Anderson Serangoon Junior College

2023 JC2 H2 Chemistry Preliminary Examination Paper 3 Suggested Solutions

1 **(a)** **(i)** Describe and explain the relative basicities of methylamine, dimethylamine and trimethylamine in the gas phase. [3]

Order of increasing basicity in the gas phase:
methylamine < dimethylamine < trimethylamine

The **increasing number** of **electron-donating methyl / alkyl group from methylamine to dimethylamine to trimethylamine** **increases** the **availability of the lone pair of electrons on N atom** to accept a proton.

[1]: trend
[1]: more electron donating alkyl group
[1]: greater availability of lone pair

(ii) Explain why amides are neutral. [1]

Amides are neutral because the **lone pair on nitrogen atom is delocalised into the π bond of the adjacent C=O** by resonance and hence **not available** for donation to a proton. [1]

(b) Deuterium (symbol D or $^{2}_{1}H$) was discovered in 1931. Deuterium accounts for 0.0156% of all the naturally occurring hydrogen in the oceans, while the most common isotope $^{1}_{1}H$ accounts for 99.98%. Tritium (symbol T or $^{3}_{1}H$), a rare and radioactive isotope of hydrogen account for only 0.0044%.

Chemically, deuterium behaves similarly to ordinary hydrogen.

(i) Calculate the average A_r of hydrogen. Give your answer to four decimal places. [1]

$$A_r = (\frac{0.0156}{100}\times 2) + (\frac{99.98}{100}\times 1) + (\frac{0.0044}{100}\times 3)$$
$$= 0.000312 + 0.9998 + 0.000132$$
$$= 1.000244$$
$= \underline{\mathbf{1.0002}}$ (4 decimal places) [1]

(ii) On the same diagram, sketch how a beam of singly positively charged deuterium ions and a beam of hydrogen ions will behave in an electric field.

In your diagram, indicate clearly the relative angle of deflection for each beam. (You may let the angle of deflection of hydrogen ions be x°) [2]

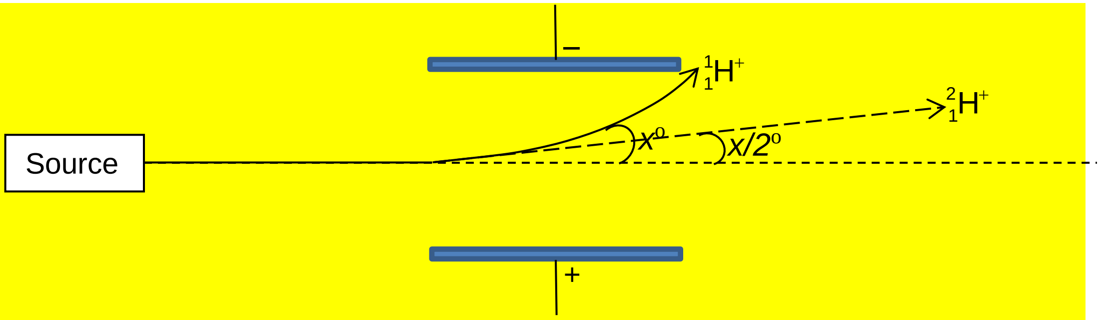


Diagram should show charged deuterium ion deflecting less than hydrogen ion. Deuterium ion and hydrogen ion must deflect in the same direction and towards negative plate.

Above two points [1]
Since angle of deflection ∝ e/m ratio: ∠ of Deuterium ion is half of ∠ of hydrogen ion [1]

(iii) Explain the difference in the thermal stability of DC*l*, DBr and DI. [2]

Down Group 17 from chlorine to bromine to iodine, the **size of valence orbitals increases** and become **more diffused**. This causes **a decrease in effectiveness of orbital overlap** between the valence orbital of halogen and s–orbital of hydrogen. / **Electronegativity difference** between the halogen and deuterium **decreases**, resulting in a **decrease in bond polarity**. [1]

D–X bond becomes weaker and hence the **D–X bond energy decreases** from DC*l* to DBr to DI. So, **thermal stability decreases** from DC*l* to DBr to DI. [1]

(c) Deuterium can replace the normal hydrogen in water molecules to form heavy water, D_2O.

Some data of light water and heavy water are given in Table 1.1.

Table 1.1

Property	D_2O (Heavy water)	H_2O (Light water)
Freezing point (°C)	3.82	0.00
Boiling point (°C)	101.4	100.0
Density at standard temperature and pressure (g cm^{-3})	1.106 (solid)	0.998 (solid)

(i) Suggest if distillation is effective in separating heavy water from light water. [1]

The boiling point of light water and heavy water is too close for distillation to take place effectively. [1]

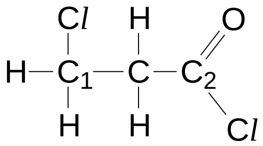
(ii) Using Table 1.1, suggest with reasoning, how a scientist can differentiate the two types of water without the use of a temperature measuring device.
(Density of liquid light water is 1.0 g cm^{-3}) [2]

Freeze the heavy water and light water separately. [1]
Drop the heavy water ice cube and light water ice cube into a glass of light water.

Heavy water having a higher density than light water will sink in the glass of light water.[1]

(d) Deuterated solvents (such as D_2O) are a group of compounds where one or more hydrogen atoms are substituted by deuterium atoms. It may be assumed that they have similar chemical reactivity as their hydrogen analogues.

(i) D_2O is added to 3-chloropropionyl chloride.



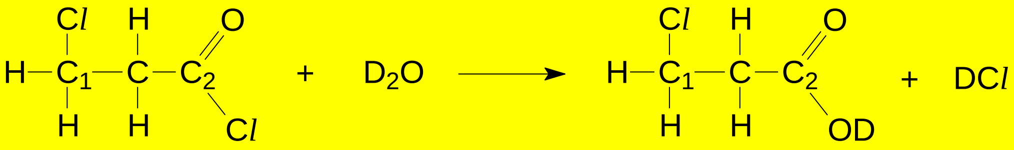
3-chloropropionyl chloride

Comment on the reactivity of C_1 and C_2 and write a balanced chemical equation for the reaction. [2]

C_2 is more reactive than C_1

C_2 is **highly electron–deficient** because it is bonded to **TWO highly electronegative** atoms, oxygen and chlorine. [1]

This makes the carbon very susceptible to reaction with nucleophiles.



