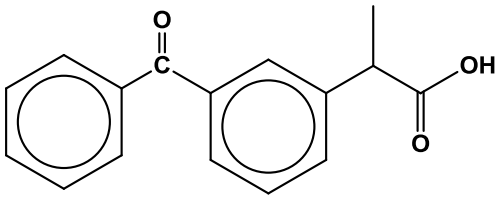
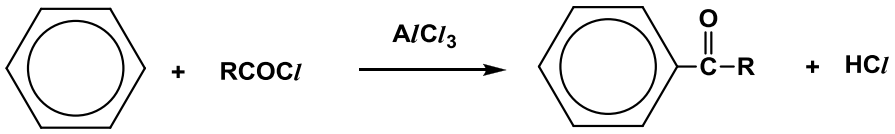
Solutions for 2015 SAJC H2 Chemistry Prelim Paper 3

1 (a) Organic compounds have various applications. For instance, Ketoprofen is a kind of nonsteroidal anti-inflammatory drug, which can be used as a substitute for aspirin.

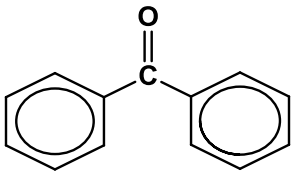


Ketoprofen

(i) Friedel Craft Acylation was first discovered by Charles Friedel and James Crafts in 1877. This reaction allowed for the acylation of an aromatic ring with acyl chloride. One such example is given below.



Benzophenone, which can be used to synthesise Ketoprofen, has the structure below.

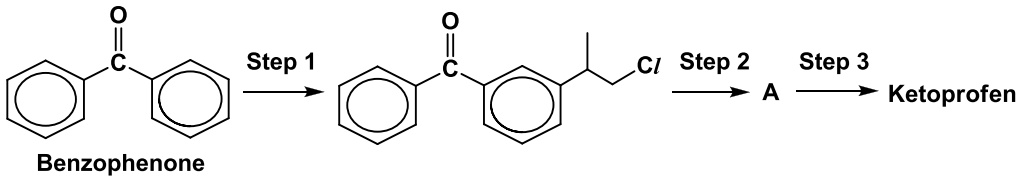


Benzophenone

Suggest the reagent needed to convert 2 moles of benzene into 1 mole of benzophenone. **[1]**

$COCl_2$

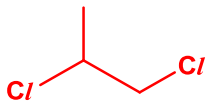
1 (a) (ii) Ketoprofen may be synthesised from benzophenone in the following route.



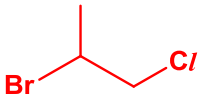
State the reagents and conditions for **Steps 1** to **3**.

Draw the structural formula of **A**. **[4]**

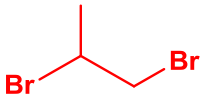
Step 1:



$AlCl_3$ or $FeCl_3$

OR 

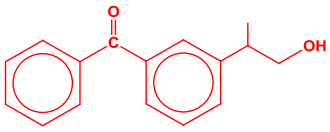
$AlBr_3$ or $FeBr_3$

OR 

$AlBr_3$ or $FeBr_3$

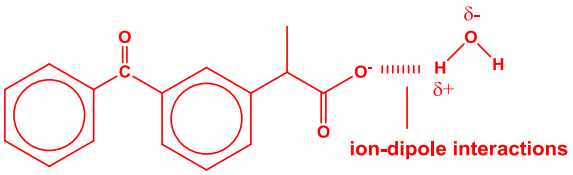
Step 2: **NaOH(aq), heat**

Step 3: **H_2SO_4 (aq), $K_2Cr_2O_7$, heat**

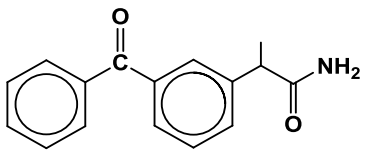
Structure of **A**: 

(iii) Ketoprofen is commonly sold as its sodium salt form for better absorption by the body, which is made up of 70% water. Explain, with the aid of a diagram, how this better absorption comes about. **[2]**

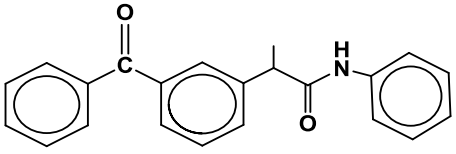
The ions in the sodium salt form can form **ion-dipole interactions with water**, thus enhancing its solubility and absorption by the body.



(iv) Nitrogen-containing derivatives of Ketoprofen may be synthesised and some examples are as shown.



Compound D



Compound E

Describe a simple chemical test to distinguish between compound **D** and compound **E**. **[2]**

Add **NaOH(aq)** to each of the unknown, followed by **heating**.

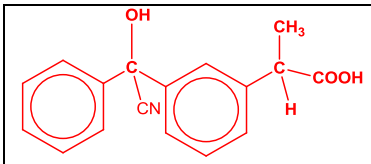
Add **Br_2 (aq) at room temperature** to each of the resultant products. **Orange Br_2 (aq) will decolourise, forming a white ppt** in the presence of compound E while the **orange colour remains** in compound D.

