Answers for MJC 2008 H2 Chem Prelim Paper 2

1(a) Phosgene gas, $COCl_2$, can be prepared by allowing gaseous chlorine and carbon monoxide to react under pressure. A scientist needed to prepare isotopically-labeled phosgene for use in an organic synthesis.

$$^{13}CO\ (g) + Cl_2\ (g) \rightleftharpoons {}^{13}COCl_2\ (g)$$

Some Cl_2 (g) and 5.00 atm of isotopically-labeled ^{13}CO (g) were pumped into a steel cylinder set at 25 °C which was then sealed. The cylinder was subsequently heated to 227 °C and the partial pressure of Cl_2 (g) was found to be 5.59 atm at 227 °C.

The cylinder was then maintained at 227 °C for an extended period of time to allow dynamic equilibrium to be reached. The new partial pressure of Cl_2 (g) was found to be 4.50 atm.

(i) Calculate the partial pressure of ^{13}CO (g) at 227 °C.

[1]

$P_{^{13}CO}$ at 227 °C = $\dfrac{5.00}{(273+25)} \times (273+227)$ = **8.39 atm**

(ii) Write an expression for the equilibrium constant, K_p. Hence, or otherwise, calculate the K_p value for the equilibrium at 227 °C, stating its units.

[2]

$$K_p = \frac{P_{^{13}COCl_2}}{\left(P_{^{13}CO}\right)\left(P_{Cl_2}\right)}$$

	^{13}CO (g)	+	Cl_2 (g)	$\rightleftharpoons$	$^{13}COCl_2$ (g)
Initial partial pressure / atm	8.39		5.59		0
Δ in partial pressure / atm	– 1.09		– 1.09		+ 1.09
Eqm partial pressure / atm	7.30		4.50		+ 1.09

K_p = **0.0332 atm^{-1}**

(iii) Calculate the average molecular mass of the gaseous mixture at equilibrium.
[A_r of ^{13}C: 13.0, O: 16.0, Cl: 35.5]

[2]

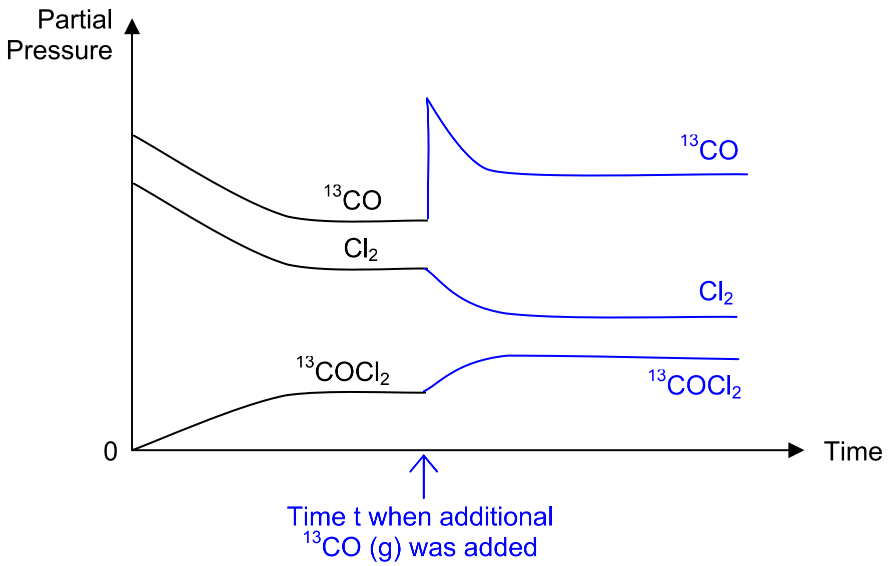
Total pressure, P_{total} = 12.89 atm

$$\text{Average } M_r = \frac{P_{^{13}CO}}{P_{total}} \times (M_r \text{ of } {}^{13}CO) + \frac{P_{Cl_2}}{P_{total}} \times (M_r \text{ of } Cl_2) + \frac{P_{^{13}COCl_2}}{P_{total}} \times (M_r \text{ of } {}^{13}COCl_2)$$

= **49.7**

(iv) Sketch on the graph below to show what the scientist should expect to observe if additional ^{13}CO (g) was added at time t to the cylinder which was maintained at constant temperature of 227 °C. Label the graph extensions for each species till equilibrium is reached.

[2]



(b)(i) State **one** of the assumptions of the kinetic theory of gases.

