinguished from each other by chemical tests. State clearly how each compound behaves in each test. Preliminary breaking up of the compounds may be required.		**[4]**	
		(i)	 and 		
			Test: Acidified $KMnO_4$, heat **Observations:**  **decolourises purple $KMnO_4$ and produces effervescence of a gas that forms white ppt in limewater.**  **decolourises purple $KMnO_4$ but no effervescence seen.**		
		(ii)	 and 		
			Test: Acidified $KMnO_4$, heat **Observations:**  **does not decolourise the purple solution.**  **decolourises the purple solution**		

			and produces effervescence of a gas that forms white ppt in limewater. **OR** **Test: HCl (aq), heat. Add Br_2 (aq).** **Observations:**  **decolourises orange/reddish-brown Br_2 solution and forms a white ppt.**  **does not decolourises orange/ reddish-brown Br_2 solution.** **Test: NaOH (aq), heat. Add $AgNO_3$ followed by NH_3 (aq), warm.** **Observations:**  **forms a silver mirror while the other does not.**		
				[Total: 14 marks]	
3	Carbonyl compounds can react with halogens in acidic or alkaline medium to form different products. Kinetic studies are then done to investigate the orders and mechanism of these reactions.				
	(a)	In acidic medium, propanone reacts with iodine to form iodopropanone as shown in the equation below: $CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$ The kinetic studies of the above reaction suggest that a three-step mechanism is involved in this reaction. $CH_3COCH_3 + H^+ \rightleftharpoons CH_3\overset{+}{C}(OH)CH_3$ (fast) $CH_3\overset{+}{C}(OH)CH_3 \rightleftharpoons H_2C{=}C(OH)CH_3 + H^+$ (slow) $H_2C{=}C(OH)CH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$ (fast)			
		(i)	Explain the term, *order of reaction*. **The order of reaction with respect to a reactant is the power to which that reactant's concentration is raised to in an experimentally determined rate equation.**	**[1]**	
		(ii)	Based on the kinetic studies, state the rate equation for the above reaction. **Rate = k $[CH_3COCH_3][H^+]$**	**[1]**	

		(iii)	Given that the initial [CH_3COCH_3], [H^+], and [I_2] are 0.200, 0.200 and 0.008 mol dm^{-3} respectively and the initial rate of the reaction is 1.92×10^{-5} mol dm^{-3} s^{-1}, calculate the rate constant, stating its units clearly. $k = \frac{\text{Rate}}{[CH_3COCH_3][H^+]} = \frac{1.92 \times 10^{-5}}{0.20 \times 0.20}$ = **4.80×10^{-4} mol^{-1} dm^3 s^{-1}**	**[1]**	
		(iv)	Sketch a labelled graph of [I_2] versus time. Your labels should include the information given in **(a)(iii)**.  **Linear graph with** **- axes and units** **- initial concentration of I_2**	**[1]**	
		(v)	Explain what will happen to the rate of reaction if chlorine is used in place of iodine, assuming that the mechanism remains unchanged? **There will be no change to the rate of reaction as halogen is not involved in the rate determining step.**	**[1]**	
		(vi)	The above data was obtained based on a sampling method, which requires a sample of the chemical reaction to be extracted at various time intervals from a reaction mixture followed by titration. Suggest another method and briefly explain how it can be used to determine the rate of the reaction between acidified propanone solution and iodine. **Colorimetry method can be used.** **Colour intensity of a chemical species/absorbance is directly proportional to its concentration. As the concentration of iodine decreases and the brown/yellow colour intensity of the reacting solution also decreases. A graph of colour intensity/absorbance against time can be plotted. The rates at various times are obtained by drawing tangents to the curve and then calculating the gradients.**	**[2]**	
	(b)	In alkaline medium, propanone reacts with iodine to form ethanoate ion and triiodomethane as shown in the overall equation below: $CH_3COCH_3 + 3I_2 + 4OH^- \longrightarrow CH_3COO^- + CHI_3 + 3I^- + 3H_2O$			

This is commonly known as the iodoform reaction.

The reaction in the alkaline medium cannot be limited to monohalogenation since polyhalogenation can occur instead.

