Answer **all** the questions in the spaces provided.

1 **(a)** Table 1.1 shows the solubility of two organic molecules at 25 °C.

Table 1.1

	solubility in water / g dm^{-3}
propanone	miscible
chloromethane	5.04

(i) Identify the type of intermolecular force present between the molecules.

propanone: ……

chloromethane: ……[1]

(ii) Give a reason for the difference in their solubilities in water.

……

……[1]

(b) The boiling point of three ligands are shown in Table 1.2.

Table 1.2

ligand	formula	boiling point / °C
water	H_2O	100
ammonia	NH_3	–33.3
hydrazine	N_2H_4	114

(i) Explain what is meant by the term *ligand*.

……

……[1]

(ii) Explain the difference in the boiling points of the three ligands.

……

……

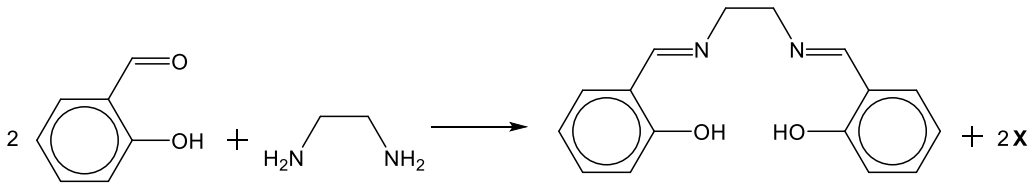
……

……

……[2]

(c) Polydentate ligands are ligands which form more than one bond with the metal atom or ion.

Salicylaldehyde, ethane-1,2-diamine and H_2salen are examples of such ligands. H_2salen can be synthesised from salicylaldehyde and ethane-1,2-diamine.



salicylaldehyde ethane-1,2-diamine H_2salen

When the phenolic groups of H_2salen are deprotonated, salen^{2-} acts as a ligand. It has a high affinity for Co^{2+} ions and forms a planar complex Co(salen).

(i) Suggest the identity of molecule **X**.

……[1]

(ii) Draw the structure of a salen^{2-} ligand and circle the atoms which are used to coordinate to a Co^{2+} ion.

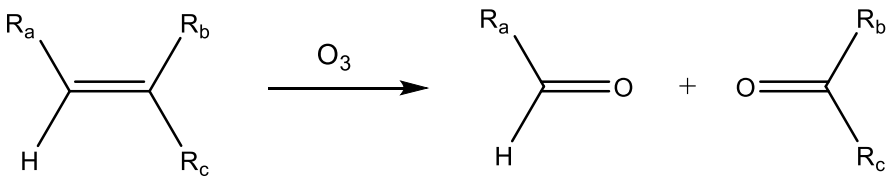
salen^{2-}

[2]

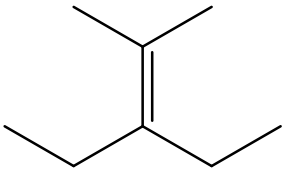
(iii) State the coordination number of the Co^{2+} ion in Co(salen).

……[1]

(d) Ozonolysis is a method to oxidatively cleave alkenes using ozone, O_3, to form carbonyl compounds.



(i)



2-methyl-3-ethylpent-2-ene

Draw the structure of the organic products when 2-methyl-3-ethylpent-2-ene undergoes ozonolysis.

[2]

(ii) Ozonolysis of **A**, C_6H_{10}, gives a single compound, **B**, $C_6H_{10}O_2$.

B gives a yellow precipitate when treated with alkaline aqueous iodine and forms a red-brown precipitate when treated with Fehling's solution.

Draw the structures of the compounds **A** and **B**.

A **B**

[2]

[Total: 13]

2 Chromium is a transition metal that is valued for its high resistance to corrosion and is added to steel to form stainless steel.

While chromium can exist in various oxidation states, the most common oxidation state is the +3 state.

(a) Hydrated chromium (III) chloride exists as isomers, with the general formula of $CrCl_3.6H_2O$. One such isomer is $[CrCl_2(H_2O)_4]Cl.2H_2O$ and it appears dark green.

Suggest the formula of two other isomers of hydrated chromium (III) chloride.

isomer 1 ……..……..

isomer 2 ……[2]

(b) When a sample of hydrated chromium (III) chloride is added to excess water, a green solution of $CrCl_3(aq)$ is obtained. Fig. 2.1 shows the reactions that aqueous $CrCl_3$ can undergo.