[1]

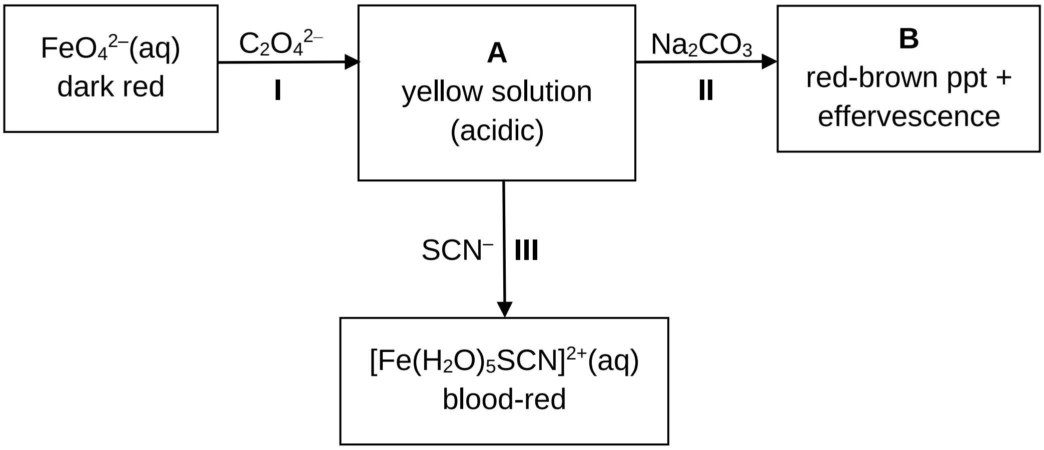
(ii) Construct a balanced chemical equation to show how deuterated ethanol, C_2D_5OD, reacts with ethanoic acid, CH_3CO_2H in the presence of acid catalyst. [1]

$CH_3COOH + C_2D_5OD \rightleftharpoons CH_3COOC_2D_5 + DOH$ [1]

[Total: 15]

2 **(a)** Iron is a transition metal.

The following scheme illustrates a series of reactions involving various oxidation states of iron.



(i) Explain why $[Fe(H_2O)_5SCN]^{2+}(aq)$ is blood-red. [3]

In the presence of water and SCN^- ligands, the partially filled 3d orbitals of Fe^{3+} are split into two levels with a small energy gap (that falls within the visible light spectrum). **[1]**

When white light passes though the solution, 3d electron absorbs light energy that is equal to the energy gap and gets excited from the lower energy 3d orbital to the higher energy 3d orbital. **[1]**

Red colour of $Fe^{3+}(aq)$ observed is complementary to the green colour absorbed. **[1]**

(ii) State the formula of the cation present in **A** and identify **B**. [1]

A: $[Fe(H_2O)_6]^{3+}$; **B**: $Fe(OH)_3$ **[1]**

(iii) State the type of reaction that occurred in **I, II** and **III**. [3]

I – Redox reaction **[1]**
II – Acid-base **[1]**
III – Ligand exchange **[1]**

(iv) With the aid of relevant equations, explain why

- solution **A** is acidic.
- effervescence was observed from reaction **II**. [3]

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + \mathbf{H_3O^+}(aq)$$ **[1]**

Why acidic?

Fe^{3+} has a high charge size and small cationic radius , giving rise to high charge density. Thus, it polarises water ligands to a large extent, hence weakening the O-H bond and liberating H_3O^+ ions readily. **[1]**

Why effervescence?

H_3O^+ ions will react with carbonate to give effervescence of CO_2.
$H_3O^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$ **[1]**

(b) The electrolysis of an aqueous solution of potassium hydroxide was carried out using an iron anode and a platinum cathode. After a current was passed through the cell for some time, 360 cm^3 of gas was collected at the cathode (measured at r.t.p.) while there was a loss of mass of 0.279 g at the anode.

Determine the oxidation state of iron in the iron-containing product after electrolysis. [2]

Amount of gas produced at the cathode = 360/24000 = 0.015 mol

$2H_2O + 2e \rightarrow H_2 + 2OH^-$ or $H_2 \equiv 2e$

Amount of electrons required = 0. 015 x 2 = 0.030 mol **[1]**

$Fe \rightarrow Fe^{n+} + ne$

$$\frac{\text{Amount of e released}}{\text{Amount of Fe}} = \frac{n}{1} = \frac{0.030}{0.279/55.8} = 6$$

Final oxidation state of Fe = +6 **[1]**

(c) Fig. 2.1 shows the octahedral geometry of a transition metal complex with six monodentate ligands, **L**.

(i) Explain what is meant by a *transition element*? [1]

A transition element is a **d block element** that can form **one or more stable ions** with **partially filled d subshells. [1]**

(ii)

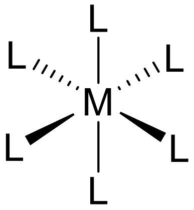


Fig. 2.1

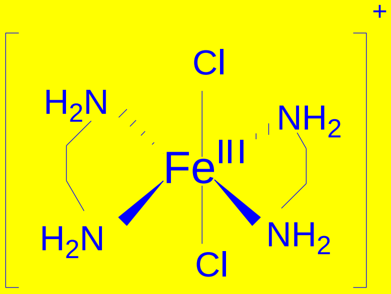
With reference to an octahedral complex, the *cis-trans* isomers are defined as follows:

Cis isomer: Same groups of atoms are on the same side of the central metal atom, i.e. 90° from each other.

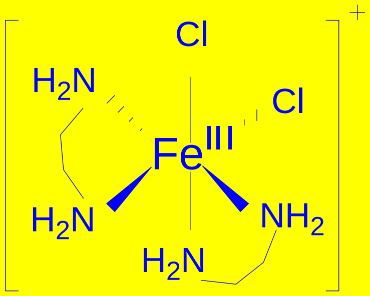
Trans isomer: Same groups of atoms are on directly opposite sides of the central metal atom i.e. 180° from each other.

$Fe(H_2NCH_2CH_2NH_2)_2Cl_2]^+$ forms an octahedral cationic complex where each $H_2NCH_2CH_2NH_2$ ligand forms 2 bonds with the central Fe(III) ion. Similar to organic molecules, this complex can exist as a pair of *cis-trans* isomers.

Using the information above, draw the 3-dimensional structures of the *cis-trans* isomers of $[Fe(H_2NCH_2CH_2NH_2)_2Cl_2]^+$ and label the isomers. [2]



trans-isomer



cis-isomer

[1]- for drawing correct isomers
[1]- correct identity

(iii) Identify the isomer in **(c)(ii)** that is optically inactive. Explain your answer. [1]

The trans-isomer has an internal plane of symmetry and has no effect on the plane polarised light, hence not optically active. **[1]**

A chemist used the set-up shown in Fig. 2.2 to investigate if a solution which consists of concentrated hydrochloric acid and iron(II) chloride, can be used to produce iron metal via electrolysis. An organic fuel cell, the direct ethanol fuel cell, is used to drive the electrolysis.