Monohalogenation:

$$CH_3COCH_3 + I_2 + OH^- \longrightarrow CH_3COCH_2I + I^- + H_2O$$

Halogenation continues:

$$CH_3COCH_2I + I_2 + OH^- \longrightarrow CH_3COCHI_2 + I^- + H_2O$$

$$CH_3COCHI_2 + I_2 + OH^- \longrightarrow CH_3COCI_3 + I^- + H_2O$$

Formation of triiodomethane:

$$CH_3COCI_3 + OH^- \longrightarrow CH_3COO^- + CHI_3$$

(i) Using the information below, propose a two-step mechanism that is involved in the **monohalogenation** reaction. Indicate the slow step clearly in your answer. **[2]**

- Propanone reacts with hydroxide ion in the first step reversibly to form a carbanion, which is a negatively charged carbon based anion.
- The overall order of the reaction is 2.

Step 1: $CH_3COCH_3 + OH^- \rightleftharpoons [CH_3CO\overset{-}{C}H_2] + H_2O$ (slow)

Step 2: $[CH_3CO\overset{-}{C}H_2] + I_2 \longrightarrow CH_3COCH_2I + I^-$

(ii) In the last step of forming triiodomethane, one of the carbon-carbon bond breaks to form CI_3^- when all the acidic protons have been replaced by iodine atoms. Suggest why this reaction takes place readily? **[1]**

CI_3^- is a stable anion/good leaving group as it is stabilized by three electron-withdrawing iodine atoms.

Alternatively:

That particular carbon-carbon bond is weakened due to the presence of electron-withdrawing groups.

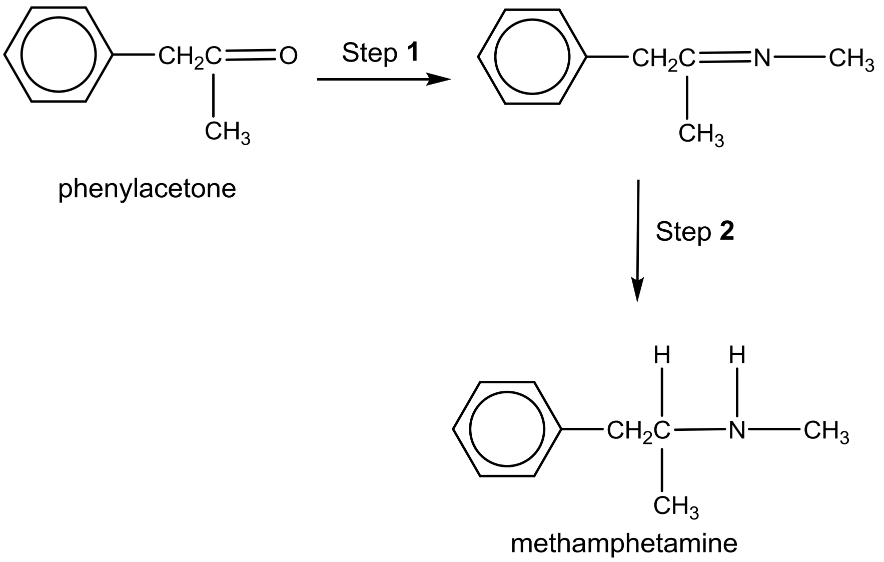
(c) In a two-step synthesis of phenylacetone, $C_6H_5CH_2COCH_3$ from propanone, the basis of reaction in **3(a)**, and the knowledge of Friedel-Crafts reaction can be used. It is known that Friedel-Crafts reaction is an electrophilic substitution reaction, involving the alkylation or acylation of an aromatic ring in the presence of a Lewis acid catalyst. **[3]**

Hence or otherwise, propose the synthesis route for the conversion, stating the reagents and conditions clearly for each step and the intermediate which is formed.

$CH_3COCH_3 \longrightarrow CH_3COCH_2Cl$ [1] $\longrightarrow CH_3COCH_2(C_6H_5)$

First step: <u>Cl_2</u> in acidic condition, e.g dilute H_2SO_4
Second step: <u>benzene,</u> anhydrous <u>$AlCl_3$</u>, room temperature

(d) Phenylacetone can then be used to synthesise methamphetamine as shown below:



(i) Given that condensation reaction takes place in step **1**, state the reagent needed for this step. **[1]**

CH_3NH_2

(ii) Name the type of reaction taking place in step **2**. **[1]**

Reduction

[Total: 15 marks]

4 **(a)** When propan-1-ol is heated with acidified potassium dichromate(VI) solution, it can be oxidised to form either propanal (Figure I) or propanoic acid (Figure II)