[1]

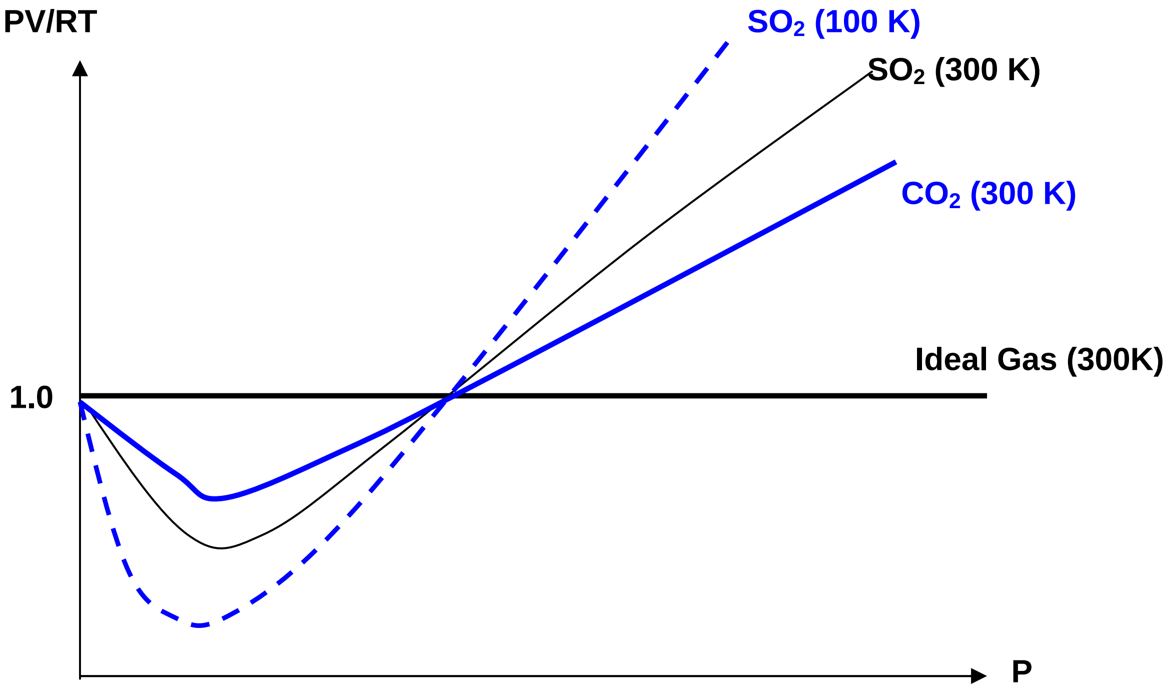
Any 1 of the following assumptions

1) The intermolecular forces of attraction between gas particles are negligible.
2) The total volume of gas particles is negligible compared to the volume of the container. *(i.e. gas particles are widely spread and far apart)*
3) Gas particles are in continuous random linear motion.
4) All collisions between gas particles (and that of gas particles with the walls of the container) are perfectly elastic so that no kinetic energy is lost on collision.

(ii) The plots of PV/RT against P for one mole of an ideal gas and one mole of SO_2 at 300K are given below.

Show, on the same axes, how one mole of CO_2 will behave at the same temperature of 300K. Label your graph clearly.

[1]



(iii) Explain the difference in behaviour between carbon dioxide and sulphur dioxide at 300K. **[1]**

SO_2 deviates more from ideal gas behaviour as compared to CO_2.
SO_2 is a polar molecule while CO_2 is a non-polar molecule

Hence, there is stronger permanent dipole-permanent dipole attractions between SO_2 molecules as compared to induced dipole- induced dipole attractions between CO_2 molecules.

(iv) Explain what happens when sulphur dioxide gas is cooled to 100K. Illustrate your answer clearly on the same axes in **b(ii).**

[2]
[Total: 12]

At lower temperature of 100K, the SO_2 molecules possess less kinetic energy and they move slower.
⇒ Thus, intermolecular forces of attraction between SO_2 molecules becomes significant.

2 (a) One method that is used to determine the concentration of ozone in the ozone layer is to pass air through acidified potassium iodide and to measure the amount of iodine liberated. In the process O_2 is also being liberated as one of the products.

