1 The Periodic Table shows many interesting and recurring trends.

(a) The variation of 1st ionisation energies across Period 4 is similar to that of Period 3. Table 1.1 shows the 1st ionisation energies of six consecutive elements in Period 4.

Table 1.1

element	Ga	Ge	As	Se	Br	Kr
1st ionisation energy / kJ mol^{-1}	580	760	950		1140	1350

(i) Explain why the 1st ionisation energies show a general increase from gallium to krypton.

.....

.....

.....

.....

.....

.....

..... [2]

(ii) Using your knowledge of the variations, complete Table 1.1 with a suggested value for the first ionisation of selenium. [1]

(b) Electrical conductivity is measured in Siemens per meter, S m^{-1}, where a higher value represents higher electrical conductivity. Calcium is a Group 2 metal and has an electrical conductivity of 2.9×10^7 S m^{-1} while copper is a transition metal and electrical conductivity of 5.9×10^7 S m^{-1}.

(i) State the full electronic configuration of copper.

..... [1]

(ii) Explain the difference in electrical conductivity between calcium and copper.

.....

.....

.....

..... [2]

(c) Other transition metals such as nickel and platinum are sometimes found in copper ores. To obtain pure copper, the ore was made the anode of an electrolysis cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.

Explain, with reference to relevant $E^{\ominus}$ values from the *Data Booklet* what happens to the platinum impurities during this purification procedure. You should also use the following information:

$$Pt^{2+} + 2e \rightleftharpoons Pt \qquad E^{\ominus} = +1.20\ V$$

.....

.....

.....

.....

.....

.....

..... [2]

(d) Propene undergoes reaction with Br_2 to form 1,2-dibromopropane. This reaction mechanism features a carbocation intermediate.

(i) Draw a labelled diagram to show orbital overlap in the C=C double bond of propene.

[2]

(ii) Name and draw the mechanism of the reaction between propene and Br_2 to form 1,2-dibromopropane.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

[3]

(iii) Hence, draw the dot-and-cross diagram for the carbocation intermediate in the mechanism drawn in **(ii)**.

State the shape and bond angle at the positively charged carbon in the carbocation intermediate.

shape:.....

bond angle: ..... [3]

[Total: 16]

2 Nitrosyl fluoride, NO_2F, is a colourless gas which is used as a nitrating agent in organic synthesis.

(a) NO_2F is formed from the reaction between nitrogen dioxide and fluorine according to the following reaction.

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

The reaction kinetics for this reaction was studied. The experimental rate equation for this reaction can be expressed as rate = k $[NO_2]^m[F_2]^n$, where m and n are non-zero constants.

The concentration of NO_2 gas was determined at regular time intervals as the reaction progressed.

In this experiment, the concentration of NO_2 and F_2 used were at 0.080 mol dm^{-3} and 1.20 mol dm^{-3} respectively. The results obtained are shown in Fig. 2.1.