For Examiner's use

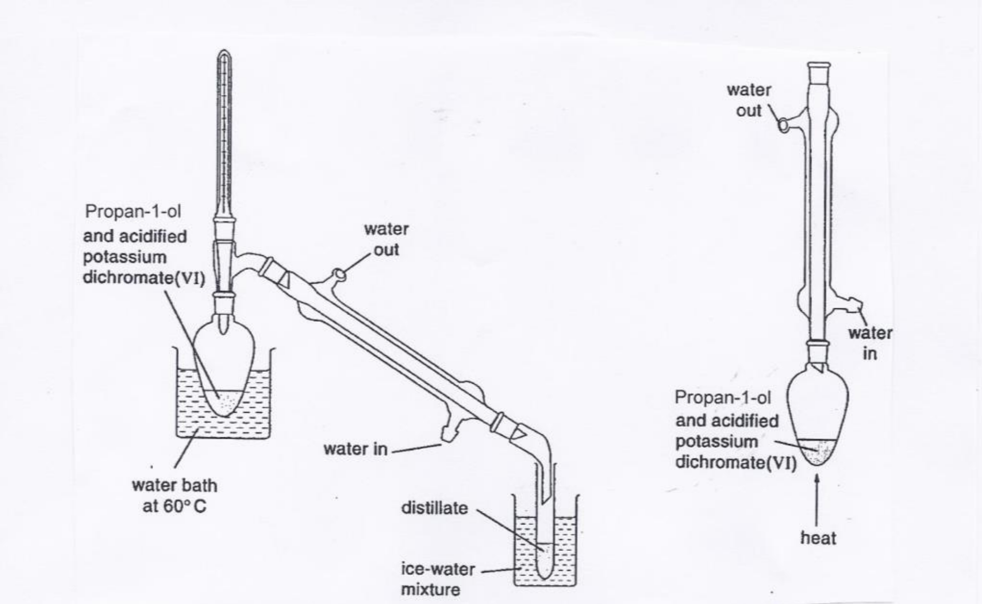


Figure I **Figure II**

The boiling points of propan-1-ol, propanal and propanoic acid are given in the table below.

	$CH_3CH_2CH_2OH$	CH_3CH_2CHO	$CH_3CH_2CO_2H$
Boiling point/^oC	97	49	141

Use this table of boiling points to explain

(i) why the organic product is likely to be propanal if the apparatus shown in **Figure I** is used.

As water bath is at 60^{o}C, propanal would distil off and will not be oxidised further. **[1]**

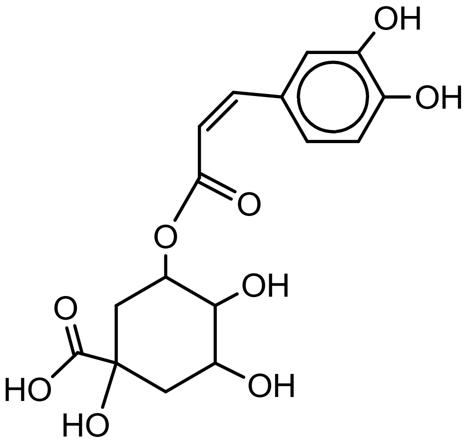
(ii) why the organic product is likely to be propanoic acid if the apparatus shown in **Figure II** is used.

In the cooler region of the condenser, propanal will condense back into mixture and further oxidation into propanoic acid can take place. **[1]**

(iii) Suggest why the flask in which the product is collected is surrounded by iced water.

Propanal is volatile (b.p. is 49^{o}C). Hence by reducing the temperature, it can reduce the loss of propanal. **[1]**

(b) Coffee beans contain chlorogenic acid as shown below.