OR

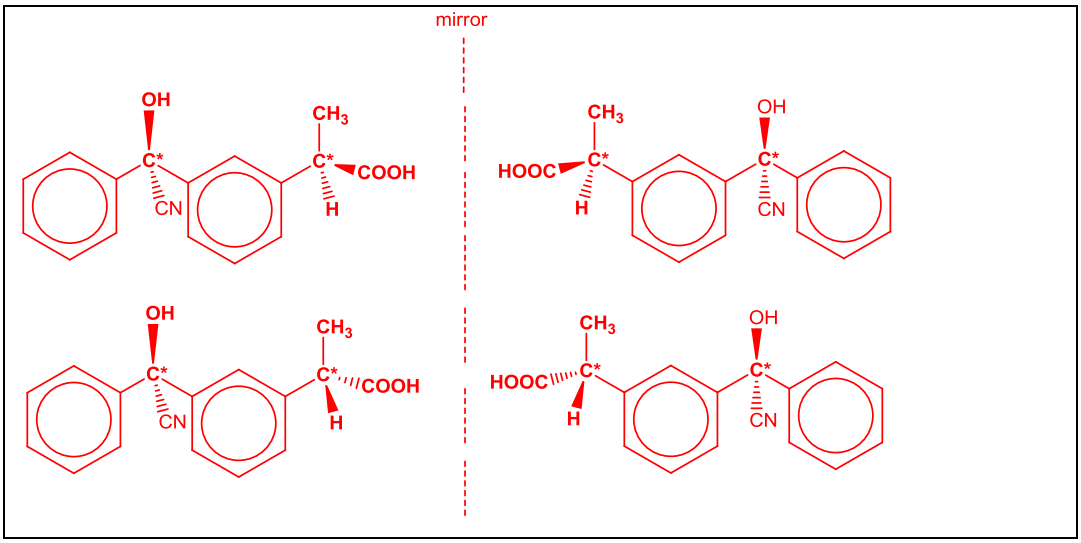
Add **NaOH(aq)** to each of the unknown, followed by **heating.** Compound D will produce a **colourless, pungent gas which turns moist red litmus paper blue / forms white fumes with a glass rod dipped in concentrated HCl**. Compound E does not produce such gas.

(v) Ketoprofen can react with cold alkaline HCN to form a product which exists as a mixture of 4 stereoisomers.

Give the structure of the product formed. Hence, state the type of isomerism exhibited by this product and draw the stereoisomers. **[4]**



Optical isomerism



1 (b) Another use of organic compounds is in the area of food preservation. To prevent food spoilage, the pH of food should not fluctuate too much. Hence, a mixture of lactic acid, $CH_3CH(OH)COOH$, and sodium lactate is commonly added in yoghurt to act as a pH regulator.

(i) Explain how the mixture of lactic acid and sodium lactate can function as a pH regulator when an acid is added. Include any relevant equation.

[2]

Addition of H^+: $CH_3CH(OH)COO^- + H^+ \rightarrow CH_3CH(OH)COOH$

When a **small amount** of H^+ is added, the presence of **large reservoir** of $CH_3CH(OH)COO^-$ neutralise the excess H^+. Hence, $[H^+]$ does not change significantly and **pH is kept almost constant**.

(ii) The pH of yoghurt is usually maintained at about 4.2.

Calculate the ratio of the concentrations of lactate ion to lactic acid in yoghurt, given that the pK_a of lactic acid is 3.86. **[1]**

$K_a = [CH_3CH(OH)COO^-][H^+] / [CH_3CH(OH)COOH] = 10^{-3.86}$

$= 1.380 \times 10^{-4}$ mol dm^{-3}

$[H^+] = 10^{-4.2} = 6.309 \times 10^{-5}$ mol dm^{-3}

Ratio of [lactate ion] to [lactic acid] = $10^{-3.86} : 10^{-4.2}$ = **2.19 : 1**

or 2.19

OR

$pH = pK_a + lg ([lactate ion] / [lactic acid])$

$4.2 = 3.86 + lg ([lactate ion] / [lactic acid])$

$([lactate ion] / [lactic acid]) = 10^{0.34}$ = **2.19**

(iii) Given that the concentration of lactic acid in a sample of yoghurt is 0.05 mol dm^{-3} and using your ratio in **(b)(ii)**, calculate the concentration of lactate ion. **[1]**

[lactate ion] = 0.05 x 2.19 = 0.110 or 0.109 mol dm^{-3}

(iv) Perfluorooctanoic acid is a common food contaminant. In yoghurt, this monobasic acid will dissociate completely. Calculate the new pH of the yoghurt when 0.05 mol of perfluorooctanoic acid is added to 5 dm^3 of the yoghurt in **b(iii)**.

Hence, calculate the change in pH. **[3]**

No. of moles of lactate ion in the yoghurt = 5 x 0.109 = 0.545 mol

No. of moles of lactate ion left after reacting with added H^+

= 0.545 – 0.05 = 0.495 mol

No. of moles of lactic acid after adding H^+ = (5 x 0.05) + 0.05 = 0.3 mol

OR

	$CH_3CH(OH)COO^-$	+ H^+	→ $CH_3CH(OH)COOH$
Initial amount / mol	0.545	**0.05**	5 x 0.05 = 0.25
Change in amount / mol	-0.05	-0.05	+0.05
Final amount / mol	0.495	0	0.3
Final concentration / mol dm^{-3}	0.495 / 5 = 0.099	0	0.3 / 5 = 0.06

OR

	$CH_3CH(OH)COO^-$ + H^+ →		$CH_3CH(OH)COOH$
Initial conc./ $moldm^{-3}$	0.545/5 = 0.109	0.05/5 = 0.01	0.05/5 = 0.01
Change conc./ $moldm^{-3}$	-0.01	-0.01	+0.01
Final conc. / mol dm^{-3}	0.099	0	0.06

Step ②

$K_a = [CH_3CH(OH)COO^-][H^+] / [CH_3CH(OH)COOH] = 10^{-3.86} = 0.5[H^+] / 0.3$

pH = - lg(8.282×10^{-5}) ≈ **4.08** **[1]**

OR

pH = pKa + lg [salt]/[acid]

= 3.86 + lg (0.5/0.3) = **4.08** **[1]**

Step ③

Change in pH = 4.2 – 4.08 = **0.12** **[1]**

[Total: 20 marks]

2 (a) Transition metals are known to have many uses, ranging from materials, medicine to

catalysts. Explain what is meant by the term *transition metal*. **[1]**

A transition element is a **d-block element** which forms at least one stable **ion** with an **incomplete d sub-shell of electrons / partially filled or incomplete d orbitals of electrons**.