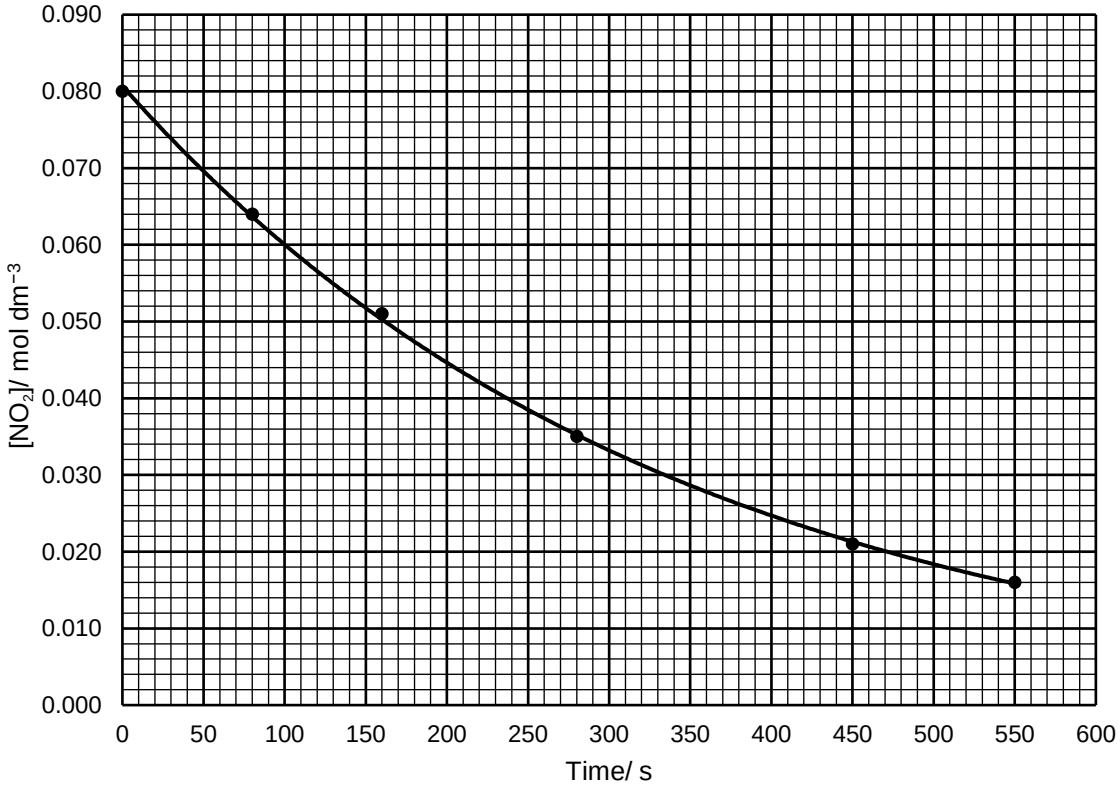
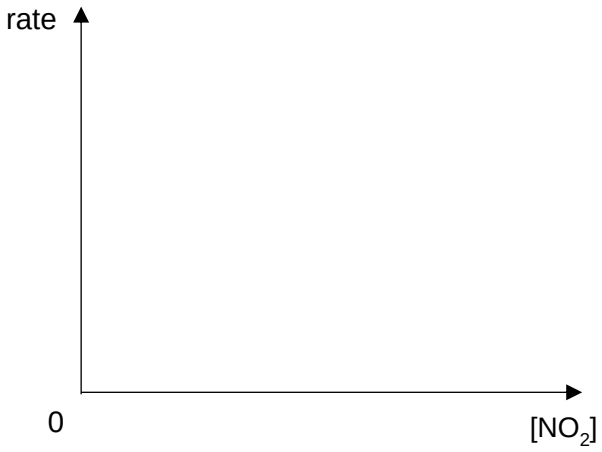


Fig. 2.1

(i) Using Fig. 2.1, determine the value of m. Show all your working and any construction lines clearly on your graph.

[2]

(ii) Hence, sketch on the given axes, a graph to show how the rate of reaction changes with concentration of NO_2.



[1]

(iii) Determine the initial rate using the graph in Fig 2.1.

[1]

(iv) Hence, or otherwise, calculate the value of the rate constant and its units, given that the value of n = 1.

[2]

(v) The experiment was repeated using a larger concentration of 1.80 mol dm^{-3} for F_2 instead. Determine the half-life of NO_2 in this experiment.

[1]

(b) NO_2 is among the exhaust gases produced by petrol-driven cars. Catalytic converters are fitted in petrol-driven cars to reduce the emission of these harmful NO and NO_2 gases by converting them to less harmful products such as H_2O and N_2. Platinum is used as a catalyst inside the catalytic converter.

(i) Name the type of catalysis that occurs in the catalytic converter. Outline the mode of action of the platinum catalyst in the reaction.

.....

.....

.....

.....

.....

..... [3]

(ii) Carbon monoxide is another harmful exhaust gas produced in car exhaust that leads to poisoning for humans because it reduces the capacity of haemoglobin to transport oxygen around the body.

Explain how carbon monoxide prevents oxygen from being transported around the body.

.....

.....