The iodine liberated is measured using a platinum/aqueous iodine/ aqueous iodide electrode against a standard silver/aqueous silver nitrate reference electrode. The e.m.f. of the system, $\mathbf{E_{cell}}$, is given by the following equation.

$$E_{cell} = 0.32 + 0.029 \lg ([I_2])$$

To determine ozone in the atmosphere above New Zealand, a balloon was used to carry a sampling device. A 1.0 dm^3 sample of the air, at room temperature and 0.24 atm pressure, was passed through 15 cm^3 of acidified potassium iodide. When the iodine liberated was measured using the above cell, the e.m.f of the system was 0.21 V.

(i) Write a balanced equation for the reaction of ozone and iodide.

[1]

$\mathbf{O_3 + 2I^- + 2H^+ \rightarrow H_2O + O_2 + I_2}$

(ii) Calculate the percentage of ozone in this sample of air.

[2]

$[I_2] = 1.61 \times 10^{-4}$ mol dm^{-3}

No. of mole of $I_2 = 2.415 \times 10^{-6}$

No of mole of $O_3 = 2.415 \times 10^{-6}$

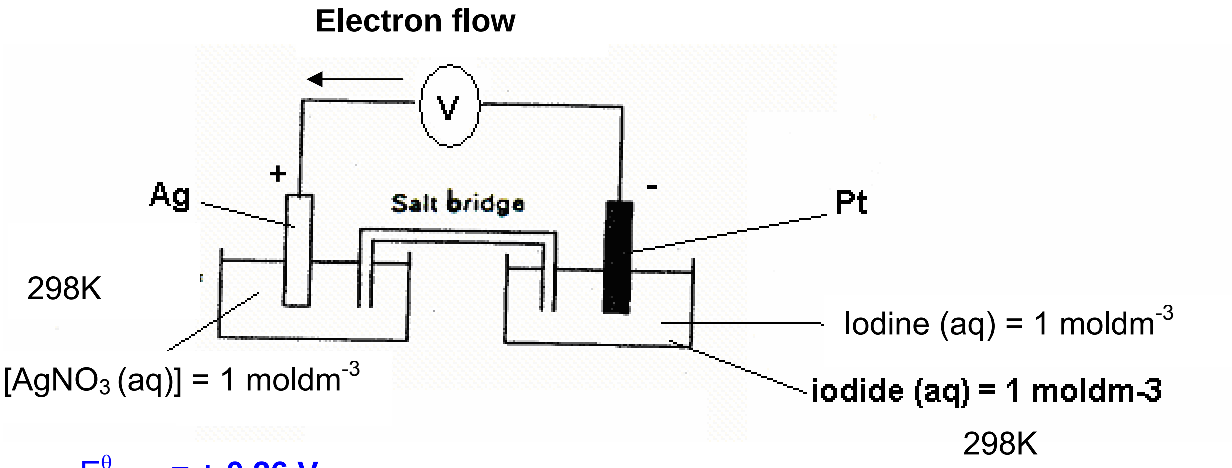
Volume of $O_3 = 2.47 \times 10^{-7}$ m^3

Percentage of ozone = **0.0247 %**

(iii) Draw a labeled cell diagram to show the set-up for measuring the e.m.f of the cell using silver/aqueous silver nitrate and aqueous iodide/aqueous iodine half cells.

In your diagram, show clearly the polarity of the electrode and the direction of the electron flow in the external cell. Calculate the E^{θ}_{cell} for this set-up.

[3]



E^{θ}_{cell} = **<u>+ 0.26 V</u>**

(iv) 20 cm^3 of 0.1 mol dm^{-3} sodium iodide solution is added into the standard platinum/iodine(aq)/iodide electrode cell, describe what would happen to E^{θ}_{cell} value measured.

[2]

$I_2 (aq) + 2e \rightleftharpoons 2I^- (aq)$ $\quad E_{oxid} \quad (1)$

By adding in sodium iodide solution, the concentration of iodide increases. By Le Chatelier's principle, the position of equilibrium (1) shifts to the left to decrease the amount of iodide.

E_{oxid} will be reduced

Thus E^{θ}_{cell} > + 0. 26 V

(b) Stratospheric ozone that protects the earth against harmful ultraviolet radiation is being depleted by the anthropogenic introduction of various gases into the atmosphere. The most destructive ozone depletion processes are catalytic cycles in which trace amounts of gases are able to destroy large quantities of ozone.

