ANDERSON SERANGOON JUNIOR COLLEGE

2019 JC 2 PRELIMINARY EXAMINATIONS

CHEMISTRY **9729/03**

Higher 2 **18 September 2019**

Paper 3 Free Response **2 hours**

Candidates answer on separate Answer Booklet.

Additional Materials: Answer Booklet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **15** printed pages and **1** blank page.

Section A

Answer **all** the questions from this section.

1 **(a)** Iron(III) cation complexes with a thiocyanate anion (SCN^-) to form the iron(III) thiocyanate complex, $[Fe(SCN)]^{2+}$ at 298 K, according to the following equation.

$$\underset{\text{yellow}}{Fe^{3+}(aq)} + \underset{\text{colourless}}{SCN^-(aq)} \rightleftharpoons \underset{\text{blood red}}{[Fe(SCN)]^{2+}(aq)} \qquad \Delta H < 0$$

(i) Write an expression for K_c for this reaction, stating its units. [2]

(ii) The K_c value of this reaction is 4.99×10^2. Calculate the percentage of $[Fe(SCN)]^{2+}$ in a Fe^{3+}–$[Fe(SCN)]^{2+}$ mixture when $[SCN^-] = 5.00 \times 10^{-3}$ mol dm^{-3}. [2]

(iii) State and explain the difference in observations when the reaction is carried out at 500 K. [2]

(b) Describe the variations in melting points of the elements sodium to chlorine and explain these variations in terms of their structures and bonding. [5]

(c) Compounds **B**, **C**, **D** and **E** are oxides or chlorides of Period 3 elements.

B and **C** have high melting points while **D** and **E** have low melting points.

B is insoluble in water but soluble in hot concentrated sodium hydroxide.

When water was added separately to 0.100 mol each of **C**, **D** and **E**, a neutral solution was obtained for **C** while an acidic solution was obtained for **D** and **E**. The resulting solution of **D** required 0.500 mol of silver nitrate for complete precipitation.

1 mol of **E** requires 2 mol of aqueous sodium hydroxide for complete neutralisation.

Identify compounds **B** to **E**, and write equations for the reactions described above. [6]

[Total: 17]

Question 2 starts on the next page.

2 (a) Helium is used to fill party balloons.

A 60.0 dm^3 industrial tank of helium gas at 27 °C and 125 atm was used to fill up some balloons. After some balloons were filled, the pressure in the tank was reduced to 50 atm.

(i) How many moles of helium was used to fill the balloons? [2]

(ii) Assuming each filled balloon is a sphere with a radius, r, of 0.15 m and has an internal pressure of 1.2 atm, what is the maximum number of balloons that can be filled with the **remaining** gas in the tank at the same temperature?

(volume of sphere $= \frac{4\pi r^3}{3}$)

[2]

(iii) State and explain if helium gas behaves more ideally in the tank, or when present in balloons. [2]

(b) (i) Using the thermochemical data shown in Table 2.1, draw a fully labelled energy cycle to calculate the standard enthalpy change of combustion of liquid propan–2–ol.

Table 2.1

Standard enthalpy change of formation of liquid propan–2–ol	–318 kJ mol^{-1}
Standard enthalpy change of combustion of carbon	–394 kJ mol^{-1}
Standard enthalpy change of formation of water	–286 kJ mol^{-1}
Standard enthalpy change of vapourisation of water	+41 kJ mol^{-1}

[2]

(ii) By using your answer to **(b)(i)**, and relevant data from the *Data Booklet* and Table 2.1, calculate the standard enthalpy change of vapourisation of propan–2–ol. [2]

(iii) Hence, explain why combustion of liquid propan–2–ol takes place at all temperatures. [2]

(c) (i) State and explain how the acidities of 2–methylpropan–2–ol, 2–chloro–2–methylpropanoic acid and 2,2–dimethylpropanoic acid might compare with each other.

$(CH_3)_3COH$ — 2–methylpropan–2–ol

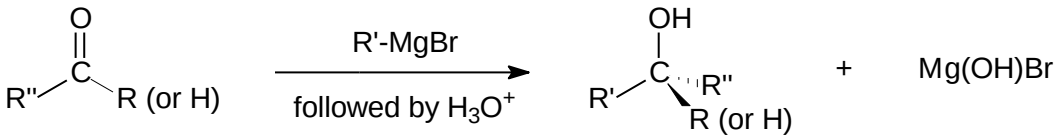
$(CH_3)_3CCO_2H$ — 2,2–dimethylpropanoic acid

$(CH_3)_2CClCO_2H$ — 2–chloro–2–methylpropanoic acid

[3]

(ii) Outline how 2,2–dimethylpropanoic acid may be produced from 2–chloro–2–methylpropane, $(CH_3)_3CCl$. Include the structure of the intermediate compound in your answer. [3]

(iii) Grignard reagents, with different alkyl or aryl groups (R'–MgBr), react with carbonyl compounds to yield alcohols.