..... [1]

(c) Car airbags is an important safety feature built in cars to minimise injury during collision. When the airbag is being activated, N_2 gas will be produced within milliseconds to inflate the airbag.

(i) Calculate the pressure in the airbag of the front passenger with a volume of 70.5 dm^3 when inflated at 25 °C with 135 g of N_2.

[1]

(ii) The plots of *pV*/R*T* against p for one mole of an ideal gas and one mole of carbon dioxide at 25 °C are given in Fig. 2.2.

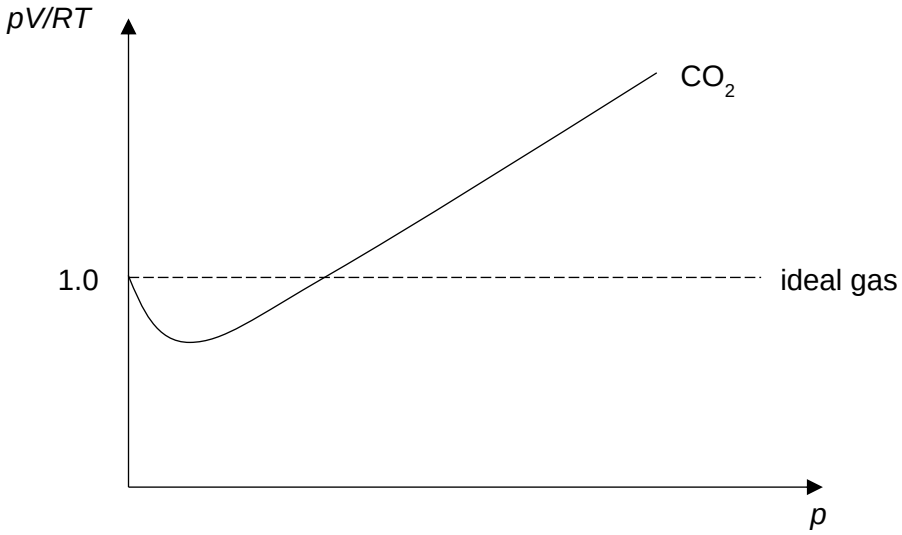


Fig. 2.2

On the axes above, sketch a graph to illustrate the behaviour of one mole of NO_2 at 25 °C. Explain your answer.

.....

.....

.....

.....[2]

[Total: 14]

3 **(a)** The aldol reaction is a useful organic reaction that involves the formation of a C–C bond between the α-carbon of a carbonyl compound with the carbonyl carbon of another carbonyl compound. The product is known as an aldol compound.

For instance, the aldol reaction between ethanal molecules involves 3 steps as shown in Fig. 3.1.