The overall reaction is shown below:

$$O_3\text{ (g)} + O\text{ (g)} \rightarrow 2\ O_2\text{ (g)}$$

(i) Given the standard enthalpy change of formation of O_3 (g) is + 142.67 kJ mol^{-1} and using relevant data from the Data Booklet, calculate the enthalpy change of the above reaction. **[2]**

ΔH_{rxn} = **$\underline{-\ 391\ kJ\ mol^{-1}}$**

(ii) The standard entropy change of the reaction between O_3 (g) and O (g) is +10.17 kJ mol^{-1} K^{-1}. Use the data to decide if the reaction is spontaneous at -273 ^oC, and predict how ΔG^θ will change with increasing temperature.

[2]

$\Delta G = \Delta H - T\Delta S$
= **$\underline{-\ 391\ kJ\ mol^{-1}}$**

Since ΔG is negative, the reaction is thermodynamically feasible at -273 ^oC

Since ΔS is positive, $-T\Delta S$ is negative.
and ΔH is negative, $\Delta G = \Delta H - T\Delta S$ is negative at all temperature.

3(a) The boiling points of three common chlorides are given in the following table.

Compound	**Formula**	**Boiling Point/ ^oC**
Magnesium chloride	$MgCl_2$	1412
Aluminum chloride	$AlCl_3$	178
Silicon tetrachloride	$SiCl_4$	58

(i) Briefly relate these boiling points to the structure of, and bonding in, each of these chlorides.

[3]

$MgCl_2$ has giant ionic lattice structure.

As large amount of energy are required to overcome the extensive and strong electrostatic forces of attraction between oppositely charged ions present in the crystal lattice.

Thus $MgCl_2$ has the highest boiling point.

Both $AlCl_3$ and $SiCl_4$ have simple molecular structures.

Hence, $AlCl_3$ and $SiCl_4$ have low boiling point as a small amount of energy is required to overcome the weak van der Waals' forces of attraction between molecules.

However, $AlCl_3$ exists as a dimer of Al_2Cl_6 Since Al_2Cl_6 has a larger molecular size, it has stronger van der Waals' forces of attraction between its molecules than $SiCl_4$.

Thus Al_2Cl_6 has the higher boiling point than $SiCl_4$.

(ii) State the pH of the solution formed when the each of the chlorides compound dissolved in water. Hence, predict the expected observation when these chlorides were added separately to test-tubes containing sodium carbonate solution. Give reasons to support your answers.

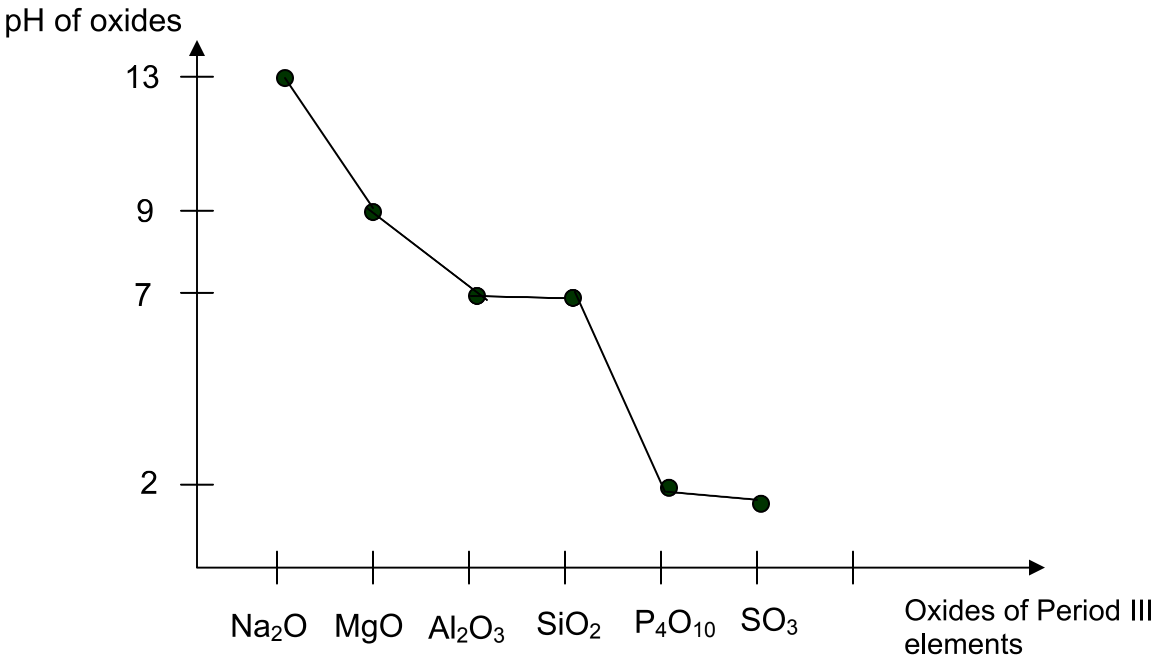
[3]