(b) Aqueous copper(II) sulfate is blue and this is due to the presence of hexaaquacopper(II) ion, $[Cu(H_2O)_6]^{2+}$. When 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, and ammonia are added separately to a sample of copper(II) sulfate solution, the following reactions occur. (Note: "en" represents $H_2NCH_2CH_2NH_2$)

Reaction 1:

$[Cu(H_2O)_6]^{2+}$ (aq) + en (aq) $\longrightarrow$ $[Cu(en)(H_2O)_4]^{2+}$ (aq) + $2H_2O$ (*l*)

$\Delta H^{\ominus}$ = - 52 kJ mol^{-1}

Reaction 2:

$[Cu(H_2O)_6]^{2+}$ (aq) + $2NH_3$ (aq) $\longrightarrow$ $[Cu(NH_3)_2(H_2O)_4]^{2+}$ (aq) + $2H_2O$ (*l*)

$\Delta H^{\ominus}$ = - 48 kJ mol^{-1}

(i) State the full electronic configuration of Cu^{2+}. **[1]**

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

(ii) With reference to relevant bonds, suggest why the two enthalpy changes are similar in value. **[1]**

Both reactions involve the **breaking of 2 Cu-O bonds (bond between Cu and H_2O)** and **forming of 2 Cu-N bonds**, hence they have similar ΔH values.

(iii) By considering the entropy and enthalpy changes of **Reaction 1** and **Reaction**

2, suggest and explain the difference in magnitude of the standard Gibbs free energy change of the two reactions. **[2]**

The number of species increased in reaction 1 but remains the same for reaction 2. Hence, $\triangle S^{\ominus}$ is positive for reaction 1 but almost 0 for reaction 2.

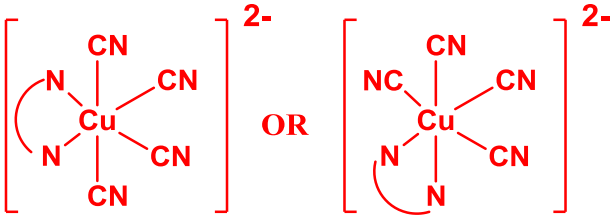
$|T\triangle S^{\ominus}|_{reaction\ 1} > |T\triangle S^{\ominus}|_{reaction\ 2}$

Since **$\triangle G^{\ominus} = \triangle H^{\ominus} - T\triangle S^{\ominus}$** and **$\triangle H^{\ominus}$ is almost the same and negative in value for both reactions,** $\triangle G^{\ominus}$ will be more negative and hence numerically larger for reaction 1.

(iv) Copper(II) sulfate can combine with $H_2NCH_2CH_2NH_2$ and sodium cyanide to form a compound, where the co-ordination number of copper is 6. The formula unit of this compound contains two sodium ions and an anion.

Draw the structure of the anion to illustrate its shape.

You may use N⌒N to represent $H_2NCH_2CH_2NH_2$. **[1]**



2 (c) Partition coefficient, K_D, is an example of an equilibrium constant. It is the ratio of equilibrium concentrations of a species in a mixture of two immiscible solvents. From the value of K_D, the difference in solubility of a species in two immiscible solvents can be determined.

When an aqueous solution of ammonia was shaken with dichloromethane at room temperature, an equilibrium was established as shown.

$$NH_3\ (aq) \rightleftharpoons NH_3\ (in\ CH_2Cl_2) \qquad K_D = 0.04$$

(i) State the solvent in which ammonia has a higher solubility. With reference to interactions involved, explain your answer. **[2]**

NH_3 is **more soluble in H_2O**.

NH_3 form hydrogen bonds with H_2O molecules which releases more energy

to **overcome** the **hydrogen bonds between ammonia and between water**. However, NH_3 can only form weak **permanent dipole-permanent dipole interactions / van der Waals' forces with CH_2Cl_2.**

(ii) Write the K_D expression. **[1]**

$$K_D = \frac{[NH_3\ (CH_2Cl_2)]}{[NH_3\ (aq)]}$$

(iii) 100 cm^3 of 1.00 mol dm^{-3} aqueous ammonia solution was mixed with dichloromethane. 100 cm^3 of 0.0133 mol dm^{-3} chromium(III) sulfate was then added to the water-dichloromethane mixture. This resulted in complex formation as shown below. All the Cr^{3+} reacted with some ammonia in the aqueous layer.

$$Cr^{3+} + n\ NH_3 \rightleftharpoons [Cr(NH_3)_n]^{3+}$$

The setup was then left to stand and the dichloromethane layer was found to contain 0.0184 mol dm^{-3} of ammonia.