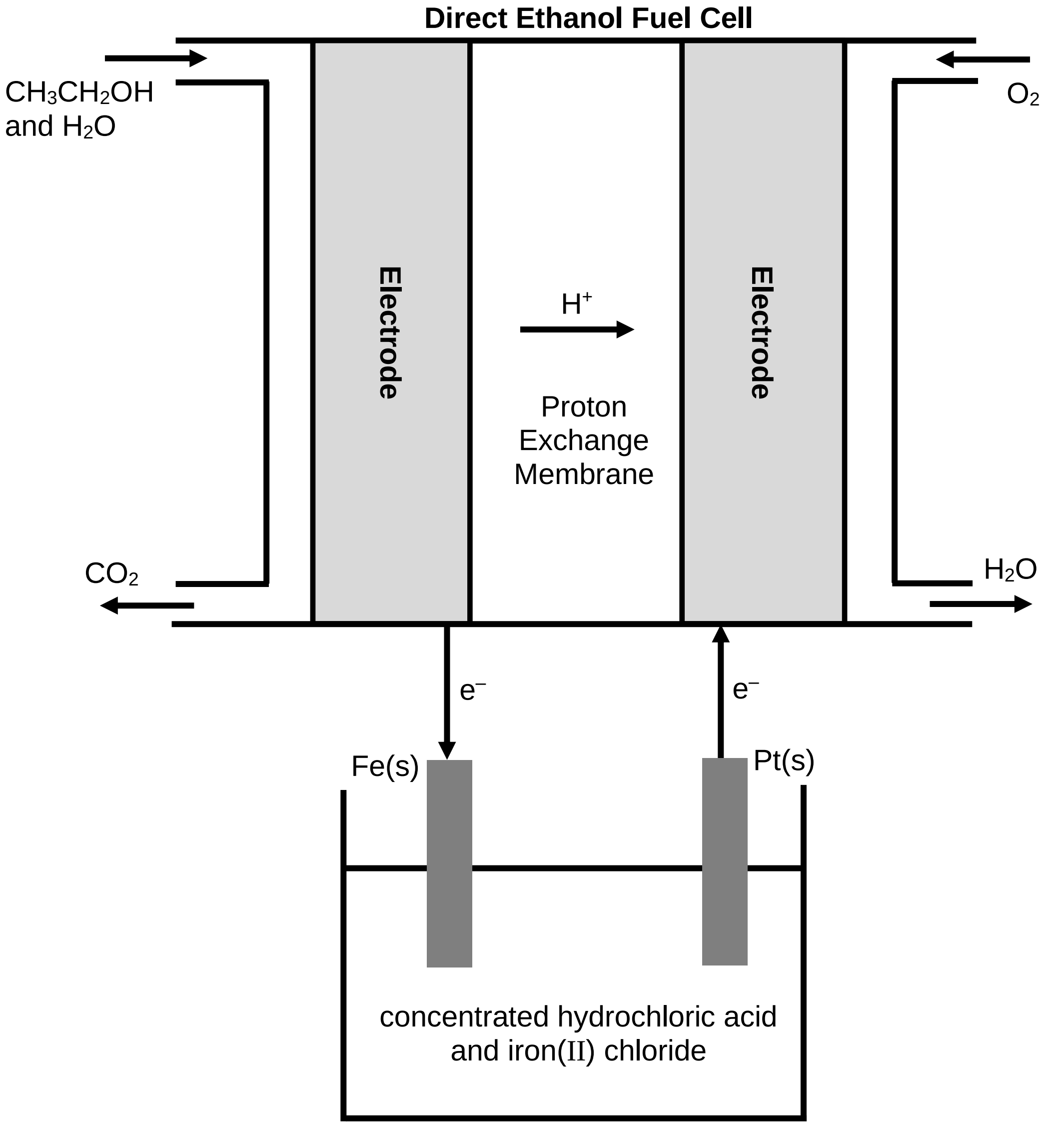


Fig. 2.2

(d) The reaction that takes place at one of the electrodes of the direct ethanol fuel cell involves the reduction of oxygen gas as follows.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

(i) Construct the half equation at the anode of the direct ethanol fuel cell, given that carbon dioxide is produced at the anode. Hence, write the overall equation for the reaction that occur in the fuel cell.

[2]

Oxidation: $CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e$ [1]

Reduction: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Overall: $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ [1]

(ii) The direct ethanol fuel cell generates an e.m.f. of 1.56 V.

By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the CO_2/CH_3CH_2OH electrode reaction. [1]

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxd}$
$1.56 = +1.23 - E^\ominus_{oxd}$
$E^\ominus_{oxd} = -0.33$ V [1]

(iii) Use data from the *Data Booklet* to predict the reaction that will occur at the iron electrode of the electrolytic cell. Write equation for the reaction.

Hence, deduce if iron can be produced using the set up in Fig. 2.2. [2]

From Fig 2.2 the electrons flow in the external circuit of the electrolytic cell is an important information. Since electron moves from anode to cathode, in the electrolytic cell, the platinum electrode is the anode while the iron electrode is the cathode.

At the cathode there will be presence of water and Fe^{2+}
$Fe^{2+} + 2e \rightleftharpoons Fe$ (–0.44 V)
$2H_2O + 2e \rightleftharpoons H_2 + OH^-$ (–0.83 V)
$2H^+ + 2e \rightleftharpoons H_2$ (0.00V)
Since reduction process takes place at the cathode.
Iron electrode (Cathode reaction): $2H^+ + 2e \rightarrow H_2$ [1]

Iron cannot be produced. [1]

(iv) Suggest why chlorine gas is preferentially produced at the platinum electrode. [1]

At the anode there is water and concentrated Cl^- present.
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ --------(1) (+1.36V)
$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ (+1.23V)
Chloride ion is preferentially oxidised as high concentration of chloride ions causes POE of (1) to shift to the left. [1]

[Total: 22]

3 **(a)** The position of substitution in the electrophilic substitution of mono-substituted arenes can be explained based on the stability of the intermediate carbocation formed.

Fig. 3.1 shows three possible first steps in the nitration of methylbenzene.

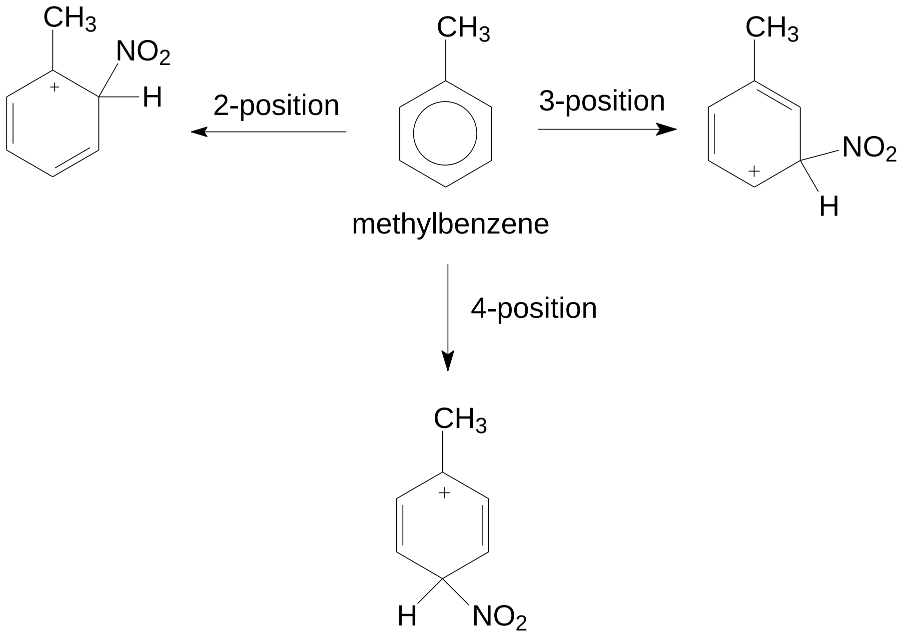


Fig. 3.1

(i) Use the information in Fig. 3.1 to suggest why the –CH_3 group directs incoming electrophiles to the 2– and 4–positions in preference to the 3–position. [2]

Substitution at 2– and 4– position forms tertiary carbocations which are more stable compared to the secondary carbocation [1] formed when-NO_2 is at the 3–position.