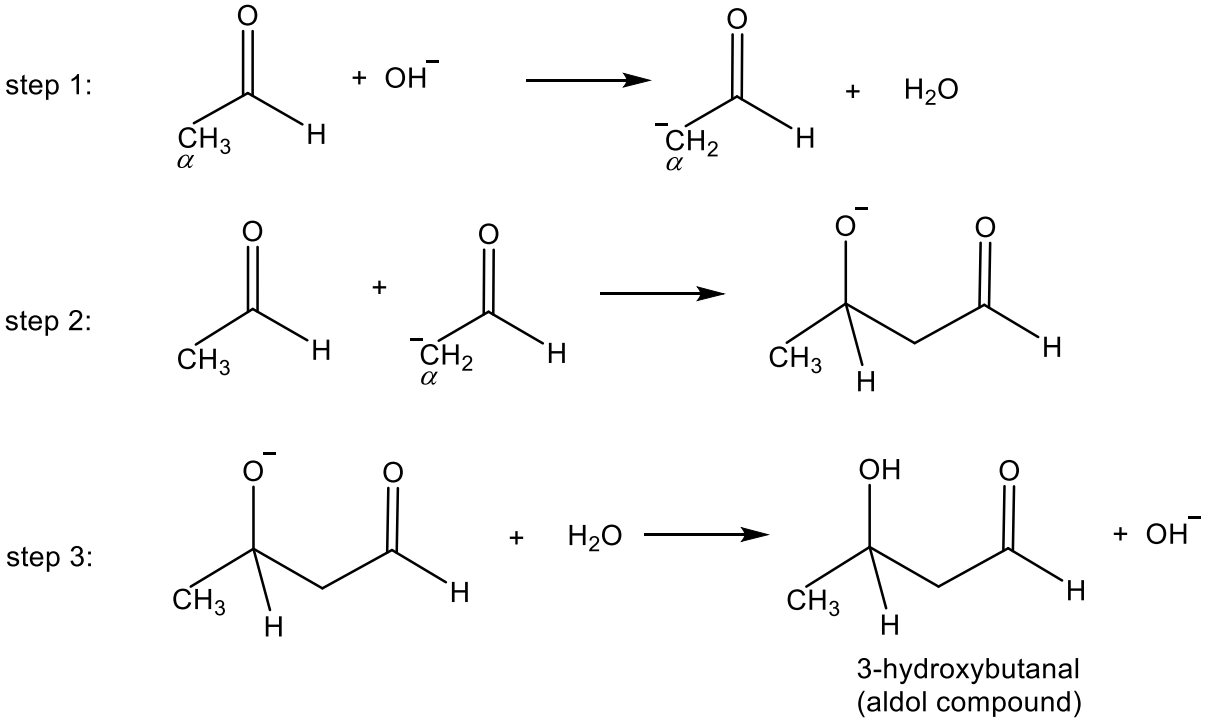


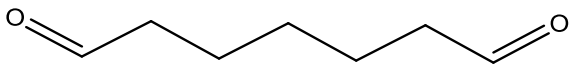
Fig. 3.1

(i) State the type of reaction for steps 2 and 3 given above.

step 2: .....

step 3:..... [2]

(ii) Heptanedial undergoes aldol reaction to form a compound with the same number of carbon atoms.



heptanedial

Suggest the structure of the product formed.

[1]

(iii) Hydrogen atoms in alkyl groups do not deprotonate easily. However, in step 1, the α-carbon in the carbonyl compound is deprotonated. Suggest a reason to explain why this deprotonation occurs. Use the concepts of electronic effects or delocalisation in your answers.

.....

..... [1]

(b) Succinic anhydrides are primarily used in the production of various polymers and resins.

Fig. 3.2 shows a possible reaction scheme to form succinic anhydrides.

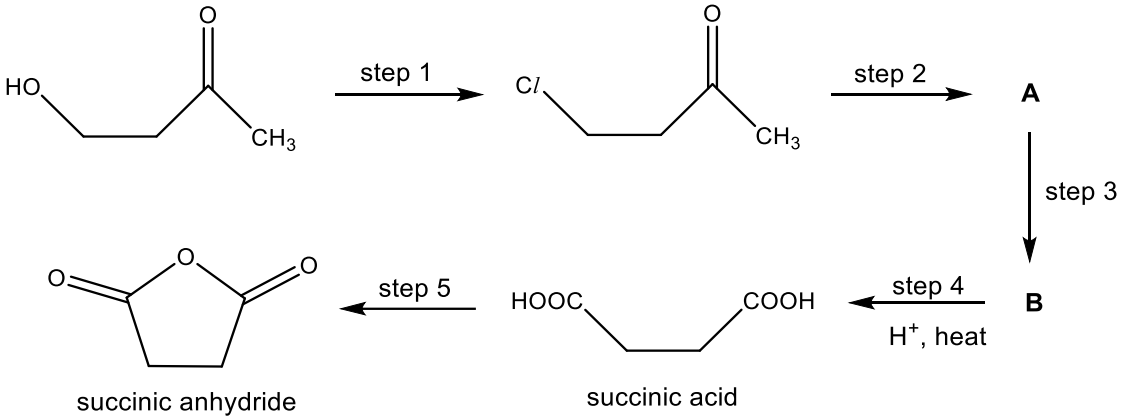


Fig. 3.2

(i) State the reagents and conditions for step 2 and 3.

step 2: .....

step 3: ..... [2]

(ii) Draw the structures for compound **A** and **B**.

A	**B**

[2]

(iii) Suggest the type of reaction occurring in step 5.