Compound	**pH of solution when the compound dissolves in water**	**Observation on reaction of aqueous solution with Na_2CO_3**	**Reasons**
$MgCl_2$	6.5	No Effervescence	$MgCl_2$ undergoes both hydration and slight hydrolysis in water to give a slightly acidic solution.
$AlCl_3$	3	Effervescence	Al^{3+} has very high charge density which polarises its surrounding water molecules, weakening the O-H bond such that H^+ ions is released into the solution.
$SiCl_4$	2	Effervescence	$SiCl_4$ undergoes complete hydrolysis in water to give a strongly acidic solution.

(b) The highest oxides of the Period 3 elements (from sodium to sulphur) are separately added to water.

(i) Using the grid provided below, sketch a graph to show the variation of pH of the resulting mixtures.

[2]



(ii) Describe and explain the trend of the graph you have drawn in **(b)(i).**

[2]

- Na_2O dissolves in water to give an alkaline solution of NaOH (pH ≈ 13)
- MgO dissolves slightly in water to give a weakly alkaline solution (pH ≈ 9). It is partially insoluble in water because of its high lattice energy.

- Al_2O_3 does not dissolve in water because of its very exothermic lattice energy.
- SiO_2 does not dissolve in water as large amounts of energy are required to break the numerous strong covalent bonds between the Si and O atoms. Hence, pH of Al_2O_3, SiO_2 = 7.
- P_4O_6, P_4O_{10}, SO_2 and SO_3 react with water to form H_3PO_3/ H_3PO_4 and H_2SO_3/H_2SO_4 respectively. (pH ≈ 2)

4 In the analysis of drinking water, the method known as Mohr's titration is used to determine the chloride content present. Chloride ions present in a water sample is titrated against $AgNO_3$ (aq).

As $AgNO_3$ is slowly added, sparingly soluble AgCl precipitate is formed. The indicator used in the titration is yellow aqueous K_2CrO_4. The end-point of the titration is obtained when almost all the chloride present has been precipitated. Addition of $AgNO_3$ beyond this point causes the formation of a red-brown precipitate of Ag_2CrO_4.

This method can be used to determine the chloride ion concentration of water samples from many sources.

However, Mohr's titration should be carried out under conditions of pH 6.5 – 9. At higher pH, the $AgNO_3$ titrant added becomes ineffective, while at lower pH, the K_2CrO_4 indicator is affected. Chromate (VI) ions, CrO_4^{2-}, may be removed by an acid-base reaction to form hydrogen chromate ions ($HCrO_4^{2-}$) or dichromate ions ($Cr_2O_7^{2-}$), causing the end-point to be inaccurate.

The following are relevant K_{sp} values in Mohr's titration:

Salt	K_{sp}
AgCl	1.8×10^{-10} mol^2 dm^{-6}
AgBr	7.7×10^{-13} mol^2 dm^{-6}
AgI	8.3×10^{-17} mol^2 dm^{-6}
Ag_2CrO_4	1.1×10^{-12} mol^3 dm^{-9}

(a)(i) Calculate the concentration of Cl^- (aq) ions at the end-point of the titration.

[1]

At the end point, all the Cl^- in the solution would be precipitated out as AgCl. The sparingly soluble salt would be in equilibrium with the saturated solution.

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$$

At end-point,
K_{sp} of AgCl = $[Ag^+ (aq)][Cl^- (aq)]$
s = $[Cl^- (aq)]$ = $\underline{\mathbf{1.34 \times 10^{-5}\ mol\ dm^{-3}}}$

(ii) Explain what would be observe if excess aqueous ammonia is added to the resultant solution in **(a)(i)** at the end point. Support your answers with relevant equations.

[3]

$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$ … (1)
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+ (aq)$ ... (2)

On addition of aqueous NH_3, white precipitate of AgCl dissolves to form a colourless soluble complex, $[Ag(NH_3)_2]^+ (aq)$.

Adding NH_3 (aq) removes the free Ag^+. By Le Chatelier's Principle, position of equilibrium (1) shifts to the left.