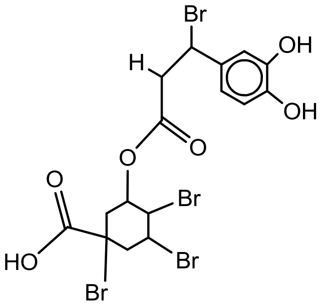
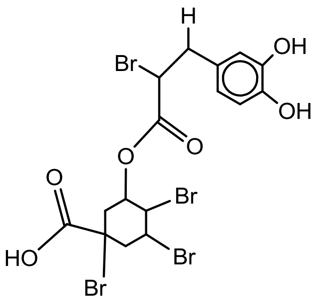
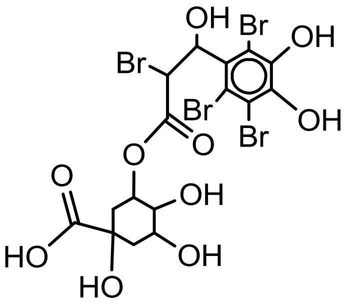
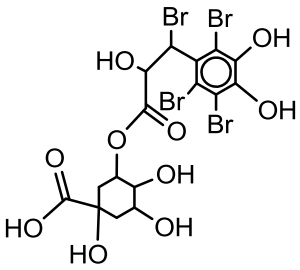
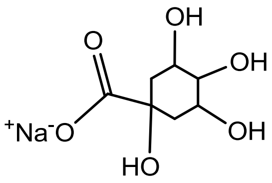
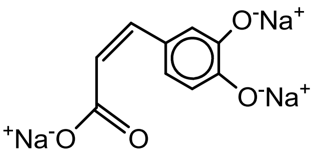
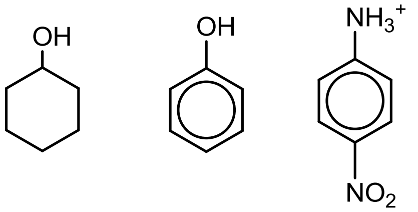
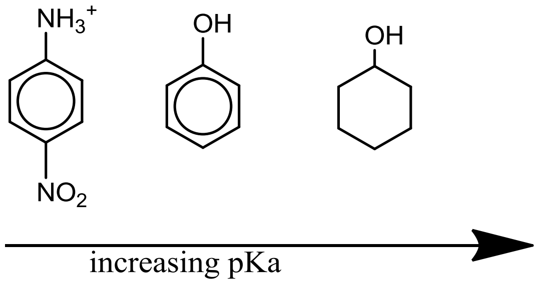


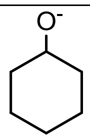
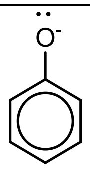
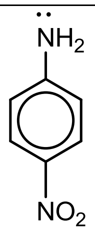
chlorogenic acid

Draw the structural formula of the main product(s) when chlorogenic acid is reacted with each of the following reagents.

(i) HBr(g)

[1]

			 or 		
		(ii)	An excess of Br_2(aq)  or 	**[1]**	
		(iii)	Hot NaOH(aq)  	**[2]**	
	(c)	**(i)**	Arrange the following three compounds in order of increasing pK_a and explain the trend.   $HA \rightleftharpoons A^- + H^+$	**[1]**	

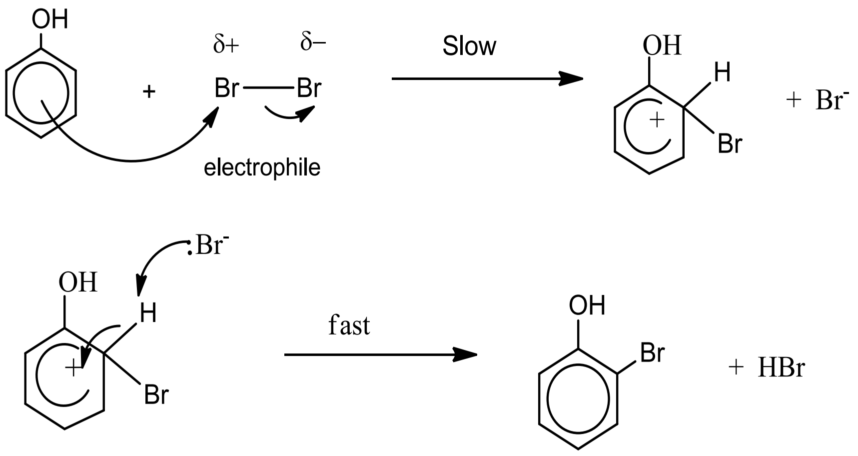
		
Increasing stability of conjugate base→		
Alkyl group is electron-donating, intensified the negative charge	**Lone pair of electrons is delocalised into ring, dispersing the negative charge**	**Lone pair of e is delocalised into ring and NO_2 is a powerful electron-withdrawing group**

(ii) Phenol reacts much more readily with bromine than benzene does. Explain why electrophiles, such as bromine, react much more readily with phenol than with benzene.

Lone pair of electrons from O is delocalised into the ring thus electron density of the ring is increased so electrophiles are more attracted to the ring or dipole in electrophile is more easily induced. **[1]**

(iii) Phenol reacts with Br_2/CCl_4 to produce 2-bromophenol. Outline the mechanism of the reaction between phenol and Br_2/CCl_4. [2]

You should include all charges and use curly arrows to represent the movement of electron pairs.