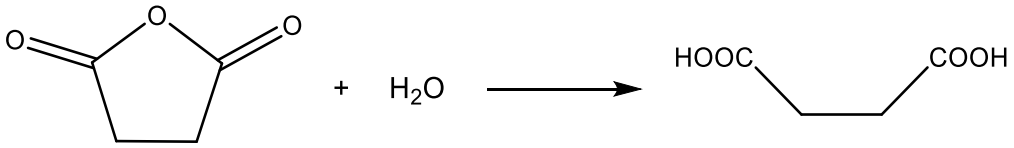
.....[1]

(iv) Propose a chemical test used to confirm that succinic acid has been completely reacted in step 5. State your expected observation.

.....

..... [2]

(v) Succinic anhydride reacts with water in a 1:1 ratio as shown.



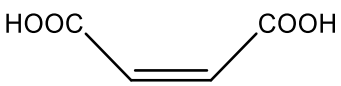
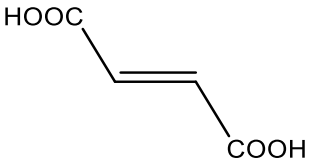
succinic anhydride

succinic acid

With reference to the above reaction, suggest the structure of the product when succinic anhydride reacts with ethanol in a 1:1 ratio.

[1]

(vi) Maleic acid and fumaric acid are unsaturated forms of succinic acid. The boiling points of both compounds are given below.

compound	boiling point / °C
 maleic acid	135
 fumaric acid	280

Account for the difference in boiling points of the two compounds.

.....

.....

.....

.....

.....

.....

..... [2]

(c) Other than succinic anhydrides, alcohols and acids are commonly used as industrial solvents in cleaning products and disinfectants. Explain why ethanoic acid is a stronger acid compared to ethanol.

.....

.....

.....

.....

.....

..... [2]

[Total: 16]

4 **(a)** When a beam of particles containing protons and electrons approach an electric field at the same speed, the particles are deflected as shown in Fig. 4.1.

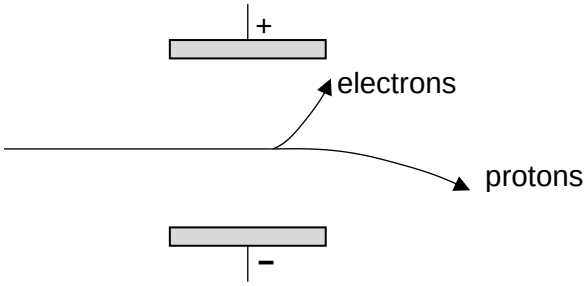


Fig. 4.1

(i) Explain the differences in the behaviour of the electrons and protons in the electric field. Account for both direction and magnitude of deflection.

.....

.....

.....

.....

..... [2]

(ii) If the protons are deflected by an angle of +24.0°, predict the angle of deflection of a beam containing $^{32}S^{2-}$ ions travelling at the same speed in the same electric field. Show your working clearly.

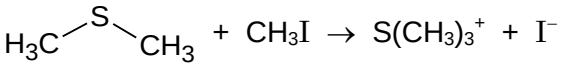
[1]

(b) Sulfur forms compounds that can behave as either Lewis acids or bases.

(i) Explain what is meant by a Lewis acid.

..... [1]

(ii) Deduce whether the sulfur containing compound in the following reaction behaves as a Lewis acid or base.



.....

.....

..... [1]

(c) When mixed with water at 25 °C, hydrogen sulfide (H_2S) dissociates in two steps:

equation 1 $H_2S + H_2O \rightleftharpoons HS^- + H_3O^+$ $K_{a_1} = 8.9 \times 10^{-8}$ mol dm^{-3}

equation 2 $HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+$ $K_{a_2} = 1.0 \times 10^{-15}$ mol dm^{-3}

(i) Explain why the value of K_{a_2} is much smaller than K_{a_1}.

.....

..... [1]

(ii) Write the expression for the acid dissociation constant, K_{a_1}.

[1]

(iii) Hence show, by calculating the $[HS^-]/[H_2S]$ ratio, that an aqueous H_2S solution which has pH 3.16 contains H_2S as the predominant sulfur-containing species.