Hence, ionic product $[Ag^+][Cl^-]$ decreases

Since K_{sp} of AgCl is relatively high, ionic product of $[Ag^+][Cl^-]$ will easily decrease to a value lower than its K_{sp}. Hence, white ppt of AgCl dissolves.

(b)(i) In a 100 cm^3 sample of treated tap water, 6.95 cm^3 of 0.01 mol dm^{-3} $AgNO_3$ was required for Mohr's titration. Calculate the concentration of Cl^- (aq) ions in the treated water.

[2]

No. of mol of Ag^+ = 6.95×10^{-5}

No. of mol of Cl^- before titration in 100 cm^3
= 6.95×10^{-5}

Concentration of $[Cl^- (aq)]$ in treated water
= **6.95×10^{-4} mol dm^{-3}**

(ii) Determine the minimum concentration of CrO_4^{2-} (aq) ions in the titration mixture that is required to precipitate only Ag_2CrO_4 immediately after the end-point.

[1]

Ag_2CrO_4 (s) $\rightleftharpoons$ $2Ag^+$ (aq) + CrO_4^{2-} (aq)

For precipitation of Ag_2CrO_4 just after end-point,

Ionic product of Ag_2CrO_4 > K_{sp} of Ag_2CrO_4
$[CrO_4^{2-}$ (aq)] > 6.13×10^{-3} mol dm^{-3}

Minimum $[CrO_4^{2-}$ (aq)] = **6.13×10^{-3} mol dm^{-3}**

(iii) Suggest a reason why the $AgNO_3$ titrant becomes ineffective at higher pH.

[1]

The added Ag^+ (aq) ions would combine with OH^- (aq) ions in the basic solution to form insoluble AgOH instead of reacting with the Cl^- (aq) ions.

(c) An aqueous solution of chlorine can be used as a disinfectant, for example, in swimming pools. The disinfecting action is due to the presence of chloric (I) acid, HClO, formed by the reaction of chlorine with water:

Cl_2(aq) + H_2O (l) $\rightleftharpoons$ HClO(aq) + HCl(aq)

Chloric (I) acid ionizes as a weak acid:

HClO(aq) $\rightleftharpoons$ H^+(aq) + ClO^-(aq)

In many swimming pools, chemicals other than chlorine gas used to form the chloric (I) acid. This is partly because the use of chlorine gas causes much more corrosion of metal parts in the pool than does chloric (I) acid. Compounds used to chlorinate pool water in this way include calcium chlorate (I) and chlorine dioxide, ClO_2.

(i) Explain why chlorine in water causes more corrosion to the metal parts compared to pure chloric (I) acid.

[2]

In chlorine water, there are HCl and HClO.

HCl is a strong acid which dissociates completely to give a high $[H^+]$ while HClO is a weak acid that dissociates partially in water to give a low $[H^+]$.