Use the above information to suggest a synthesis of 2–methylpropan–2–ol from 2–chloropropane according to the scheme in Fig. 2.1. Include reagents and conditions for all steps, and the structures of the intermediate organic compounds, **G** and **H**, in your answer.

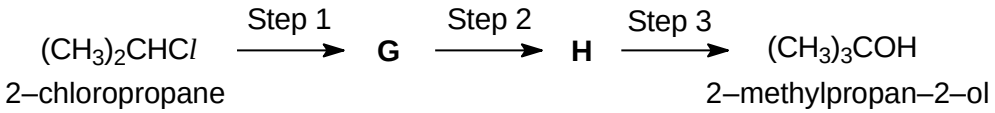


Fig. 2.1

[5]

[Total: 23]

3 **(a)** Nitrate, NO_3^-, and phosphate, PO_4^{3-}, are oxoanions of nitrogen and phosphorous respectively.

(i) Draw dot–and–cross diagrams to show the bonding in NO_3^- and PO_4^{3-}. Hence, suggest the shape of **each** of these ions. [3]

(ii) The 2s and 2p orbitals of nitrogen atoms can hybridise in the same way as the 2s and 2p orbitals of carbon atoms.

Suggest the hybridisation state of nitrogen in NO_3^-. [1]

(iii) Table 3.1 shows the bond lengths of two nitrogen–oxygen bonds.

Table 3.1

Bond	N–O	N=O
Bond length (pm)	136	115

The experimental bond length of each nitrogen–oxygen bond in the nitrate ion, NO_3^-, is 128 pm.

By reference to your answers to **(a)(i)** and **(a)(ii)**, explain this observed bond length in NO_3^-. [1]

(b) Fig. 3.1 shows the synthesis of compound **K** from phenylamine.