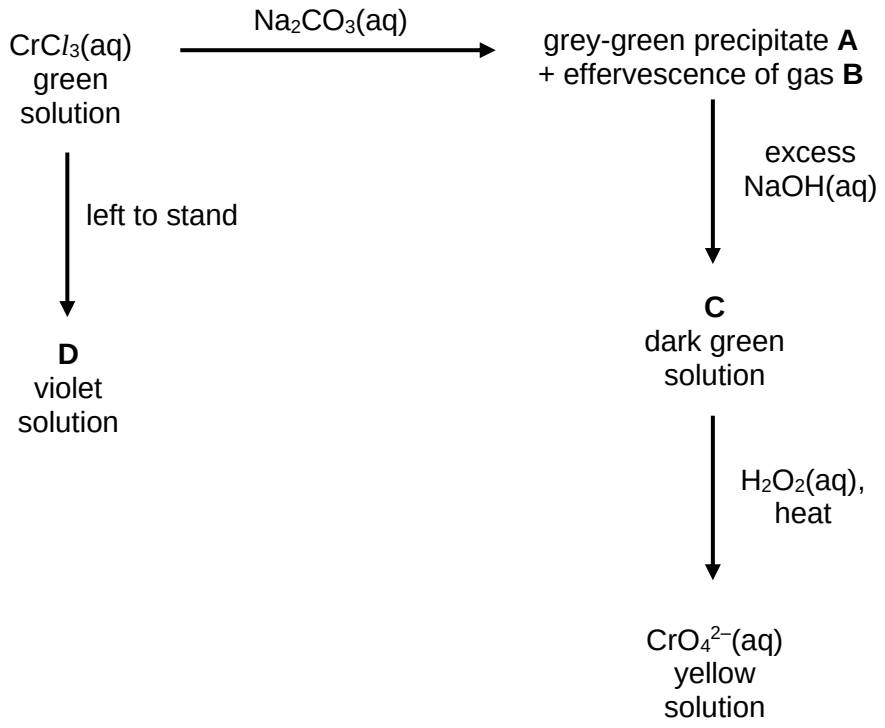


Fig. 2.1

(i) Identify precipitate **A** and gas **B**.

precipitate **A**: ……..…

gas **B**: ……[2]

(ii) Suggest the formula of compound **C**.

……[1]

(iii) Explain why solutions of transition metal compounds are often coloured.

………………………………………………………………………………………..…….

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………………………………………………………………………………………... [3]

(iv) Given that the oxidation state of chromium in compound **D** is still +3, suggest what happened that caused the colour change from green to violet.

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……………………………………………………………………………………………[2]

(v) State the role of H_2O_2(aq).

……………………………………………………………………………………………[1]

(vi) Write a balanced equation for the formation of CrO_4^{2-} from **C**.

……………………………………………………………………………………………[1]

(c) Fig. 2.2 shows the first seven ionisation energies of calcium and chromium.

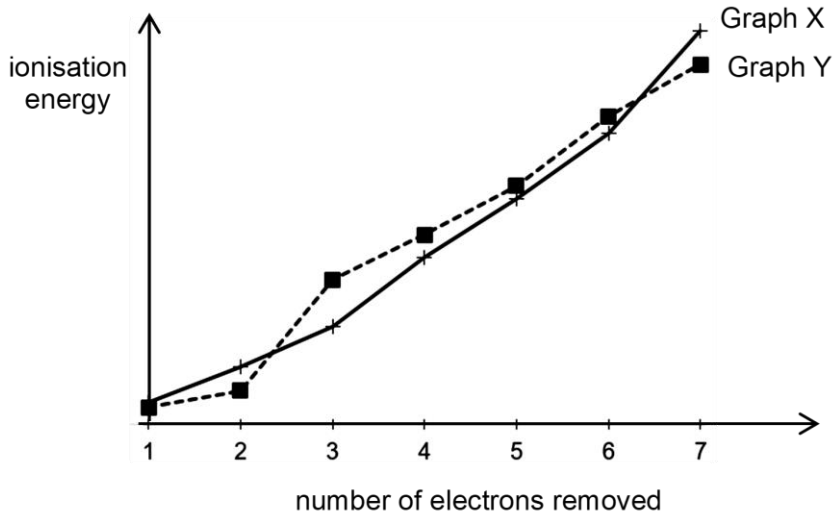

Fig. 2.2

State and explain which graph shows the successive ionisation energies for calcium.