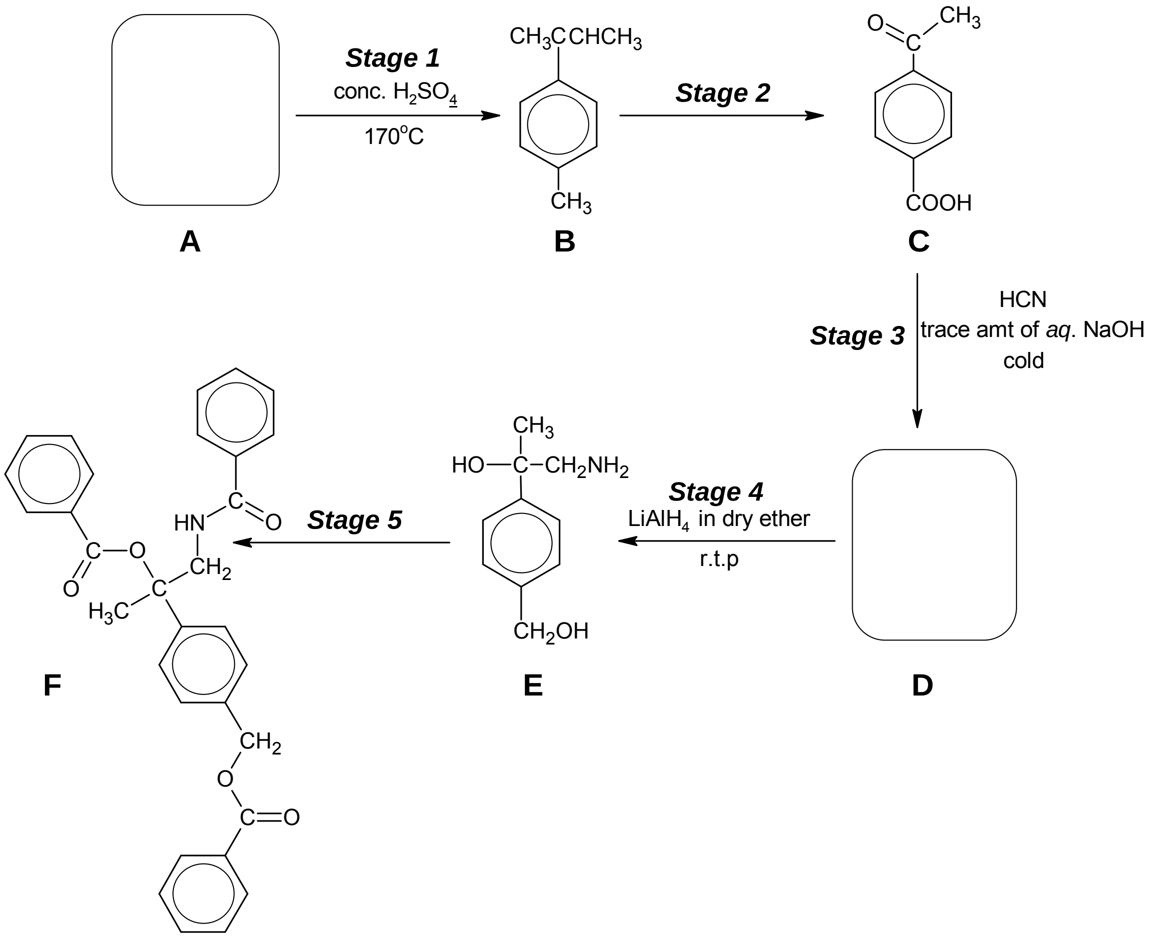
Due to the high $[H^+]$ in chlorine water, corrosion of metal parts occur more readily.

(ii) Chlorine dioxide undergoes a disproportionation reaction in water to give a mixture of chloric (I) acid and chloric (V) acid. Write a balanced equation, including state symbols, for this reaction.

[1]
[Total: 11]

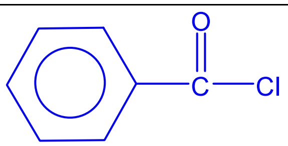
$4ClO_2(aq) + 2H_2O(l) \rightarrow HClO(aq) + 3HClO_3(aq)$

5 Compound **B** is an active ingredient used typically as a fungicide. Its low toxicity and well-known properties makes it ideal for agriculture.



(a)(i) Suggest the reagents and conditions for Stages **2** and **5**.

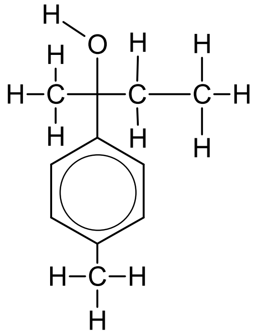
[2]

	Reagents	Conditions
Stage 2	**H_2SO_4 (aq), $KMnO_4$ (aq)**	**Heat**
Stage 5		**r.t.p**

(ii) Compound **A** is optically active. Draw the displayed formula of compound **A** in the box provided below.

[1]

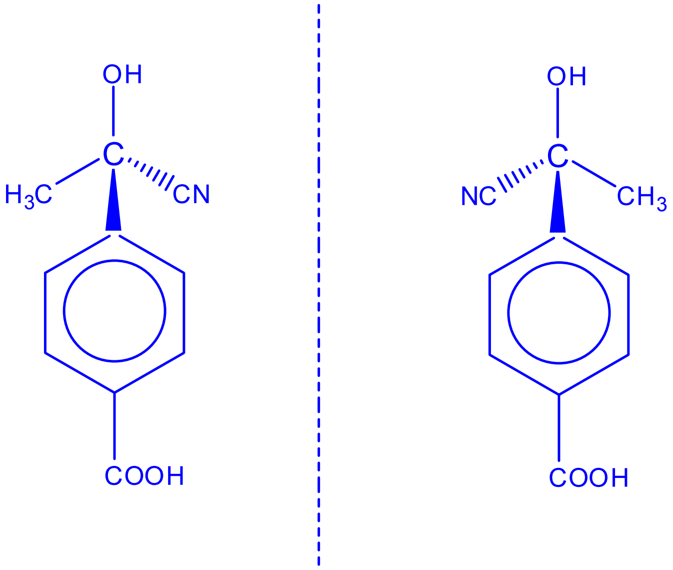
Compound **A**



A

(iii) Compound **D** contains a chiral centre and it consists of a 50:50 mixture of two isomers. Draw structural formulae of these isomers of **D**.