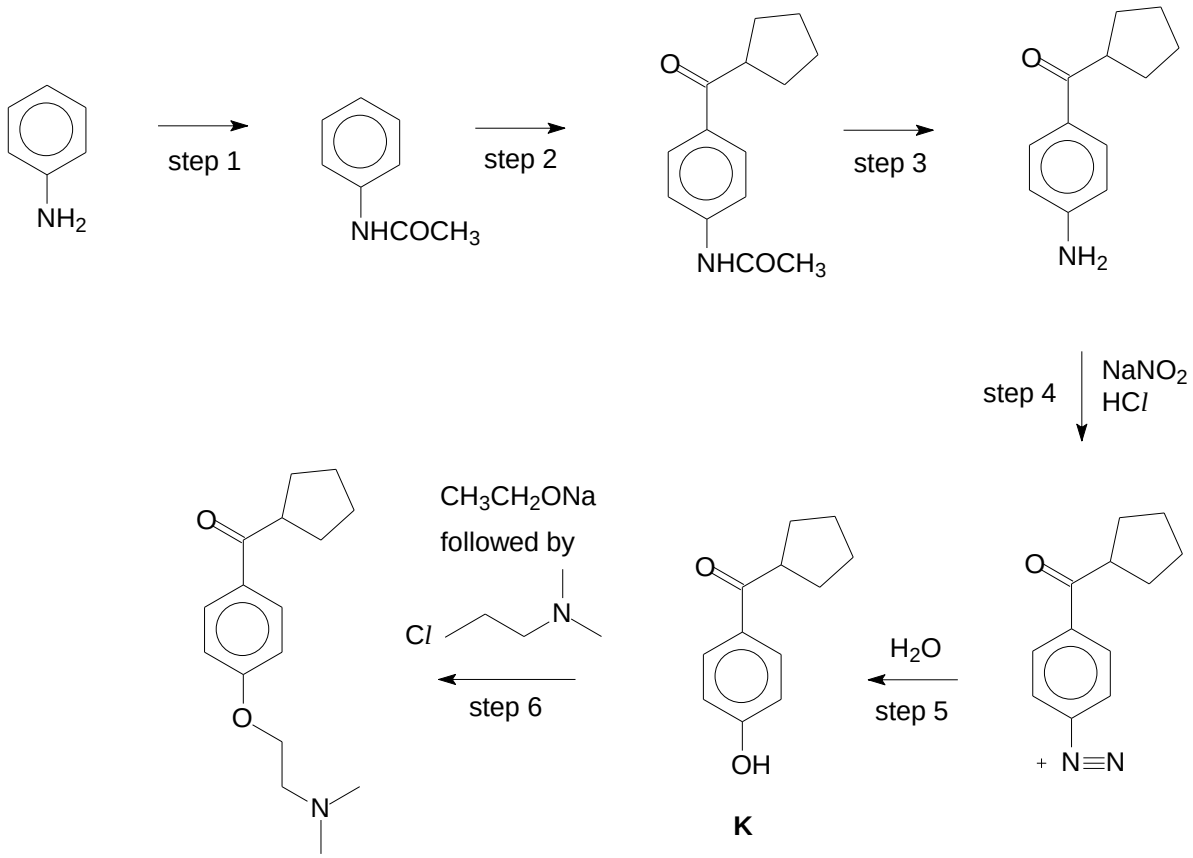


Fig. 3.1

(i) Suggest the reagents and conditions in steps 1 and 2. [2]

(ii) Explain why step 1 needs to be carried out **before** step 2. [1]

(iii) Explain why step 6 would **not** occur in the **absence** of sodium ethoxide, CH_3CH_2ONa. [1]

The reaction in step 6 is carried out in a suitable solvent and is found to be bimolecular.

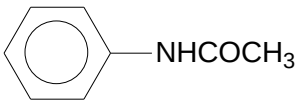
(iv) Describe the mechanism for this reaction. In your answer, you should show all charges, lone pairs and the movement of electrons using curly arrows.

You may use R to represent any part of the molecule that does not take part in the reaction. [3]

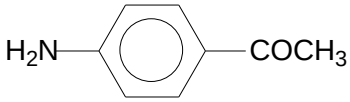
(v) Predict the effect on the rate of the reaction in step 6 if the volume of solvent used is doubled. [1]

(vi) Explain whether compound **K** or phenol undergoes electrophilic substitution more readily. [2]

(c) Both acetanilide and 4–aminoacetophenone are solids at room temperature and pressure.



acetanilide



4-aminoacetophenone

(i) Suggest and explain, with the aid of equations, the solubility of **each** of the compounds in HC*l*(aq). [3]

(ii) Using your answer to **(c)(i)**, outline how these two compounds could be separated from each other in a mixture and recovered in their original solid forms using chemicals normally found in the laboratory. [2]

[Total: 20]

Question 4 starts on the next page.

Section B

Answer **one** question from this section.

4 (a) Alkenes have many diverse industrial applications. They are used as starting materials for many chemicals.

One of the reactions of alkenes involves the addition of hydrogen to form alkanes. This process of hydrogenation of alkenes at room temperature requires the use of a catalyst. The Wilkinson's catalyst precursor, $RhCl(PPh)_3$ (where Ph represents a phenyl group), is one of them.

When the Wilkinson's catalyst precursor was added to propene dissolved in benzene with hydrogen gas being passed through the solution, the following dissociation took place:

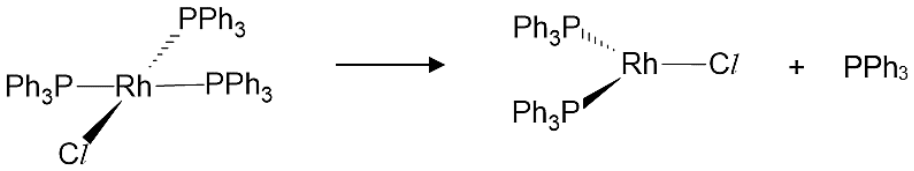


Fig. 4.1 shows the proposed mechanism for the hydrogenation of propene.