The greater number of electron–donating alkyl groups attached to the positively charged carbon in the tertiary carbocation help to disperse the positive charge more [1], making the tertiary carbocation more stable than a secondary carbocation.

(ii) When nitration of methylbenzene is carried out and the isomers are analysed, it was found that the mole ratio between 2-nitromethylbenzene and 4-nitromethylbenzene is about 2 : 1.

Suggest an explanation for this. [1]

Two C atoms in methylbenzene would give rise to the formation of 2-nitromethylbenzene while 4-nitromethylbenzene can be formed at only one C atom. Hence, substitution at the 2-position would occur twice as much as at the 4-position.
[1]: idea of why the substitution at 2-position is twice that of 4-position

(iii) 3–aminobenzoic acid can be synthesised from methylbenzene as shown in Fig. 3.2.

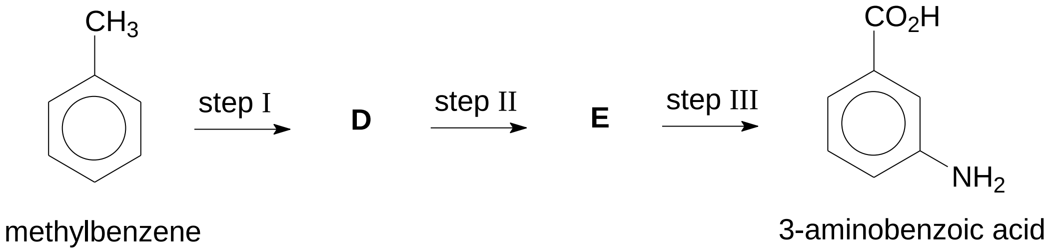
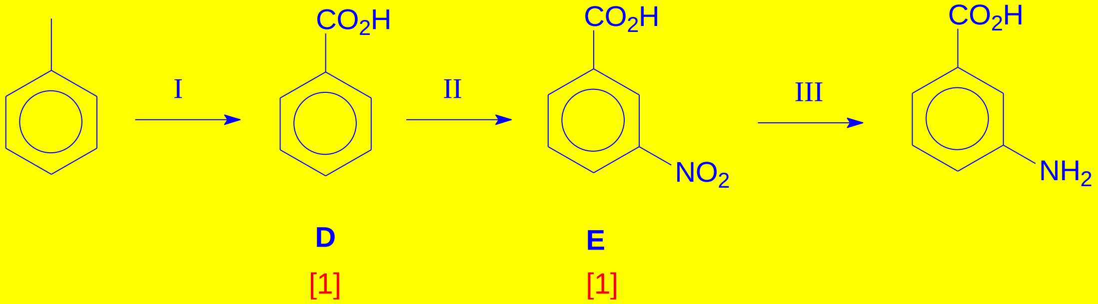


Fig. 3.2

Suggest structures for the intermediates **D** and **E** and the reagents and conditions for steps I, II and III. [5]



I [1]	$KMnO_4$, dil. H_2SO_4, heat (accept alkaline with corresponding base for product)
II [1]	concentrated HNO_3, concentrated H_2SO_4, heat
III [1]	(granulated) Sn, concentrated HC*l*, heat

(b) Friedel–craft alkylation, using A*l*C*l*$_3$ as a catalyst, is usually carried out in anhydrous conditions.

(i) Suggest why the reaction has to be carried out under anhydrous condition. [1]

A*l*C*l*$_3$ hydrolyses in water, resulting in absence of catalyst to generate electrophile for Friedel–craft alkylation to take place. [1]

In the presence of A*l*C*l*$_3$ and under suitable conditions, benzene reacts with CC*l*$_4$ via electrophilic substitution to form a mixture of trichlorophenylmethane, $C_6H_5CCl_3$ and dichlorodiphenylmethane, $(C_6H_5)_2CCl_2$.

The reaction occurs in several steps.

- The first step is an acid–base reaction between A*l*C*l*$_3$ and CC*l*$_4$.

$$AlCl_3 + CCl_4 \rightarrow AlCl_4^- + CCl_3^+$$

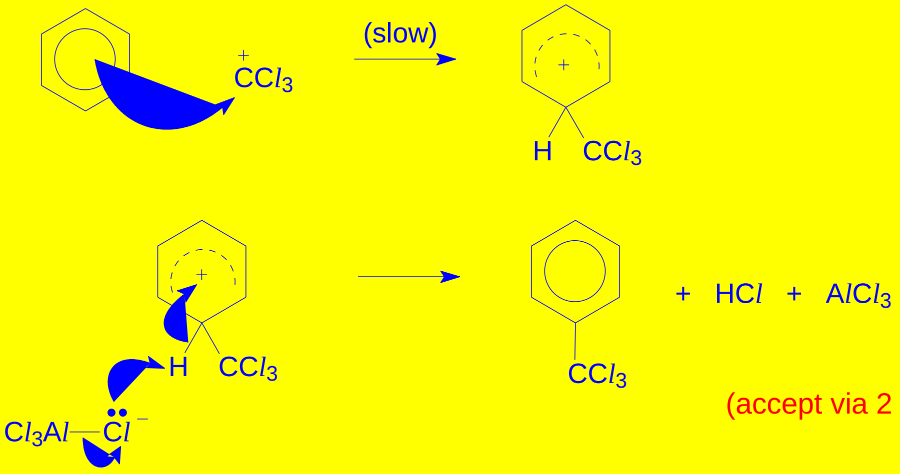
- The benzene ring is then attacked by the CCl_3^+ electrophile in the second step.

(ii) A*l*C*l*$_3$ behaves as a Lewis acid in the first step. Explain what is meant by the term *Lewis acid*. [1]

$AlCl_3$ is an electron pair acceptor. [1]
(no mark if 'pair' is missing)

(iii) Suggest a mechanism for the reaction between benzene and CCl_3^+ electrophile to form $C_6H_5CCl_3$. [2]

$CCl_4 + AlCl_3 \longrightarrow \overset{+}{C}Cl_3 + AlCl_4^-$ (not required)



(accept via 2 steps)

(or show single arrow from Al—Cl bond)
Can also accept a separate step 4
Step 4: $H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$

[1]: slow/fast step; curly arrows in both equations
[1]: intermediate; regeneration of benzene ring and catalyst

(iv) Suggest a reason why further alkylation of $(C_6H_5)_2CCl_2$ does not take place. [1]

Idea of steric hindrance
The two large phenyl groups bonded to the small carbon atom sterically hinders the approach of the 3rd phenyl group from attacking the electrophilic C atom. [1]

Idea of stability of electrophile.
$(C_6H_5)_2CCl^+$ electrophile generated is stable due to (extensive) delocalisation of the positive charge into the π electron cloud of the two benzene rings.