……

……

……

……

……

……

…… [2]

[Total: 14]

3 **(a)** The variation of the volume with temperature of a fixed mass of an ideal gas at constant pressure may be represented by a relationship known as Charles's law,

$$V = k\,T$$

where V is the volume of a gas, T is the temperature in Kelvin and k is a constant.

An experiment was carried out to attempt to verify this law using a gas, phosphine, PH_3.

The experiment was repeated several times at different temperatures.

Fig. 3.1 was plotted to determine the relationship between the volume of the gas and its temperature.

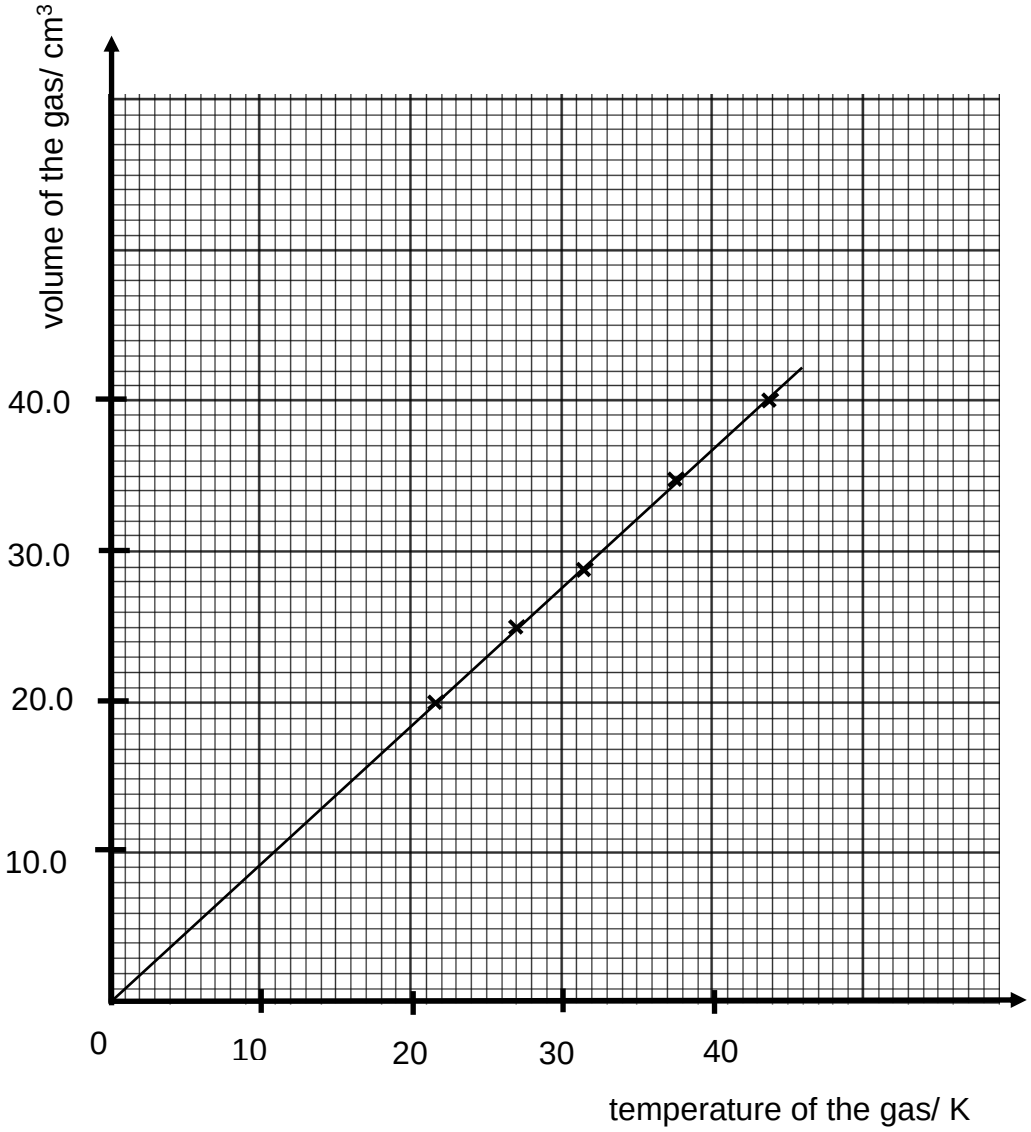

Fig. 3.1

(i) Based on Fig. 3.1, state whether the result is consistent with Charles's law. Give a reason for your answer.

……..…..

……..…..