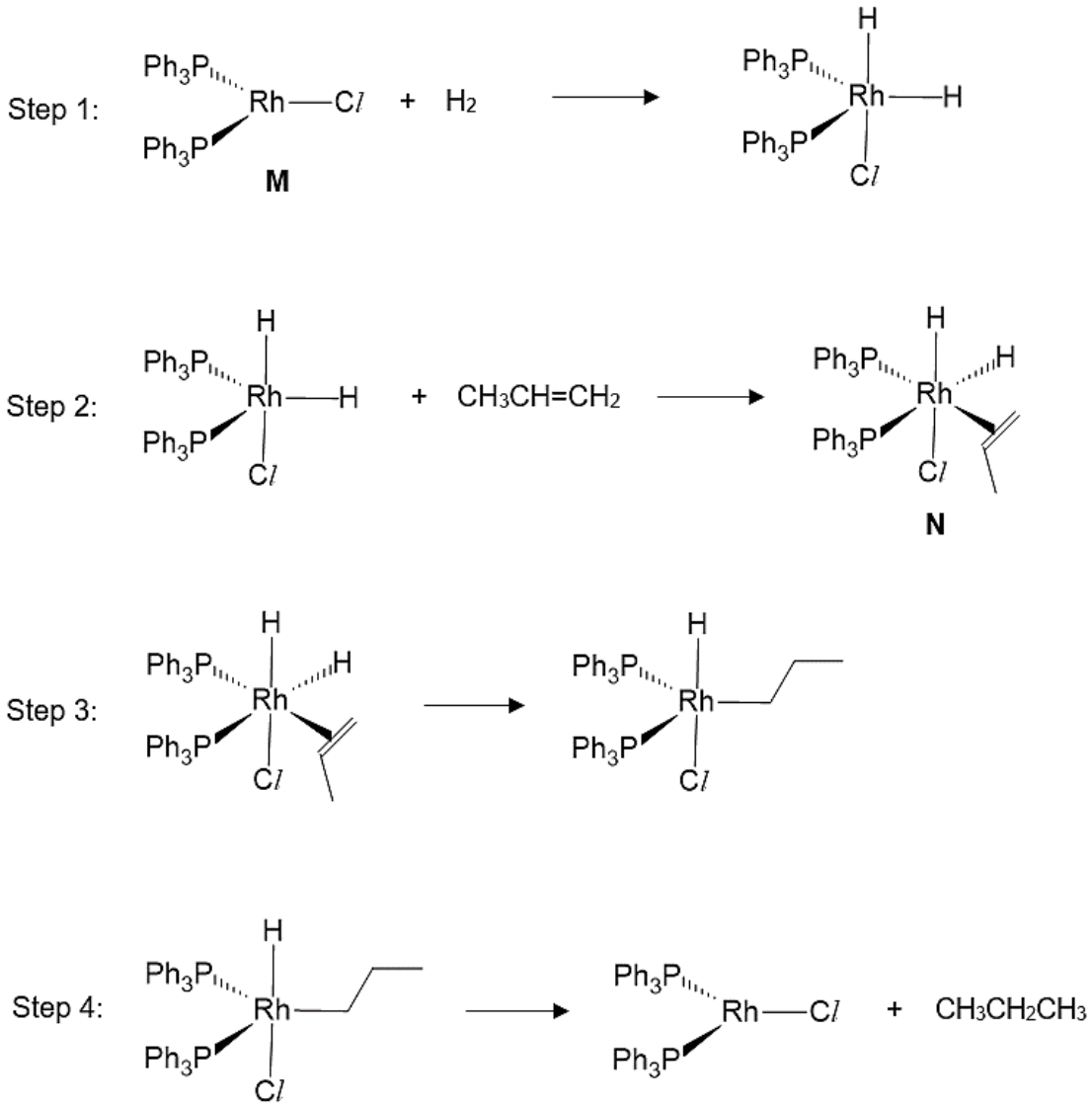


Fig. 4.1

(i) Triphenylphosphine, PPh_3, is a ligand in the Wilkinson's catalyst precursor, $RhCl(PPh_3)_3$.

Explain what is meant by the term *ligand*. [1]

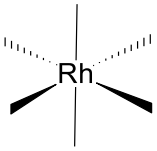
(ii) Determine the oxidation state of rhodium in $RhCl(PPh_3)_3$. [1]

(iii) The species in the equations shown in Fig. 4.1 have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason in each case, the roles of the species **M** and **N**. [2]

(iv) Rhodium can also form octahedral complexes with bidentate ligands like ethane–1,2–diamine, *en*.

Copy and complete the diagram below to suggest the structure for this complex.



(You may use  to represent *en.*) [1]

(b) Scientists have recently made vanadium into a useful catalyst for hydrogenation.

Vanadium was named after Vanadis, the Scandinavian goddess of beauty, because of the wide range of colours it exhibits in its complexes.

(i) Explain why a solution of $[V(H_2O)_6]^{2+}$ is violet whereas a solution of $[V(H_2O)_6]^{3+}$ is green. [1]

(ii) Nitric acid is an oxidising agent.