Using your answer to **c(ii)**, calculate the concentration of ammonia left in the aqueous layer after complex formation. **[1]**

$[NH_3\ (aq)]$ after complex formation = 0.0184 / 0.04 = **0.46 mol dm^{-3}**

(iv) Using your answer to **c(iii)**, calculate the value of n in the formula $[Cr(NH_3)_n]^{3+}$. **[1]**

Number of moles of NH_3 left in aqueous layer = 200/1000 x 0.46 = 0.092 mol
Number of moles of NH_3 that reacted with Cr^{3+} = 0.1 - 0.092
= 0.008 mol
Number of moles of Cr^{3+} = 2 x 0.1 x 0.0133 = 2.66 x 10^{-3} mol
Mole ratio of NH_3 : Cr^{3+} = 3.00 : 1
n = 3

2 (d) The production of "elephant toothpaste" involves the decomposition of hydrogen

peroxide. The equation for this reaction is as given.

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$$

(i) It is postulated that this reaction involves a highly reactive species with an unpaired electron. With the use of curly arrows to represent the movement of electrons, show how the reactive species may be formed from H_2O_2. **[1]**

(ii) Using data from the *Data Booklet*, calculate $E^{\ominus}_{cell}$ for the decomposition of hydrogen peroxide. **[1]**

$O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons H_2O_2 \quad E^{\ominus} = +\ 0.68\ V$

$H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O \quad E^{\ominus} = +\ 1.77\ V$

$E^{\ominus}_{cell} = +1.77 - (+0.68) =$ **+ 1.09 V**

(iii) ΔG and $E^{\ominus}_{cell}$ values are related by the following equation.

$$\Delta G = -\ zFE^{\ominus}_{cell}$$

Where ΔG is in Joules per mole, z is the number of moles of electrons transferred and F is the Faraday constant.

Based on the given information, calculate ΔG for the decomposition of hydrogen peroxide. State the significance of your answer. **[2]**

ΔG = - (2)(96500)(1.09) = **- 210370 J mol^{-1}** / **- 210.4 or - 210 kJ mol^{-1}**

The decomposition of hydrogen peroxide is **spontaneous / feasible / thermodynamically favourable**.

(iv) When a sample of hydrogen peroxide was left to decompose, the rate of

production of gas was slow. Suggest a reason for this observation. **[1]**

There is **high activation energy** involved in the decomposition of H_2O_2.

(v) Fe^{2+} is known to aid the decomposition of hydrogen peroxide. By referring to the following $E^{\ominus}$ value and relevant data from the *Data Booklet*, show how Fe^{2+} carries out its role. You should give relevant equations in your answer.

$FeO^{2+} + 2\ H^+ + 2\ e^- \rightleftharpoons Fe^{2+} + H_2O \qquad E^{\ominus} = +1.55\ V$ **[3]**

$O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons H_2O_2 \quad E^{\ominus} = +\ 0.68\ V$

$H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O \quad E^{\ominus} = +\ 1.77\ V$

Step 1: $H_2O_2 + Fe^{2+} \rightarrow FeO^{2+} + H_2O$

$E^{\ominus}_{cell} = +1.77 - (+1.55) =$ **+ 0.22 V** > 0

Step 2: $FeO^{2+} + H_2O_2 \rightarrow Fe^{2+} + O_2 + H_2O$

$E^{\ominus}_{cell} = +1.55 - (+0.68) =$ **+ 0.87 V** > 0

(vi) Besides its role in hydrogen peroxide decomposition, Fe^{2+} (aq) is commonly used in redox titration. Although both acidified potassium manganate(VII) and acidified potassium dichromate(VI) can be used to titrate Fe^{2+} (aq) in volumetric analysis, acidified potassium manganate(VII) is the preferred titrant to improve the reliability of experiment. Suggest a reason why this is so. **[1]**

The colour change is **more distinct / clearer / more obvious** for titration with potassium manganate(VII) rather than potassium dichromate(VI).

[Total: 20 marks]

3 (a) Chlorine is a useful reagent for chemical synthesis. It has desirable applications, such

as in the production of drugs, fire-fighting and purification of water.

(i) Chlorine may be produced from the electrolysis of concentrated sodium chloride. Write equations for the reactions at the anode and cathode. **[1]**

Anode: $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$

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

(ii) By considering their reactions with thiosulfate ion and with reference to changes in oxidation number, compare the oxidising ability of Cl_2 and I_2. Write relevant equations where appropriate. **[3]**

Cl_2 is a **stronger oxidizing agent** than I_2 as it can oxidise $S_2O_3^{2-}$ to SO_4^{2-} (S from +2 to +6) whereas I_2 only oxidises $S_2O_3^{2-}$ to $S_4O_6^{2-}$ (S from +2 to +2 ½).

$4\ Cl_2 + S_2O_3^{2-} + 5H_2O \rightarrow 8\ Cl^- + 2\ SO_4^{2-} + 10\ H^+$

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

(iii) A student attempted to synthesise trichloromethane from methane using an aqueous solution of chlorine. However, this was unsuccessful. Suggest and explain what went wrong in the synthesis. **[1]**

Water **polarises** chlorine molecule, resulting in **heterolytic fission / absence of homolytic fission / no formation of free radicals** (words to same effect). This prevents free radical substitution from happening.

OR

Chlorine underwent **disproportionation** in water and was **unable to form free radicals / cleave homolytically** as required in free radical substitution.