……[1]

(ii) State the **two** properties of a gas necessary for it to approach ideal behaviour.

……..…..

……..……..…

……..……

……..……..…

……[1]

(b) Orange street lamps contain sodium with a small amount of neon. The light is produced when gaseous atoms are ionised in an electric field. When it is first turned on, the lamps emit a red glow characteristic of neon, but after some time, the orange glow of sodium predominates.

Explain the order for the appearance of the colours. Use relevant data from the *Data Booklet* in your answer.

……..……

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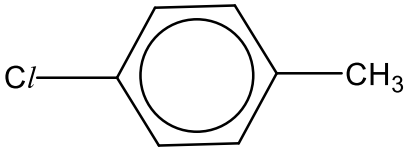
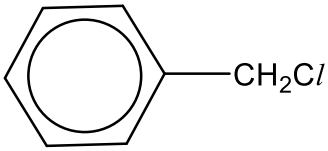
……[2]

(c) 4–chloromethylbenzene and (chloromethyl)benzene are isomers.



4-chloromethylbenzene



(chloromethyl)benzene

(i) Explain the difference in their reactivities towards hot aqueous sodium hydroxide.

……

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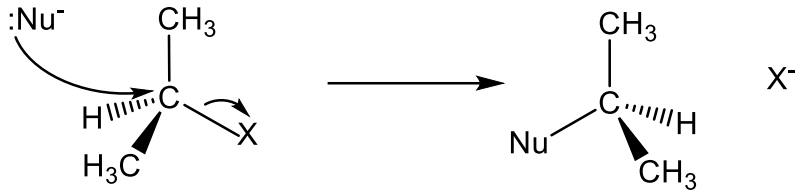
……[2]

(ii) Alkyl halides can undergo nucleophilic substitution, with the simplified general mechanism as shown below:



The mechanism involves the heterolytic fission of the C−X bond, resulting in X leaving with a pair of electrons as X^-. X^- is called the leaving group.

When alkyl halide undergoes nucleophilic substitution, one factor that affects its reactivity is the basicity of X^-. In general, when X^- is a stronger base, it is a poorer leaving group. This results in the alkyl halide being less reactive towards nucleophilic substitution.

Using the data given in Table 3.1 and relevant data from the *Data Booklet*, suggest **two** reasons to explain why (iodomethyl)benzene reacts much faster than (chloromethyl)benzene.

Table 3.1

halide	pK_b
Cl^-	21.0
I^-	24.0

……

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……

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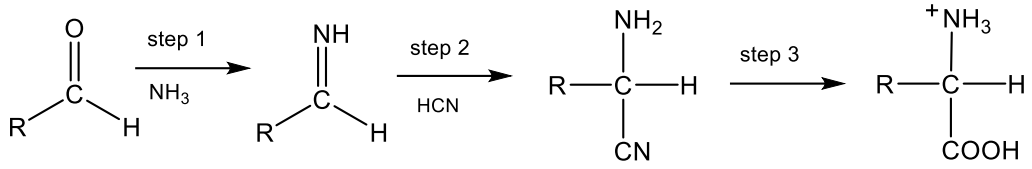
……[2]

(d) The first known synthesis of an amino acid occurred in 1850 in the laboratory of Adolf Strecker.



imine

(i) Name the type of reaction in step 1.

……[1]

(ii) In step 2, the reaction proceeds via two stages:

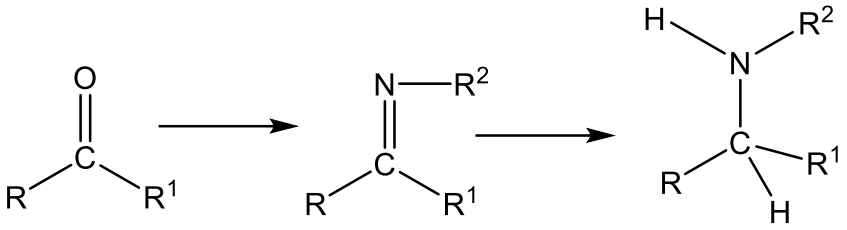
(I) acid-base reaction between the N atom in imine and HCN

(II) nucleophilic attack on C atom by CN^-

Draw the mechanism of step 2. Show all relevant charges, dipoles, lone pairs and curly arrows.

[2]

(iii) An imine intermediate is also formed in preparing secondary amines from ketones.



imine

Suggest the synthetic route by giving all the reagents, conditions and intermediate for the preparation of $(CH_3)_2CHNH(CH_2CH_3)$.