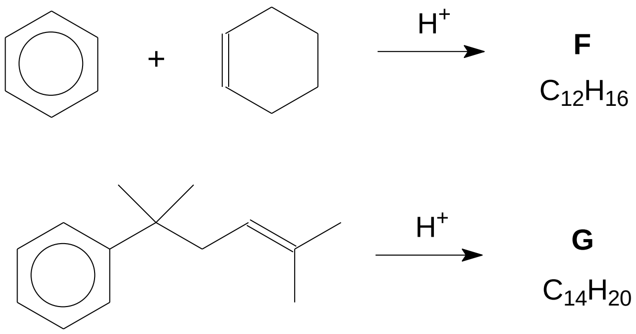
An example of Friedel–Crafts alkylation which can be done in non–anhydrous conditions is shown in Fig. 3.3.

Reaction I

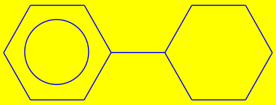
Fig. 3.3

(c) **(i)** Using the information given about **Reaction I**, suggest the structure of the product for each of the following reactions.

Both compounds **F** and **G** do not react with aqueous bromine. Only compound **F** decolourises hot, acidified potassium manganate(VII).

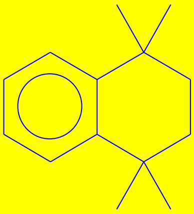


[2]



F

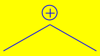
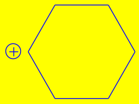
[1]

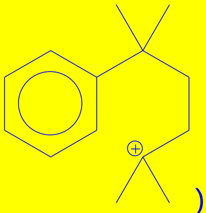
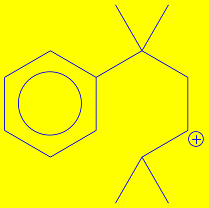


G

[1]

Thinking process
In both cases, the products **F** and **G** does not react with Br_2(aq)
⇒ suggest an absence of >C=C<.

From observation of **Reaction I**, a more stable carbocation () is formed which is then attacked by the benzene ring to form the product.
For the formation of **F**, either of the C atom of the >C=C< can form the carbocation () since it is a symmetrical alkene.

However, a more stable tertiary carbocation () is favoured over a secondary one () for the formation of **G**. Hence the benzene ring (nucleophilic centre) will attack the electrophilic C^+ to form a cyclic ring, where both benzylic C atoms are quaternary and does not decolourise MnO_4^-/H^+.

Electrophilic substitution in phenol occurs much faster, and under milder conditions, than in benzene. Fig. 3.4 shows another Friedel–Crafts alkylation carried out in acidic condition.

Reaction II

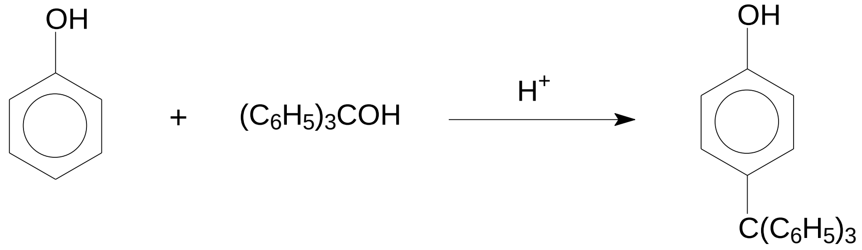
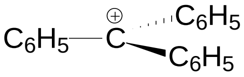


Fig. 3.4

Reaction II cannot take place if benzene is used instead of phenol.

(ii) The electrophile formed in **Reaction II** is shown below.



With reference to the structure of the electrophile formed, suggest why the activation energy of **Reaction II** is high. [1]

The triphenylmethyl cation generated is relatively unreactive / weak electrophile/stable , due to (extensive) delocalisation of the positive charge into the π electron cloud of the three benzene rings. [1]:

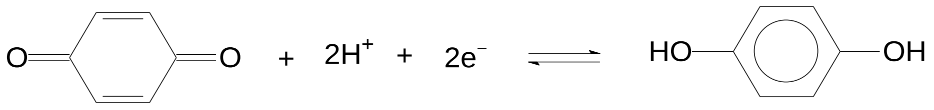
Idea of steric hindrance
The three large phenyl groups bonded to the small carbon atom sterically hinders the approach of the electrophile from attacking the electrophilic C atom. [1]:

(iii) Hence suggest why phenol is required for **Reaction II** to occur. [1]

The lone pair of electrons on the O atom of phenol can delocalise into the π electron cloud of the benzene ring, increasing the ring electron density and making it more susceptible to reaction even with a weak electrophile such as triphenylmethyl cation.

[1]: increased electron density of nucleophile

(d) Quinone, $C_6H_4O_2$, can be formed by oxidisin.g quinol, $C_6H_6O_2$ with acidified $KMnO_4$.



$E^\ominus = +0.70$ V

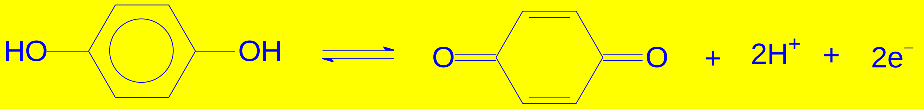
quinone

quinol

(i) Calculate $E^\ominus_{cell}$ for the overall reaction between quinol and acidified $KMnO_4$. [1]

$E^\ominus_{cell} = +1.52 - (+0.70)$
$= \underline{+0.82\ \text{V}}$ [1]

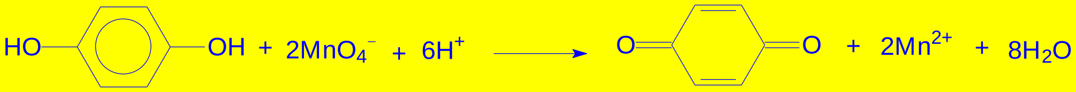
(ii) Construct a balanced equation for this reaction and hence determine its $\Delta G^\ominus$, in kJ mol^{-1}. [3]



--- (1)

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ --- (2)

$\underline{(1) \times 5 + (2) \times 2}$



OR $5C_6H_6O_2 + 2MnO_4^- + 6H+ \rightarrow 5C_6H_4O_2 + 2Mn^{2+} + 8H_2O$

$\Delta G^\ominus = -nFE^\ominus_{cell}$
$= -(10)(96500)(0.82)$
$= -791\ 300\ J\ mol^{-1}$
$= \underline{-791\ kJ\ mol^{-1}}$

[1]: balanced equation [1]: $\Delta G^\ominus$ in J mol^{-1} [1]: $\Delta G^\ominus$ in kJ mol^{-1}

(iii) Using the list of standard electrode potentials in the *Data Booklet*, identify a gas that would reduce quinone to quinol. Explain your answer. [2]

$\underline{H_2 \text{ (in acidic / alkaline) or } SO_2}$

$E^\ominus_{cell} = +0.70 - (0.00 / -0.83 / +0.17)$
$= \underline{+0.70 / 1.53 / 0.87\ V}$

[1]: choose a gas whose $E^\ominus$ is less positive than +0.70
[1[: explain in terms of $E^\ominus_{cell}$ or in words

[Total: 23]

Section B

4 **(a)** In aqueous solution, chlorine dioxide, ClO_2, reacts with hydroxide ions as shown.

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$$

A series of experiments is carried out using different concentrations of ClO_2 and OH^-. Table 4.1 shows the results obtained.