(b) Chlorine dioxide gas, ClO_2, is widely used as a bleaching agent. It is commonly manufactured from the reaction between chlorine and sodium chlorite.

$$Cl_2\ (g) + 2\ NaClO_2\ (s) \rightarrow 2\ ClO_2\ (g) + 2\ NaCl\ (s)$$

(i) Calculate the mass of ClO_2 produced when 15.0 g of $NaClO_2$ is reacted with 2000 cm^3 of Cl_2 at 290 K and under 1.50 atm. **[3]**

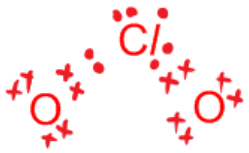
Using ideal gas equation,

Amount of $Cl_2 = (1.50 \times 101000)(2000 \times 10^{-6}) / (8.31)(290) = 0.1257$ mol

Amount of $NaClO_2 = 15.0 / 90.5 = 0.1657$ mol

Amount of ClI_2 required if 0.1657 mol of $NaClO_2$ is used
= 0.1657 ÷ 2 = 0.08287 mol
⇨ ClI_2 is in excess or $NaClO_2$ is limiting
Amount of ClO_2 produced = 0.1657 mol
mass of ClO_2 produced = 0.1657 x 67.5 = 11.18 g ≈ **11.2 g (to 3 sf)**

(ii) Draw dot-and-cross diagrams of ClO_2 and ClO_2^-. **[2]**



(iii) ClO_2 is known to oxidise Fe^{2+} easily. With reference to your answer in **(b)(ii)**, suggest a reason for this. **[1]**

There is a **lone / unpaired electron on *Cl*** **[1]** in ClO_2, thus giving it a tendency to undergo reduction to achieve pairing of electrons.

(iv) Despite being highly unstable, iodite ion, IO_2^-, has been detected as an intermediate in some reactions. State and explain if the bond angle in IO_2^- is greater or smaller than that in ClO_2^-. **[2]**

The bond angle of IO_2^- is **smaller** than that in ClO_2^-.
In IO_2^-, I has a **lower electronegativity** than Cl in IO_2^-.
Hence, **bond pair of electrons are less strongly attracted to I**,
resulting in **lesser repulsion** between the bond pairs in IO_2^-.

3 (c) Figure 1 shows the change in pV with increasing pressure at 298 K for an ideal gas and

four real gases. The amount for each gas is 1 mole.

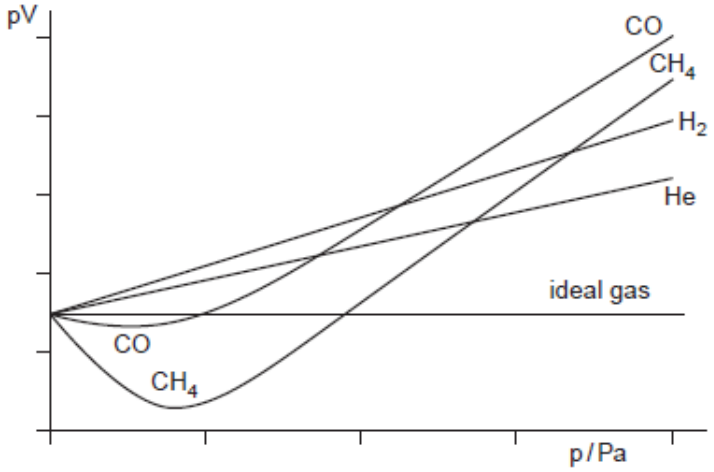


Figure 1

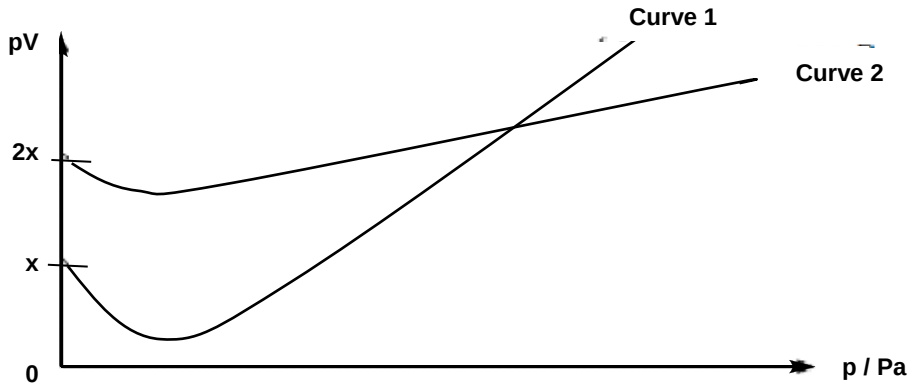
(i) Explain the deviation from ideality as shown by the real gases. **[1]**

The **gas particles have significant attractive forces / intermolecular forces of attraction between them**. OR
The **volume of each gas particle** becomes **more significant relative to the total volume occupied by the gas**.

(ii) The following curves show the behaviour of methane under different conditions.

Curve 1 shows the behavior of 1 mole of CH_4 at 298 K.

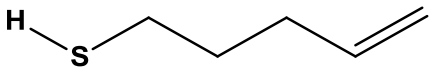
What does **curve 2** represent?