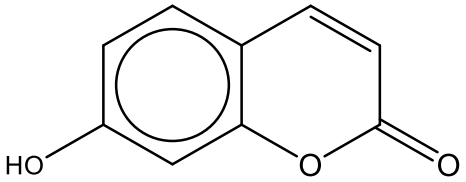
[4]

(iv) Another amine **X**, $CH_3CH(NH_2)CH_2NH_2$, reacts with ethanedioyl dichloride $(COCl)_2$ to produce compound **Y** with molecular formula $C_5H_8N_2O_2$. Suggest the structure for compound **Y**.

[1]

[Total: 16]

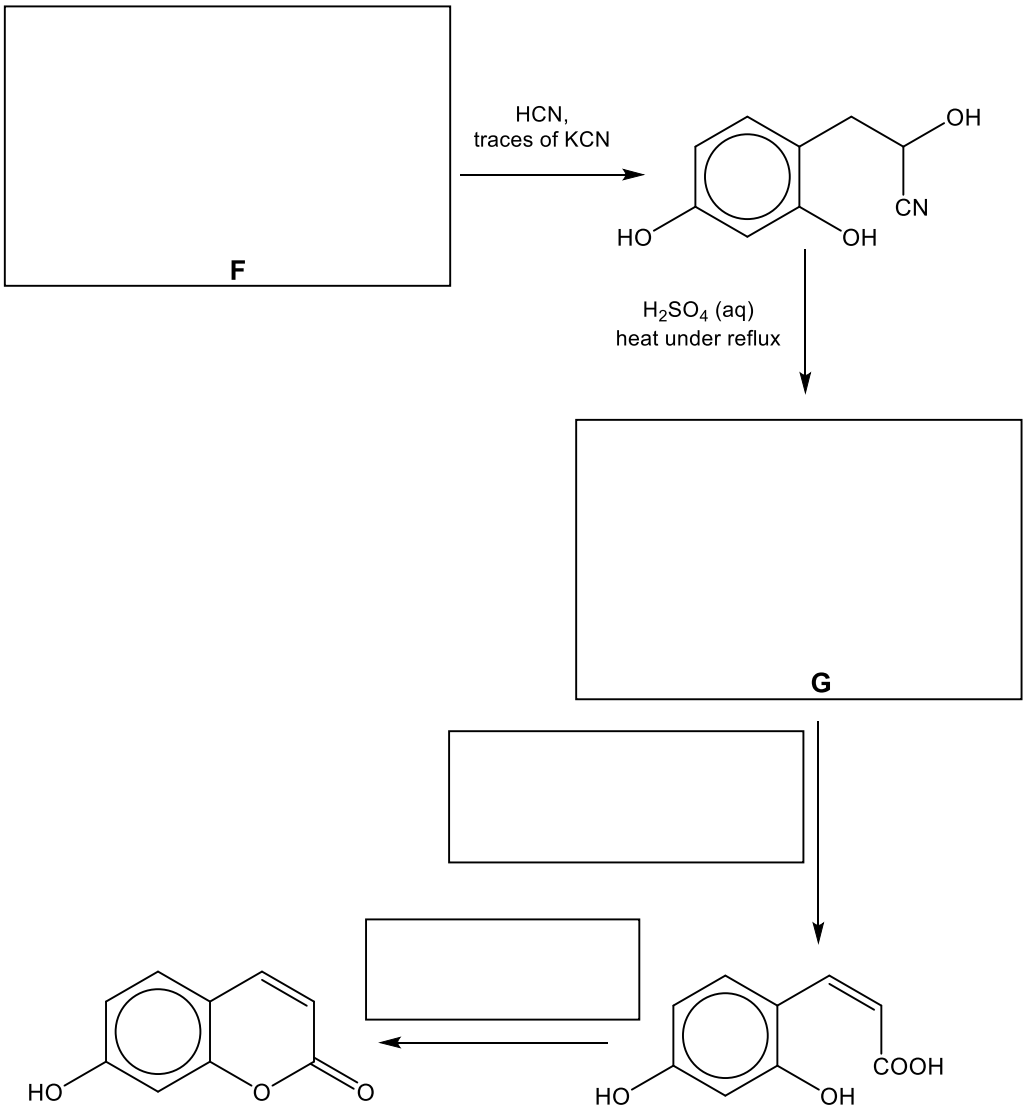
4 **(a)** Umbelliferone is a yellowish-white crystalline solid occurring naturally in carrots and is used as a sunscreen agent. It has the structure shown below:



The following reaction scheme shows how umbelliferone may be synthesised from compound **F**, which has a molecular formula of $C_8H_8O_3$.