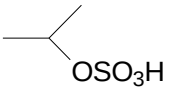
$$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O \qquad E^\ominus = +0.96\ V$$

Predict the products of, and write an equation for the reaction that occurs when nitric acid is added to a solution containing $V^{2+}(aq)$ ions. [2]

(c) Alkenes can be hydrated to form alcohols using various reagents. One such reagent is concentrated sulfuric acid.

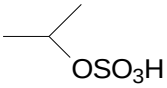
Alkenes react with concentrated sulfuric acid in the cold to produce alkyl hydrogensulfates. Addition of water with heating then produces the alcohol product.

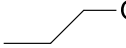
(i) Suggest a mechanism for the reaction of propene with concentrated sulfuric acid to produce the alkyl hydrogensulfate as shown.



isopropyl hydrogensulfate

Show the displayed structure of the electrophile, the structure of the intermediate and the movement of electron pairs by using curly arrows. [3]

(ii) Explain why 

is preferentially produced instead of 

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[1]

(d) Chromium(VI) is an important high oxidation state chromium and it occurs in two well–known anions, chromate(VI), CrO_4^{2-}, and dichromate(VI), $Cr_2O_7^{2-}$.

Acidified potassium dichromate(VI) is a common oxidising agent that can be used to oxidise sulfur dioxide.

(i) Construct a balanced equation for the reaction between acidified potassium dichromate(VI) and sulfur dioxide. [1]

(ii) Calculate the $E^{\ominus}_{cell}$ and hence, the standard Gibbs free energy change for this reaction. [2]

(iii) Both potassium dichromate(VI) and potassium manganate(VII) are useful oxidising agents in organic chemistry.

The scheme shown in Fig. 4.2 shows the different products formed when compound **P** is oxidised by potassium dichromate(VI) and potassium manganate(VII).

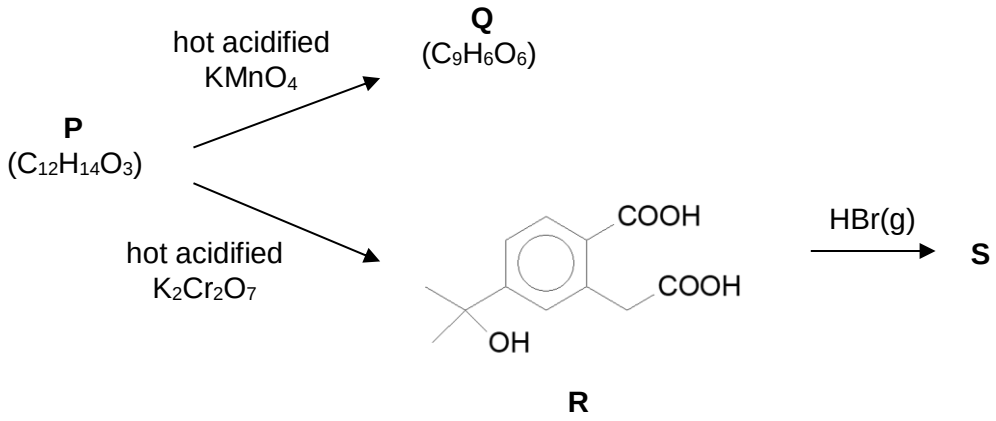
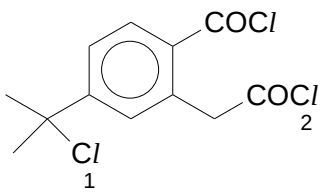


Fig. 4.2

Compound **P** does **not** react with an acid or a base at room temperature.

Suggest the structures of compounds **P**, **Q** and **S**. [3]

(iv) Compound **R** can also be converted to compound **T** which contains an acyl chloride and an alkyl chloride functional groups.



T

Explain the different reactivities of the two chlorine atoms, C*l* 1 and C*l* 2, in **T**. [2]

[Total: 20]

5 Metals like cobalt and nickel have been widely used since ancient times.

(a) In the presence of ligands, the d–orbitals in a transition metal ion are split into two levels.

Fig. 5.1 shows how the d–orbitals are split in an octahedral environment.