[1]

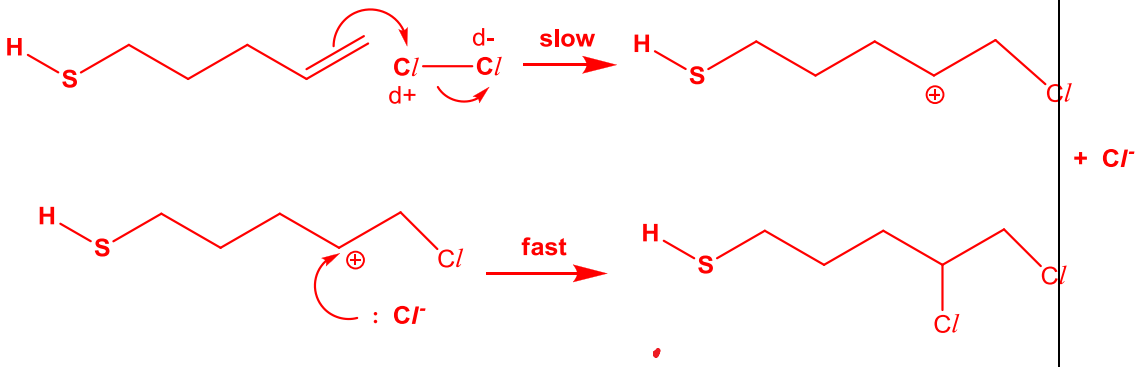
Temperature increased to 596 K

3 (d) Organic compounds which contain sulfur typically have an odour. One such example is as shown.



(i) Describe the mechanism for the reaction between this compound and chlorine molecule in CCl_4. **[3]**

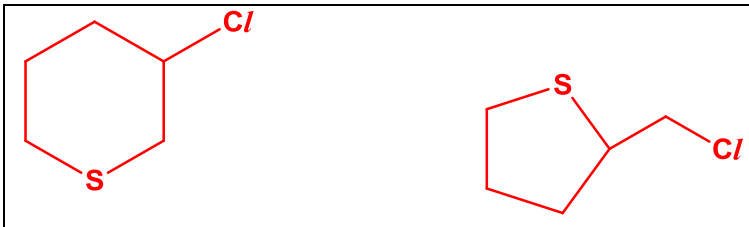
Electrophilic addition



Marking points: δ+, δ-, slow, all 3 arrows, lone pair of electrons on Cl^-, correct carbocation intermediate based on more stable 2° carbocation (Markonikov's rule), correct product

(ii) The product formed in **d(i)** can undergo further reaction to form **Z** with a molecular formula of C_5H_9SCl.

Suggest the structure of **Z** and the type of reaction involved. **[2]**



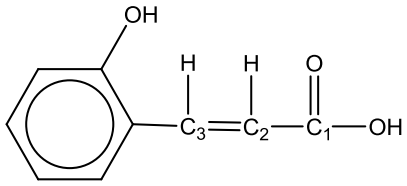
(Either 1)

Type of reaction: Nucleophilic substitution

[Total: 20 marks]

4 (a) Compound **A** is a commonly used starting material to synthesise a class of anti-

bacterial drugs known as quinolones.



Compound **A**

(i) There are two acidic groups in compound **A**.

Explain the difference in the acidities of these two groups. Show the difference in their acidities by writing an equation to represent the reaction between compound **A** with sodium carbonate. **[4]**

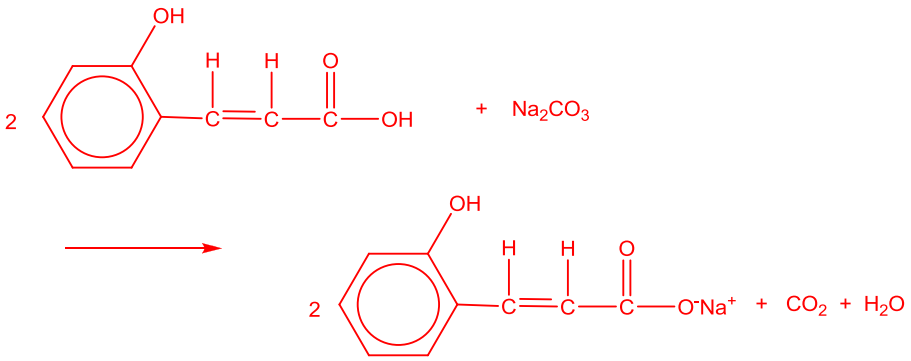
Carboxylic acid is more acidic than phenol.

Carboxylate ion/COO^-/conjugate base is **resonance stablilised by the delocalisation of negative charge over O-C-O bond**.

Phenoxide ion/conjugate base is **stabilised by the delocalisation of negative charge into the benzene ring**.

The conjugate base of carboxylic acid is **more stable / less likely to accept H^+ easily** than phenoxide ion. (i.e comparison of stability)

Hence extent of dissociation for carboxylic acid is more favoured / or eqm shift with eqm stated.



(ii) C_1, C_2 and C_3 are carbon atoms which undergo the same type of hybridisation

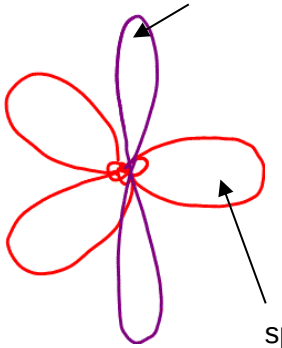
when forming compound **A**.

I – State the type of hybridisation and draw a labelled diagram to show all the orbitals of any of these carbons.

II – Explain how sigma and pi bonds arise between these orbitals. **[4]**

Type of hybridization: sp^2

unhybridised p orbital

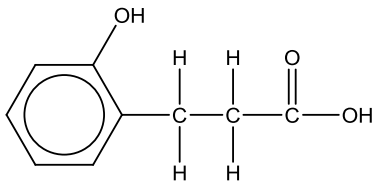


sp^2 hybrid orbital

Sigma bond arises during **head-on overlap / diagram of sigma bond** of **sp^2 hybrid orbitals.**

Pi bond arises during **side-on overlap / diagram of pi bond** of the **unhybridised p orbitals.**

(iii) Compound **B** is formed when compound **A** is hydrogenated.