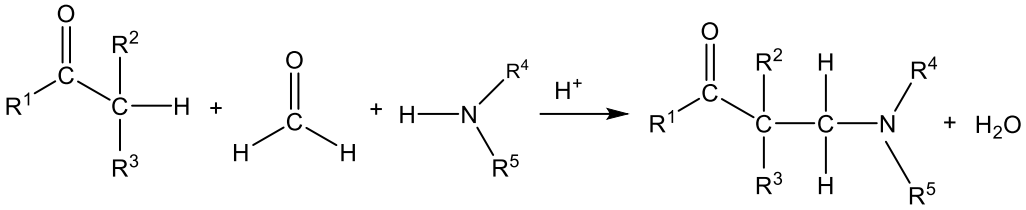
In the boxes provided, fill in the missing

- reagents and conditions,
- structures of compounds **F** and **G**.



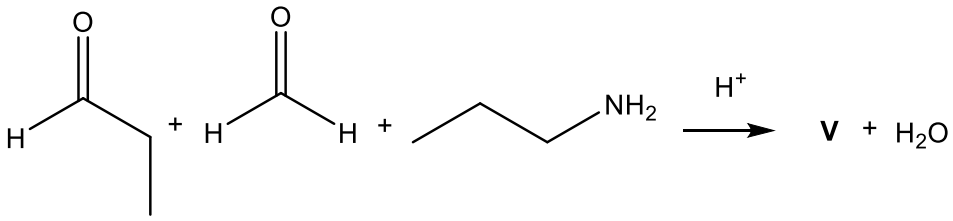
[4]

(b) The Mannich reaction is an organic reaction which consists of an amino alkylation of the hydrogen atom adjacent to a carbonyl functional group, by methanal and a primary amine, secondary amine or ammonia, in the presence of acid.



carbonyl methanal amine

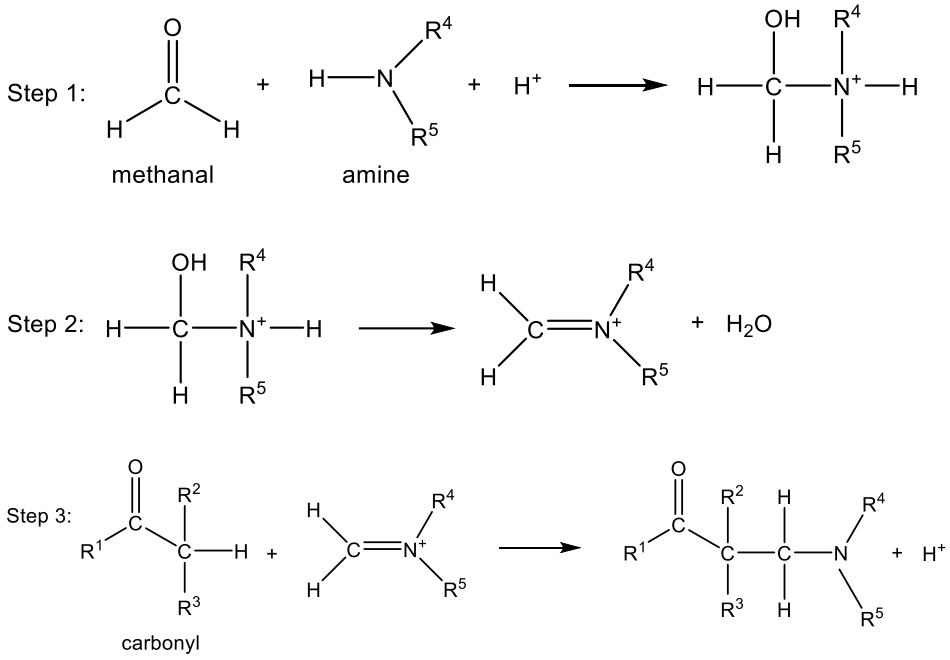
(i) Predict the structure of **V,** $C_7H_{15}NO$, when the following compounds undergo the Mannich reaction.