[1]



(b)(i) Explain why traces amount of sodium hydroxide is required for ***Stage 3*** reaction to take place.

[1]

$HCN \rightleftharpoons H^+ + CN^-$

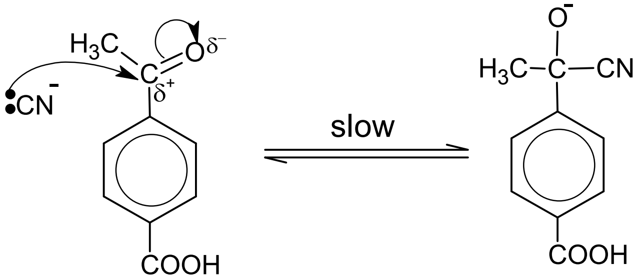
The trace amount of base is added to shift the position of the equilibrium to the right to increase the concentration of the nucleophile, CN^- ion concentration.

(ii) State and describe the mechanism for the reaction in ***Stage 3.***

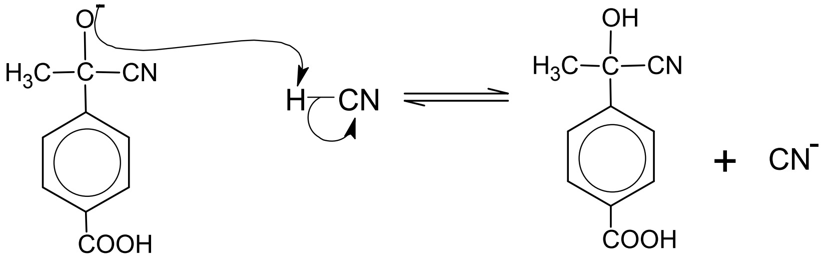
[3]

Mechanism: nucelophilic addition

Step 1 : The CN^- nucleophile attacks the electron-deficient carbonyl carbon to form an intermediate.



Step 2 : Protonation of tetrahedral intermediate to form cyanohydrin.



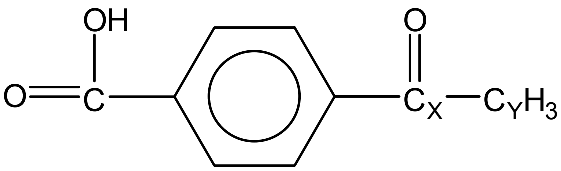
(iii) However, a sample of **D** does not rotate the plane of polarized light. Based on the mechanism in **b(ii)**, suggest a possible reason for this occurrence.

[1]

The carbonyl carbon is sp^2 hybridized or trigonal planar.

Hence, the nucleophile, CN^- can attack from either side of the carbon group with equal probability.

(c) State and describe the types of hybridisation present in the carbon atoms labelled as C_x and C_y in Compound **C** as shown below.



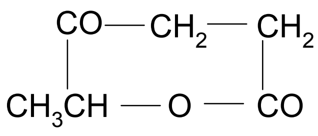
[3]

Carbon atom	**C_X**
Type of hybridisation	sp^2
Description of hybridisation	One s and two p orbitals take part in the mixing process Three sp^2 hybridised orbitals are formed.

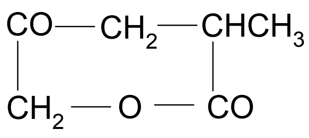
Carbon atom	**C_Y**
Type of hybridisation	sp^3
Description of hybridisation	One s and three p orbitals take part in the mixing process Four sp^3 hybridised orbitals are formed.

(d) Suggest methods by which the compounds **G** and **H** could be distinguished from each other by a simple chemical test.

Write balanced chemical equations for any reaction that has occurred.



G



H

[3]
[Total: 15]

Add dilute HCl(aq) and heat each mixture.
Add excess NaOH(aq) followed by I_2(aq) to each mixture and heat .

For G, a yellow ppt of CHI_3 is formed.
For H, no yellow ppt of CHI_3 is formed.