[Total: 14 marks]

5 Some data about hydrogen fluoride and hydrogen iodide are given below.

For Examiner's use

	HF	HI
Boiling point/^{o}C	20	-35

Bond energy/kJ mol^{-1}	562	299
Acid dissociation constant, K_a/ mol dm^{-3}	5.6×10^{-4}	---

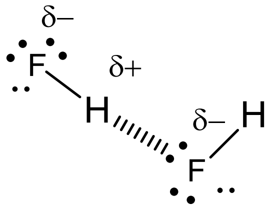
(a) Hydrogen fluoride can be prepared by the action of concentrated sulfuric acid on sodium fluoride. Explain, with the aid of an equation, why hydrogen iodide cannot be prepared by the action of the same acid on sodium iodide. **[2]**

Conc H_2SO_4 will oxidise HI to I_2

$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$

(b) Apart from the fact that H-F has a stronger bond energy than that of H-I, suggest, with the aid of a diagram, why aqueous HF is a weak acid while aqueous HI is a strong acid. **[1]**

Need to break intermolecular hydrogen bonds between molecules



(c) Calculate the pH of 0.1 mol dm^{-3} aqueous HF solution. **[1]**

$[H^+] = \sqrt{(5.6 \times 10^{-4})(0.1)} = 7.48 \times 10^{-3}$

$pH = -lg(7.48 \times 10^{-3}) = 2.13$

(d) Suggest why HF has a higher boiling point than HI. **[1]**

More energy is needed to break hydrogen bonds between HF molecules than van der Waals forces (or permanent dipoles-permanent dipoles forces) between HI molecules.

(e) When boron triflouride, BF_3, is dissolved in liquid HF, the resulting solution can conduct electricity and is acidic. Explain, with the aid of an equation, why this is so. **[2]**

$HF + BF_3 \rightarrow H^+ + BF_4^-$
BF_3 is <u>electron deficient</u> and <u>accepts F^- by dative bonding</u>, thus forming mobile BF_4^- and H^+ ions.

[Total: 7 marks]

6 (a) An experiment on the preparation of hydrated zinc sulfate involves the following steps:

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Step 1: Warm 30 cm^3 of dilute sulfuric acid in a beaker. Add zinc oxide to the acid until in excess.

Step 2: Filter the reaction mixture and collect the filtrate.

	Step 3:		Heat the filtrate until it becomes saturated at 50^{o}C. Then allow it to cool to room temperature to crystallise out hydrated zinc sulfate.		
	Step 4:		Filter off the crystals formed and then wash them with a little amount of cold distilled water.		
	Step 5:		Dry the crystals.		
		For **(i) – (ii),** refer to **Step 1**:			
		(i)	Write the balanced equation, (including state symbols) for the reaction that occurs. **$ZnO(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2O(l)$**	**[1]**	
		(ii)	Explain why zinc oxide rather than sulfuric acid is used in excess. **The unreacted ZnO can be removed by filtration but it is difficult to remove the excess H_2SO_4.**	**[1]**	
		(iii)	**Step 3** states "*Heat the filtrate until it becomes saturated*." Suggest one way to show that a saturated solution has been obtained. **Remove a drop of the solution and see if any solid is formed upon cooling.**	**[1]**	
		(iv)	Explain why ***cold distilled water*** is used to wash the crystals in Step 4. Washing with water **removes the water soluble impurities** and **cold water** is used to **reduce the loss of the salt**.	**[1]**	
		(v)	Suggest one method of drying the crystals in Step 5. **Dry the crystals between filter paper/dry in an oven at 120^{o}C/place under IR lamp**	**[1]**	
		(vi)	Suggest one chemical that can be used in place of zinc oxide in this experiment. **Zn metal or $ZnCO_3$ or $Zn(OH)_2$**	**[1]**	
	(b)	Zinc carbonate ($ZnCO_3$), another insoluble zinc salt undergoes decomposition upon strong heating.			
		(i)	Write an equation for the thermal decomposition of $ZnCO_3$. **$ZnCO_3 \rightarrow ZnO + CO_2$**	**[1]**	
		(ii)	Quoting relevant data from the *Data Booklet*, predict and explain how the thermal decomposition temperature of $ZnCO_3$ would compare to that of $CaCO_3$. **Ionic radius** **Zn^{2+}: 0.074 nm**	**[3]**	

			Ca^{2+}: 0.099 nm **The ionic radius of Zn^{2+} is smaller than Ca^{2+}. Zn^{2+} has higher power polarising power than Ca^{2+} thus able to distort the electron cloud of the CO_3^{2-} anion more and weaken the C-O bond to a larger extent.** **Hence the thermal decomposition temperature of $ZnCO_3$ would be lower than $CaCO_3$.**		
			[Total: 10 marks]		