V

[1]

(ii) The proposed mechanism for the Mannich reaction is as follows:

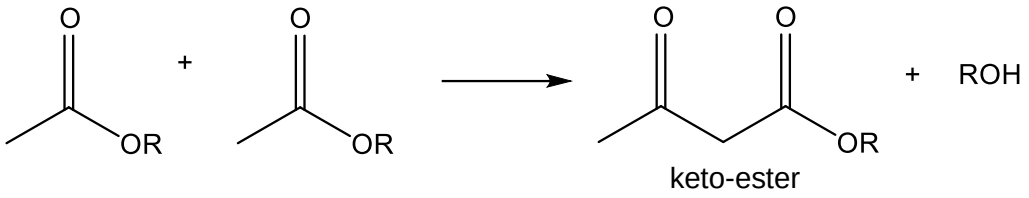


Suggest the type of reaction that occurred in step 1 and 2.

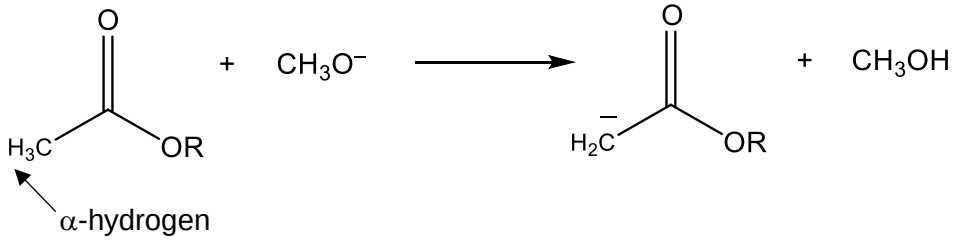
step 1 .....

step 2 ..... [2]

(c) The Claisen condensation of esters involves the formation of a new carbon-carbon bond between two esters. The products are a keto-ester and an alcohol. The reaction takes place in the presence of a strong base e.g. CH_3O^-.



(i) The first step in Claisen condensation involves the strong base CH_3O^- removing an α-hydrogen atom (i.e. the hydrogen atom bonded to the carbon atom next to the carbonyl carbon atom) in an acid-base reaction as shown below.



Suggest a reason why the α-hydrogen atom of the ester is acidic.

……

……[1]

(ii) With reference to the acid-base reaction mentioned in **(c)(i)**, suggest why each of the following reactions does not take place in the presence of CH_3O^-.

(1) $CH_3CH_3 \longrightarrow {}^-CH_2CH_3$

(2) $CH_3COOH \longrightarrow {}^-CH_2COOH$

……

……

……

……

……

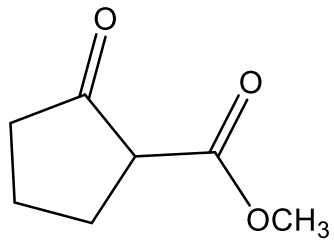
……

……[2]

(iii) Draw **two** possible structures of the keto-esters formed when a mixture of $CH_3CO_2CH_2CH_3$ and $CH_3CH_2CO_2CH_2CH_3$ undergo the Claisen condensation.

[2]

(iv) Draw the structure of the reactant that can be used to prepare the following compound by the Claisen condensation.



[1]

[Total: 13]

5 Hydrogen fuel cells use hydrogen gas with oxygen gas to form water and generate electricity. Two types of hydrogen fuel cells have been used to power vehicles.

Alkaline fuel cells (AFCs) use an aqueous solution of potassium hydroxide as the electrolyte. In recent years, novel AFCs that use an alkaline polymer membrane as the electrolyte have been developed. Fig. 5.1 shows the diagram of an AFC.