Table 4.1

Experiment	$[ClO_2]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.02	0.030	7.20 x 10^{-4}
2	0.02	0.120	2.88 x 10^{-3}
3	0.05	0.015	2.25 x 10^{-3}

(i) Define the term order of reaction. [1]

The power to which the concentration of a reactant is raised in the **experimentally determined rate equation** [1]

(ii) Use the data in the Table 4.1 to determine the order of reaction with respect to each reactant, ClO_2 and OH^-.

Explain your reasoning. [2]

Let the order of reaction wrt ClO_2 be a and OH^- be b.

Comparing Expt 1 and 2

$$\frac{2.88\times10^{-3}}{7.20\times10^{-4}} = \frac{k[0.02]^a[0.120]^b}{k[0.02]^a[0.030]^b}$$

$$4 = 4^b$$ [1]

$$b = 1$$

Comparing Expt 1 and 3 [OR]	Comparing Expt 2 and 3
$\frac{2.25\times10^{-3}}{7.20\times10^{-4}} = \frac{k[0.05]^a[0.015]^1}{k[0.02]^a[0.030]^1}$ $6.25 = 2.5^b$ $a = 2$	$\frac{2.25\times10^{-3}}{2.88\times10^{-3}} = \frac{k[0.05]^a[0.015]^1}{k[0.02]^a[0.120]^1}$ $6.25 = 2.5^b$ $a = 2$

[1]

(iii) Use your answer to **(a)(ii)** to construct the rate equation for this reaction. Hence, calculate the value of the rate constant k. [2]

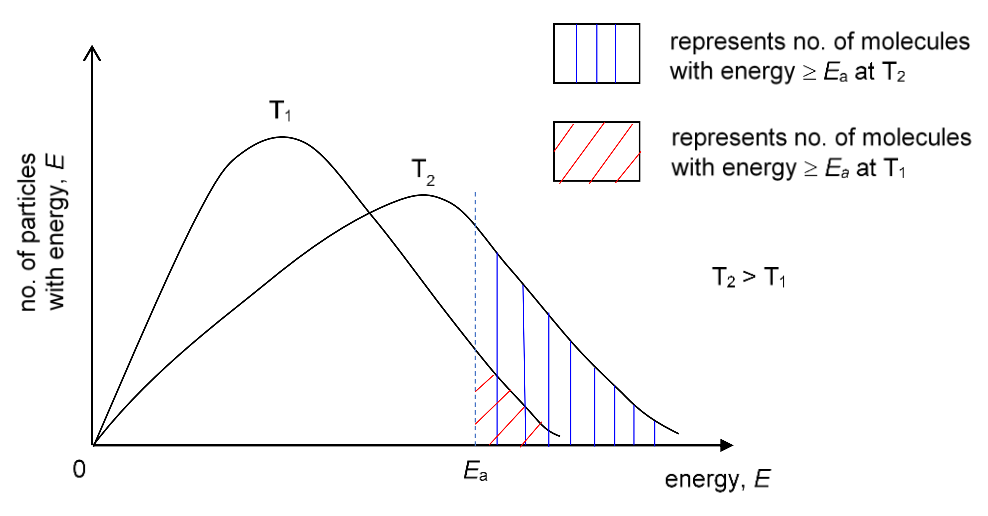
rate = $k[ClO_2]^2[OH^-]$ [1]

$$2.88\times10^{-3} = k[0.02]^2[0.120]^1$$

$$k = 60$$

[1] for value of k

(b) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect on a rate constant on increasing temperature from T_1 to T_2. [3]



[1]: diagram.
No marks if:

- graph does not start from origin
- key not provide
- absence of shading
- Peak for higher temperature is same/higher than lower temp.
- Absence of labelling on both axes/ Higher or Lower Temp not clearly indicated on graph (can use T1 to replace lower temp as stated by question)

As shown on the diagram, when temperature increases from T_1 to T_2, the average kinetic energy of the molecules increases. The number of reactant molecules with energy greater than or equal to the activation energy, E_a, increases significantly. [1]

This results in an increase in the frequency of effective collisions. The rate constant, k, increases and hence rate of reaction increases. [1]

(c) A three-step synthesis of benzaldehyde from methylbenzene is shown in Fig. 4.1.

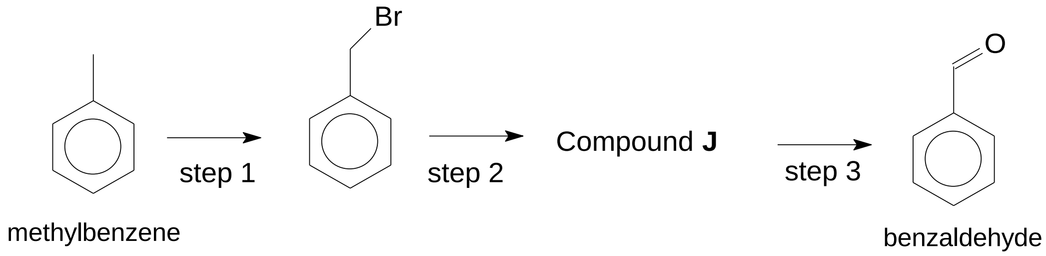
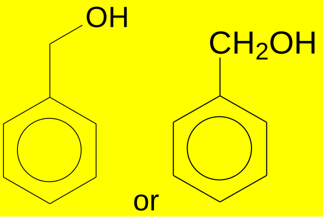


Fig. 4.1

Compound **J** does not dissolve in aqueous NaOH.

(i) Suggest the structure of compound **J**. [1]

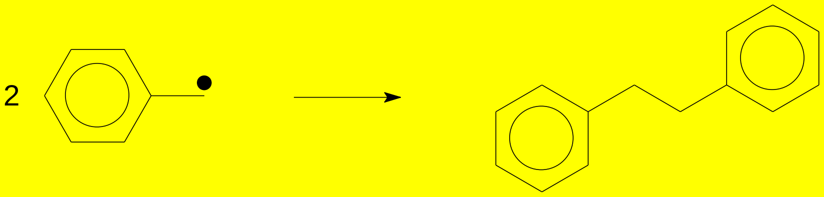


(ii) State the reagents and conditions for steps 2 and 3. [2]

Step 2: $NaOH(aq)$, heat [1]

Step 3: $K_2Cr_2O_7$, dil H_2SO_4, warm with (immediate) distillation [1]

(iii) A hydrocarbon by-product $C_{14}H_{14}$ was formed from step 1. Draw the structure of this hydrocarbon and suggest how it was formed. [1]



Two benzylic radicals ($C_6H_5CH_2\bullet$) react to form the by-product in the termination step of the free-radical substitution.

[1]: (reduced demand) structure of by-product regardless of explanation

(iv) $LiAlH_4$ reacts with benzaldehyde but not with alkenes. Explain why. [2]

$LiAlH_4$ produces H^- nucleophile which attacks the electron-deficient carbonyl carbon of benzaldehyde and reduce benzaldehyde to phenylmethanol / an alcohol.

C=C in alkenes is electron rich and it will repel the H^- nucleophile / lack of polarity of C=C bond in alkene and thus $LiAlH_4$ will not react with alkene.