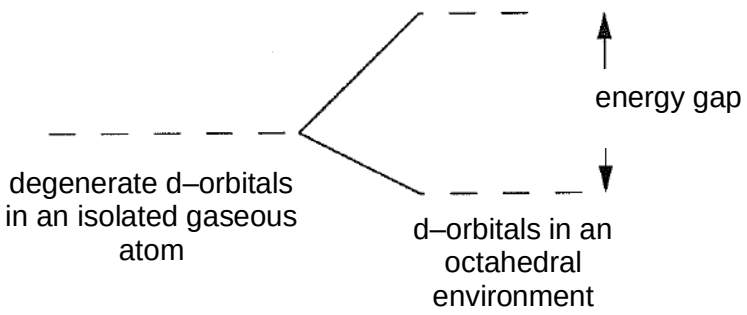


Fig. 5.1

In a 'high spin' state, the electrons occupy all the d–orbitals singly, before starting to pair up in the lower energy d–orbitals.

In a 'low spin' state, the lower energy d–orbitals are filled in first, by pairing up if necessary, before the higher energy d–orbitals are used.

(i) Use diagrams like the one above to show the electronic distribution of the cobalt(II) ion in a high spin state, and in a low spin state. Label your diagrams. [2]

(ii) Transition elements with unpaired 3d electrons are paramagnetic. In the presence of a magnetic field, these unpaired electrons align themselves in such a way that they are attracted to the field. The strength of paramagnetism shown in transition metal complexes depends on the total number of unpaired 3d electrons.

Using your answer from **(a)(i)**, explain which spin state of the cobalt(II) ion is relatively more paramagnetic. [1]

When air is bubbled through an aqueous solution containing $CoCl_2$, NH_4Cl and NH_3, and the resulting solution evaporated, crystals of a salt **Ω** can be isolated. **Ω**, which contains an octahedral cation, has the following composition by mass:

Co, 25.2%; N, 24.1%; H, 5.1%; Cl, 45.6%

(iii) Calculate the empirical formula of **Ω**. [1]

(iv) On adding an excess of $AgNO_3$(aq) to an aqueous solution containing 0.01 mol of **Ω**, 1.43 g of AgCl(s) is precipitated.

The cation in **Ω** can exist as two isomers. One of the isomers of the cation in **Ω** has **no** net dipole moment. Draw the structure of this cation. Show clearly the arrangement of the ligands and the oxidation number of the central metal ion in your diagram. [2]

(b) The nickel–cadmium (Ni–Cd) battery is a common rechargeable battery used in portable power tools and emergency lightings. It is made up of a cadmium electrode, Cd, and nickel oxyhydroxide electrode, NiO(OH), immersed in sodium hydroxide.

During discharge, cadmium hydroxide, $Cd(OH)_2$, is deposited at the cadmium electrode.

$$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$$

Nickel(II) hydroxide, $Ni(OH)_2$, is formed at the nickel oxyhydroxide electrode.

(i) Construct a half–equation for the reaction that occurs at the cathode during discharge and hence, write the equation for the overall reaction during discharge. [2]

(ii) When a Ni–Cd battery is recharged, $Cd(OH)_2$ is converted back to Cd. Given that the charging process is 86% efficient, how many hours does it take to restore 5.5 g of Cd metal using a current of 2.0 A? [3]

(c) Reduction reactions involving organic compounds are commonly carried out using reducing agents like hydrogen gas with nickel metal catalyst and lithium aluminium hydride, $LiAlH_4$.

Compound **F** is reacted with both as shown in Fig. 5.2.

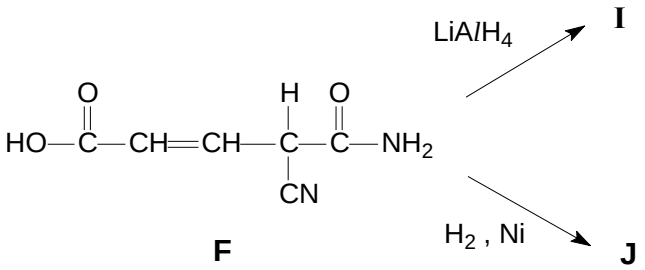


Fig. 5.2

Draw the structures of products **I** and **J**. [2]

(d) Compound **W**, $C_9H_9NO_4$, rotates plane–polarised light. **W** reacts with tin and concentrated hydrochloric acid, followed by careful neutralisation to give compound **X**, $C_9H_{11}NO_2$.

X liberates carbon dioxide with sodium hydrogencarbonate and decolourises aqueous bromine to give **Y**, $C_9H_9NO_2Br_2$. When **X** reacts with PCl_5, compound **Z**, C_9H_9NO, is formed.

Deduce the structures of **W**, **X**, **Y** and **Z**, stating clearly your reasoning. [7]

[Total: 20]

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