Compound **B**

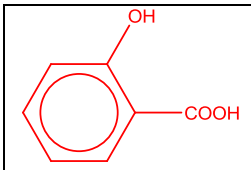
With reference to your answer in **a(ii)**, suggest why the carboxylic acid group in compound **A** is more acidic than that in compound **B**. **[1]**

The **π bonds formed between (overlapping of) the p orbitals of C_1, C_2 and C_3** enables **further delocalisation of negative charge/lone pair/electrons on O in the carboxylate anion / conjugate base** of **A** into the C=C group, hence **stabilises** the anion/conjugate further.

(iv) Upon oxidation, both compounds **A** and **B** yield compound **C** with molecular

formula $C_7H_6O_3$. Compound **C** is less soluble in water than compounds **A** and **B**. Suggest the structure of compound **C** and explain its lower solubility in water.

[2]



Compound **C**

The proximity of the 2 side groups allows for **intramolecular hydrogen bonding** which **inhibits / results in less extensive or favourable hydrogen bonding with water molecules.**

4 (b) When agricultural lime containing $CaCO_3$ is heated to a high temperature in a lime kiln, quicklime is produced. Quicklime is allowed to cool and a calculated amount of water is added. A highly exothermic reaction takes place and a white powder called slaked lime is produced.

(i) Write balanced equations for the **two** reactions described above. **[2]**

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + H_2O \rightarrow Ca(OH)_2$

(ii) Agricultural lime is used to increase the pH of the soil.

Using an equation, show how agricultural lime carries out this role. **[1]**

H^+ removed:

$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$

OR

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$

OR

OH^- produced:

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

(iii) $CaCO_3$, the main active component in agricultural lime, has a lower melting point

than quicklime.

Suggest an explanation for the difference in their melting points. **[3]**

Both $CaCO_3$ and CaO exist as **giant ionic compounds / giant ionic lattices** with **lattice energy α $(q^+q^- / r^+ + r^-)$**.
However, as the **anionic size of CO_3^{2-} is larger**,
magnitude of lattice energy of $CaCO_3$ is lower / less exo.
Hence **lesser energy** is required to overcome the / **weaker ionic bonds**, resulting in **lower melting point**.

(iv) Predict how the decomposition temperature of $Al_2(CO_3)_3$ would compare with that of $CaCO_3$ in agricultural lime.

Explain your answer using relevant data from the *Data Booklet*. **[3]**

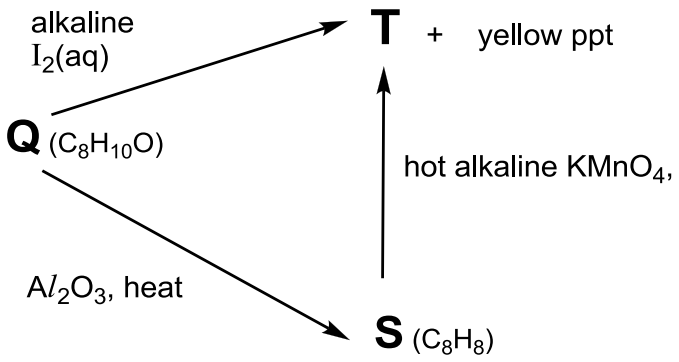
Charge density of Al^{3+} α 3/0.05 = 60
Charge density of Ca^{2+} α 2/0.099 = 20.2
OR
Al^{3+} has a **larger charge** and **smaller radius than Ca^{2+} (0.05nm for the former and 0.099nm for the latter)**. As **charge density of Al^{3+} is higher**, Al^{3+} is **more able to polarise** the electron cloud of CO_3^{2-}, hence **weakening the C-O bond to a larger extent**. This requires lesser energy to break the C-O and so, the decomposition temperature of $Al_2(CO_3)_3$ is **lower** than that of $CaCO_3$.

[Total: 20 marks]

5 (a) Compound **P**, $C_{10}H_{12}O_3$, is insoluble in water. It does not dissolve in aqueous NaOH at

room temperature but upon heating with aqueous NaOH, compound **P** gives two compounds, **Q**, $C_8H_{10}O$, and **R**, sodium 2-hydroxyethanoate.

Q was found to undergo the following reactions:



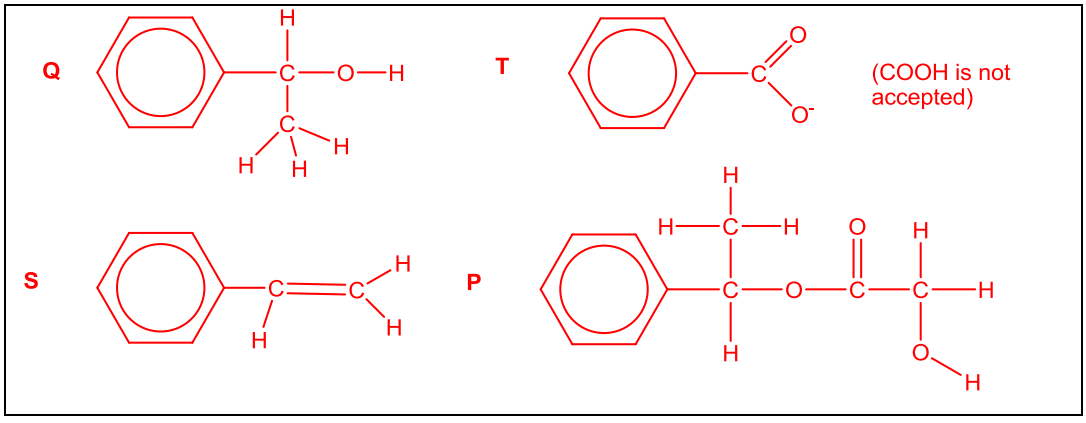
(i) Based on the above information, state the functional groups for which the three oxygen atoms in **P** belong to. Explain your answer. **[2]**