[1]: nucleophile (H^-) reacts with electron deficient carbonyl in benzaldehyde
[1]: absence of electron deficient carbon / electron rich C=C in alkenes

(d) Solid samples of **K**, **L** and **M** are added separately into hydrochloric acid and sodium hydroxide. The observations are recorded in Table 4.2.
Each sample is known to be pure and can only be Na_2O, Al_2O_3, SiO_2 or P_4O_{10}.

Table 4.2

Unknown	Observations
K	Reacts with both hydrochloric acid and sodium hydroxide
L	Reacts with hot concentrated sodium hydroxide
M	Reacts with hydrochloric acid

(i) Use Table 4.2 to identify unknown **K**, **L** and **M**. [1]

K: Al_2O_3
L: SiO_2 or P_4O_{10}
M: Na_2O [1]: All correct

(ii) Write equations to show how **K** reacts with hydrochloric acid and sodium hydroxide. [2]

$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$ [1]
$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$ [1]

(e) Salts are often used as a de-icing agent to melt ice on roads in winter. When the salt dissolves in water present on the roads, it causes the melting point of ice to drop to below 0 °C, promoting the melting of the remaining ice.

Table 4.3

Lattice energy of $CaCl_2(s)$	–2240 kJ mol^{-1}
enthalpy change of hydration of $Cl^-(g)$	–378 kJ mol^{-1}
enthalpy change of hydration $Ca^{2+}(g)$	–1579 kJ mol^{-1}

(i) Using information from Table 4.3, calculate ΔH_{sol} of $CaCl_2(s)$. [1]

ΔH_{sol} of $CaCl_2(s)$
$= -(-2240) + (-1579) + 2 \times (-378)$
$=$ **−95 kJ mol^{-1}**

(ii) By considering ΔG of the dissolution of $CaCl_2$, your answer from **(e)(i)** and assuming that ΔS_{sol} of $CaCl_2(s)$ is close to zero , state and explain if $CaCl_2$ can also be used to de-ice roads. [2]

Since ΔS is close to zero and ΔH is negative, ΔG is negative / $\Delta G = \Delta H - T\Delta S < 0$ even at low temperatures.

Hence, the dissolution of $CaCl_2$ is spontaneous even at low temperatures, and it can be used to de-ice roads.

[1]: calculate / deduce sign of ΔG_{sol} using the ΔH_{sol} from **(i)** [ecf] and the information that $\Delta S_{sol} \approx 0$
[1]: conclusion based on ΔG_{sol} calculated (i.e. if $\Delta G_{sol} < 0$, dissolving of $CaCl_2(s)$ is spontaneous and $CaCl_2(s)$ can be used and vice-versa)

5 **(a)** Diazomethane, CH_2N_2, reacts with water to give methanol and nitrogen gas.

$$CH_2N_2 + H_2O \rightarrow CH_3OH + N_2$$

When 2.50×10^{-3} mol of CH_2N_2 was added into water, the volume of nitrogen gas evolved at various time intervals after the start of the reaction were measured. The experiment results are plotted in Fig. 5.1.

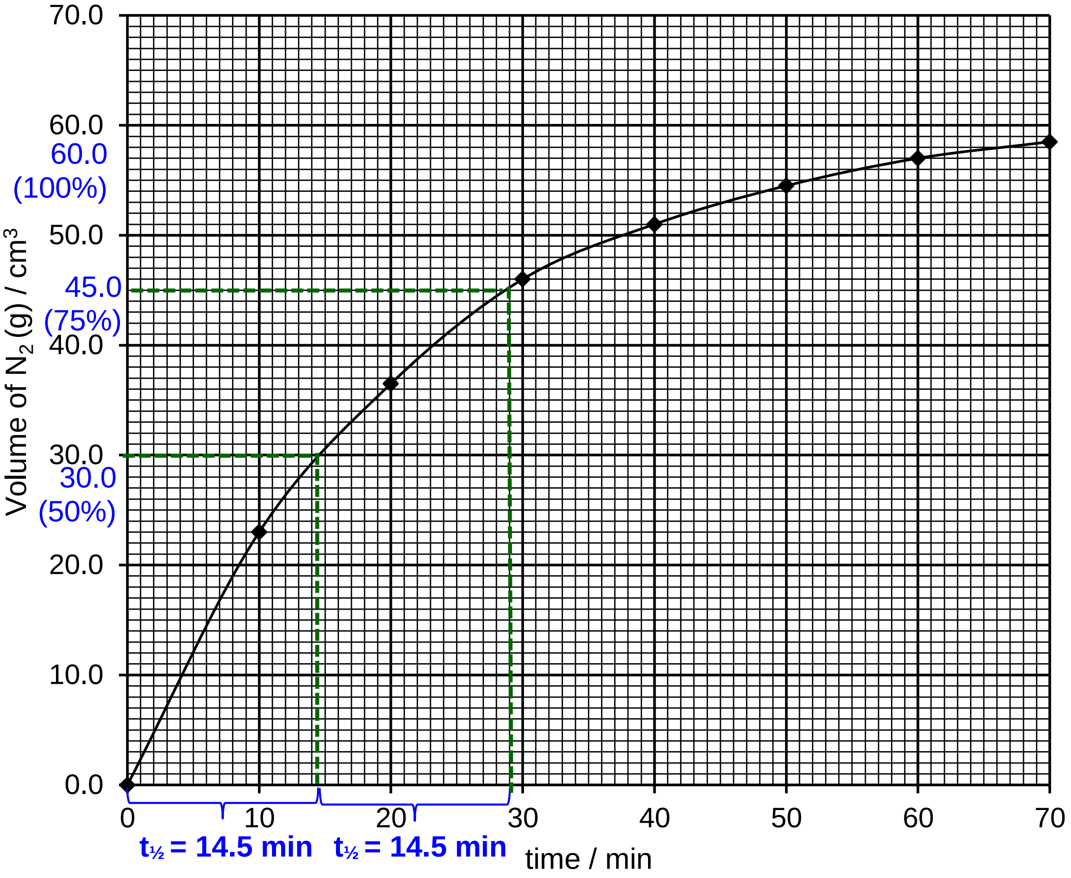


Fig. 5.1

(i) Using the information provided, show that the maximum volume of nitrogen gas, collected at room temperature and pressure is 60 cm^3. [1]

Amt of $CH_2N_2 = 2.50 \times 10^{-3}$ mol

Amt of N_2 = 2.50 × 10^{-3} mol since $CH_2N_2 \equiv N_2$

Volume of N_2 at r.t.p. = $2.5 \times 10^{-3} \times 24 \times 1000 = 60$ cm^3 [1]

(ii) Hence, use Fig. 5.1 to show that the reaction is first order with respect to $[CH_2N_2]$. [1]

Max volume of N_2 gas collected = 60 cm^3 (100%)

The two half-lives are determined from graph at volume = 30 cm^3 (50%) & 45 cm^3 (75%)

From the graph, $t_{1/2}$ is constant at about 14.5 min hence order of reaction with respect to $[CH_2N_2]$ is 1.

[1] accept construction lines on Fig 5.1 or in words how the two $t_{½}$ are determined

The reaction of CH_2N_2 with water takes place in the presence of an acid.
Two experiments were conducted at different pH values to investigate the kinetics of this reaction. The results are shown in Table 5.1.