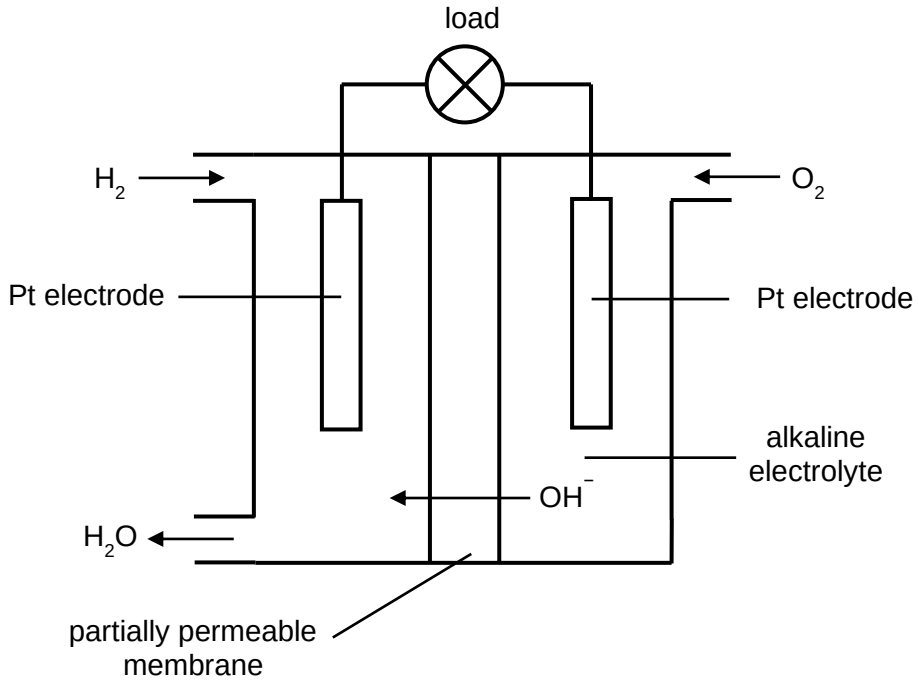


Fig. 5.1

Proton exchange membrane (PEM) fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum or platinum alloy catalyst. It has the same overall reaction as the AFC but uses an acidic electrolyte.

(a) (i) On Fig. 5.1, draw the direction of electron flow. [1]

(ii) When adjusted for standard conditions, an AFC is known to generate 1.23 V of electromotive force. With reference to the *Data Booklet*, write the half equation for each electrode and the overall equation.

anode ……..……..

cathode …….....

overall ……..…..... [2]

(iii) Using information from **(a)(ii)**, calculate the Gibbs free energy change per mol of water generated in the AFC.

[1]

(iv) Calculate the $E_{cell}^{\ominus}$ of the PEM fuel cell.

[2]

(v) Comment on the voltages generated by the AFC and PEM fuel cell.

……..…..

……..…..

…… [1]

(b) The disadvantage of transporting hydrogen gas is one of the factors limiting the use of hydrogen fuel cells. More recently, **liquid organic hydrogen carriers (LOHC)** such as the methylbenzene / methylcyclohexane system have been used to transport hydrogen safely over long distances.

At its source, hydrogen is 'loaded' on the LOHC by reacting hydrogen with methylbenzene in the presence of platinum catalyst to produce methylcyclohexane. Hydrogen is 'unloaded' from the LOHC by reacting methylcyclohexane with the catalyst to regenerate methylbenzene.

Table 5.1 contains information about hydrogen and methylcyclohexane.

Table 5.1

liquids	density under conditions for transportation / kg m^{-3}	boiling point at 1 atm / ^{o}C	flammability
hydrogen	71	–252.9	very high
methylcyclohexane	770	101	high

(i) Write a balanced equation for the loading of hydrogen on the LOHC.

…… [1]

(ii) State the **type** of catalyst used in the loading of the LOHC. Describe how it catalyses the reaction.

……..…..

……..…..

……..…..

……..…..

……..…..

……..…..

……..…..

……..…..

……..…..

……..…..

……..…..

…… [3]

(iii) Calculate the mass of H_2 transported per m^3 of methylcyclohexane.

[2]

(iv) Suggest whether it is advantageous for the transport of hydrogen to be changed from liquid hydrogen to the use of LOHC.

……..…..

……..…..

…… [1]

(c) The hydrogen supply for fuel cells has been classified according to its impact on the environment. Green hydrogen refers to the gas that is produced using renewable energy, without greenhouse gas emissions. The electrolysis of water powered by solar, wind or geothermal energy produces green hydrogen.

(i) Currently the most common method for generating hydrogen gas involves two successive reactions:

1) steam-methane reformation
2) water-gas shift reaction

Using this method, methane reacts with steam to form four times the amount of hydrogen gas along with a side product.

Write the overall balanced equation for the above method.

…… [1]

(ii) Hence suggest whether the method in **(c)(i)** is a source of green hydrogen.

……..…..

…… [1]

(iii) Hydrogen produced by steam-methane reformation may contain trace contaminants such as ethene.

Draw a 'dot-and-cross' diagram of ethene. State the bond angle and shape around the carbon atom.

shape: ……

bond angle: …….. [2]

(d) Electric vehicles (EVs) have been known as a greener form of transportation than petrol powered vehicles because greenhouse gases are not emitted from EVs.

By considering the source of the electrical energy, comment on the validity of this claim.

……....

……...….

…… [1]

[Total: 19]