Functional groups present in **P**: alcohol and ester

P contains **no** acidic group/phenol/cannot undergo neutralisation since no reaction with aq NaOH at room temperature

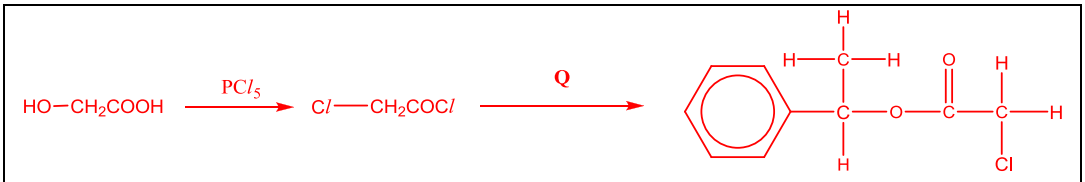
P contains ester which undergoes hydrolysis when heated with aq NaOH to give two products.

(ii) Draw the displayed formulae of **P**, **Q**, **S** and **T**. **[4]**



(iii) A student proposed to synthesise **P** from acidified **R** by the following route.

Explain what is wrong with his proposed synthetic route. Suggest how he could synthesise **P** from acidified **R** instead. **[2]**



or

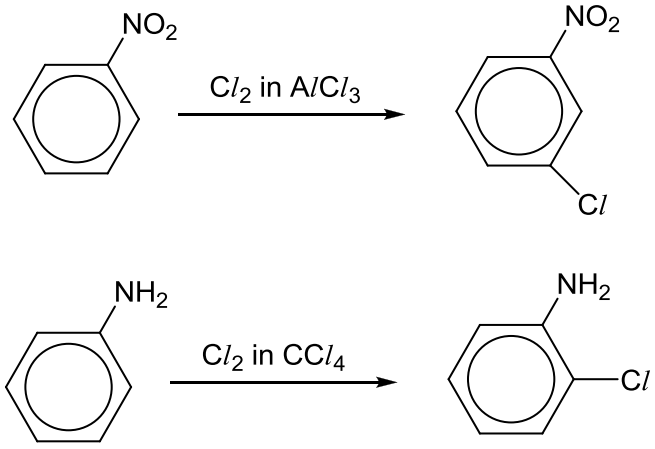
By adding PCl_5 to 2 hydroxyethanoic acid, 2-chloroethanoyl chloride will be produced. / Both alcohol and carboxylic acid in 2-hydroxyethanoic acid will undergo nucleophilic substitution with PCl_5.

He should add $HOCH_2COOH$ to **Q** in the presence of **little concentrated H_2SO_4** and **heat under reflux**.

(iv) Upon reacting acidified **R** with hot $KMnO_4$, carbon dioxide is obtained as the only carbon-containing product. Write an equation for this oxidation reaction.
Use [O] to represent the formula of the oxidising agent. **[1]**

$HOCH_2COOH + 3[O] \rightarrow 2CO_2 + 2H_2O$

5 (b) Nitrobenzene and phenylamine react with Cl_2 under different conditions as shown.



(i) State the role of $AlCl_3$ in the reaction. **[1]**

Electrophile generator / Lewis acid / (homogeneous) catalyst / halogen carrier

(ii) Explain clearly the difference in the conditions needed for the two reactions. **[2]**

The **lone pair electrons on N delocalises into the ring**, making the ring **more electron rich / activates [1/2]** the ring, and hence **more attractive to electrophile / prone to electrophilic attack**.

NO_2 is an **electron withdrawing group** which deactivates the ring. $AlCl_3$ is required to help generate electrophile.

(c) Aluminium can be combined with oxygen and chlorine to make different compounds. Alumina, Al_2O_3, is the refractory oxide of aluminium with a very high melting point of about 2070 °C. Aluminium chloride, $AlCl_3$, which can be manufactured from Al and HCl at temperatures between 650 to 750 °C, has a much lower melting point of about 192 °C.

(i) Write an equation to show how $AlCl_3$ can be manufactured from Al and HCl.

State the type of reaction involved. **[2]**

$2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2$

Redox reaction

(ii) State the type of structures of Al_2O_3 and $AlCl_3$.

Explain the difference in structures. **[3]**

Al_2O_3: **giant ionic compound / giant ionic lattice**

$AlCl_3$: **simple covalent molecule**

Cl^- is **larger** than O^{2-}, allowing it to be **more greatly polarised** by the small and highly charged / high charge density Al^{3+} resulting in overlapping of orbitals / sharing of electrons.

(iii) A student is given an unknown white solid which can either be Al_2O_3 or $AlCl_3$.

Describe how you would carry out a simple test to determine its identity. Explain the difference in observations and include relevant equations where applicable.

[3]

Add excess / limited **H_2O** to the unknown solid.

If the white solid **dissolves** (white fumes if limited H_2O added), it is $AlCl_3$

and if the white solid **does not dissolve**, it will be Al_2O_3.

Al_2O_3 has **high lattice energy /strong ionic bond** and will not dissolve in water.

In excess H_2O:

$$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$$

OR

In limited H_2O:

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$

[Total: 20 marks]