Table 5.1

Experiment	initial $[CH_2N_2]$ / mol dm^{-3}	pH	Relative initial rate
1	1.00×10^{-3}	1.00	1
2	6.00×10^{-3}	1.30	1.5

(iii) Calculate the concentration of H^+(aq) in experiment 1 and 2. [1]

Experiment	pH	**$[H^+]$ / mol dm^{-3}**
1	1.00	**$10^{-1.00} = 0.100$**
2	1.30	**$10^{-1.30} = 0.0501$**

[1]

(iv) Use the data provided to determine the order of reaction with respect to $[H^+]$, and hence write the rate equation for the reaction. [2]

Experiment	$[CH_2N_2]$ / mol dm^{-3}	pH	$[H^+]$ / mol dm^{-3}	Relative rate
1	1.00×10^{-3}	1.00	0.100	1
2	6.00×10^{-3}	1.30	0.0501	1.5

Let rate = $k\,[CH_2N_2]\,[H^+]^x$

$$\frac{rate_1}{rate_2} = \frac{k[CH_2N_2]\,[H^+]^x}{k[CH_2N_2]\,[H^+]^x}$$

$$\frac{1}{1.5} = \frac{(1.0\times10^{-3})(0.100)^x}{(6.0\times10^{-3})(0.0501)^x}$$

$$\frac{2}{3} = \frac{1}{6}(2)^x$$

$\therefore x = 2$

[1]

rate = $k\,[CH_2N_2]\,[H^+]^2$ [1]

(b) Tartrate ions, $(CHOHCO_2^-)_2$ are oxidised by hydrogen peroxide to carbon dioxide and water. The reaction can be catalysed by adding Fe^{2+}(aq) catalyst.

(i) State the property, typical of transition metals, which allows Fe^{2+}(aq) to behave as a catalyst in this reaction. [1]

Transition metals display **variable oxidation states / numbers** in their compounds. **[1]**

(ii) Using the half equation,

$$4CO_2(g) + 8H^+(aq) + 10e^- \rightleftharpoons (CHOHCO_2^-)_2(aq) + 2H_2O(l)$$

and relevant half equations from the *Data Booklet,* suggest a two-step mechanism to show how $Fe^{2+}(aq)$ functions as a catalyst in this reaction. [2]

Step 1
$2Fe^{2+} + 2H^+ + H_2O_2 \longrightarrow 2Fe^{3+} + 2H_2O$ [1]

Step 2
$(CHOHCO_2^-)_2 + 2H_2O + 10Fe^{3+} \longrightarrow 4CO_2 + 8H^+ + 10Fe^{2+}$ [1]

(c) The synthesis of HCN was developed in the early 1900s.

$$CH_4\ (g) + NH_3\ (g) + \frac{3}{2}\ O_2\ (g) \longrightarrow HCN\ (g) + 3\ H_2O\ (l) \qquad \Delta H = -506\ kJ\ mol^{-1}$$

(i) Explain why the entropy change of the above reaction is negative. [2]

Δn (gaseous particle) = **1 – 3.5 = – 2.5 mol** [1]

An decrease in number of gaseous particles result in **less gaseous particles** moving randomly. There are **less ways to distribute the particles and the energies** among these particles, resulting in a **smaller / lesser disorder** [1] in the system.

Hence entropy of the system decreases.

(ii) Hence, comment on the effect of temperature on the spontaneity of this reaction. [2]

$\Delta G = \Delta H - T\Delta S$

At **low temperature**, **ΔH is more negative than $T\Delta S$** [1], it is more likely to have **$\Delta G < 0$** at low temperature, hence reaction will become **spontaneous**. [1]

(d) **P** and **Q** are oxides of Period 3 elements.

P is a solid with a high melting point. It conducts electricity when molten. **P** is sparingly soluble in water to form a solution of pH 9.0.

Q is a solid at room temperature. It dissolves in water to form a solution of pH 2.

Identify **P** and **Q** and write equations for all reactions. [4]

P is MgO [1]
Q is P_4O_{10} [1]

$MgO(s) + H_2O(l) \rightleftharpoons Mg(OH)_2(aq)$ [1]

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$ [1]

(e) Compound **X**, $C_3H_4O_3$, liberates a gas when treated with aqueous sodium carbonate.

Compound **X** is formed as the only organic product when a neutral organic compound **Y**, $C_4H_8O_3$, is heated with acidified $KMnO_4$.

Both **X** and **Y** give yellow precipitate with alkaline aqueous iodine.

Deduce the structures of **X** and **Y.** Suggest explanations for your answer that are consistent with information provided. [4]

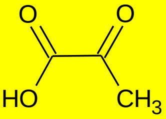
N undergoes **acid-base reaction** with Na_2CO_3, **X** contains **carboxylic acid**.

X and **Y** undergo **oxidation with alkaline aqueous iodine**

X is an oxidation product of Y, **X** has the structure, CH_3CO-

(above 2 points ➔[1])

X is

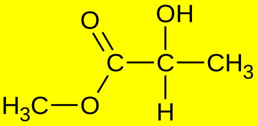

[1]

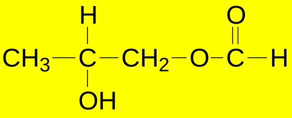
Y is a **neutral organic compound so it cannot contain the carboxylic group**. It is likely to **contain an ester** functional group given that there are three oxygen atoms in its molecular formula.

Y undergoes **acidic hydrolysis** reaction of its **ester** functional group and **oxidation** of its **2° alcohol.**

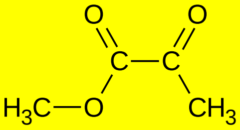
Any of the above 3 points ➔ [1]

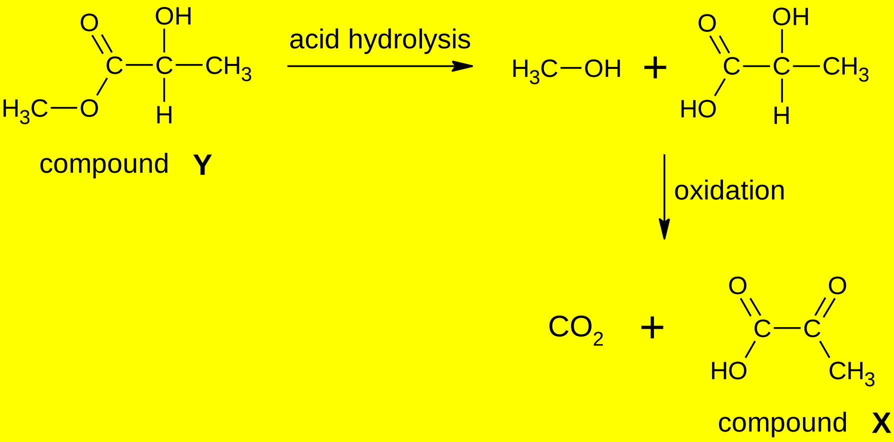
Y is


[1] or


$$CH_3-\overset{H}{\underset{OH}{C}}-CH_2-O-\overset{O}{C}-H$$

FYI:

Y cannot be  since this has a molecular formula is $C_4H_6O_3$



[Total: 20]