[You may disregard the effect of K_{a_2}.]

[2]

(iv) A solution containing $H_2S(aq)$ and $HS^-(aq)$ can act as a buffer solution, resisting changes in pH when small amounts of acid or alkali are added.

Write two equations to show how this mixture acts as a buffer.

.....

..... [2]

(v) A 1.0 dm^3 solution containing 0.50 mol each of $H_2S(aq)$ and $HS^-(aq)$ was prepared. Calculate the increase in pH when 0.020 mol of solid sodium hydroxide was added (assume no change in volume).

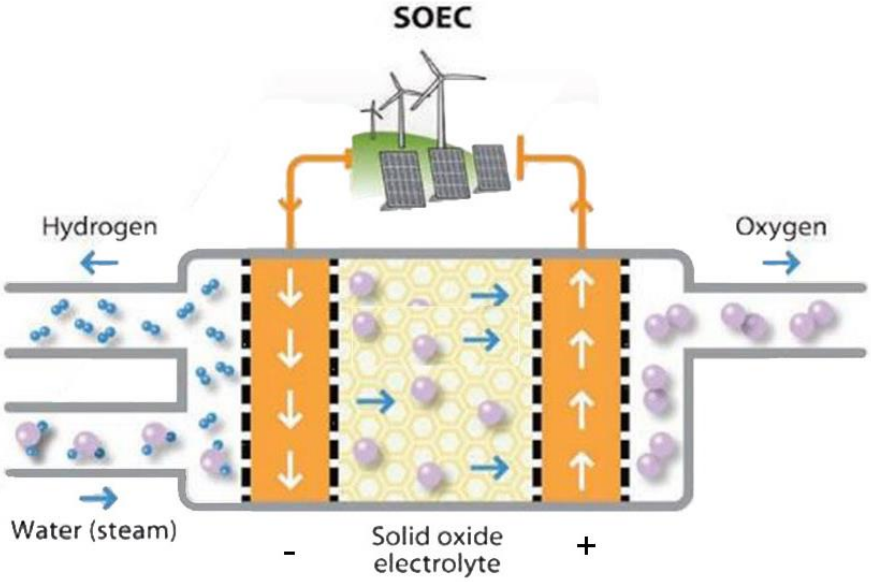
[1]

[Total: 12]

5 **(a)** Green hydrogen fuel is a promising renewable energy source and is produced through the process of electrolysis, using renewable electricity to split water into hydrogen and oxygen. The cell used is known as the Solid Oxide Electrolysis Cell (SOEC) and it offers high efficiency and scalability.

$$2H_2O(g) \longrightarrow O_2(g) + 2H_2(g) \qquad \Delta H = +241.8 \text{ kJ mol}^{-1}$$

SOEC, as shown in Fig. 5.1 below, utilises a solid oxide electrolyte such as cerium oxide (CeO_2) and nickel-based electrodes as key components in the electrolysis process. Steam goes into the cathode and produces hydrogen gas, H_2, and oxide ions, O^{2-}. The oxide ions migrate through the electrolyte to the anode, where they release electrons to become oxygen gas. Typically, the operating temperatures for SOECs are from 800 to 1,000 °C and current at 1.5 A cm^{-2} of cross section area.



Modified from: https://www.researchgate.net/figure/Alkaline-Electrolyser-Cell-AEC-working-principle-Reprinted-from-ref-9-with_fig1_354214398

Fig. 5.1

(i) Write the equation for the reaction that occurs at the cathode and the anode respectively.

cathode: .....

anode: ..... [2]

(ii) Given that the total cross section area of the anode is 1500 cm^2, calculate the mass of H_2, in kg, generated in one day of operation.

[2]

(iii) Propose an explanation, in terms of thermodynamics, why high temperature is necessary in this reaction.

.....

.....

.....

.....

..... [2]

(iv) Suggest a physical property of cerium oxide that makes it suitable to be used as the solid electrolyte in SOEC.

.....

..... [1]

(b) Fig 5.2 shows the reactions of nickel and its compounds.

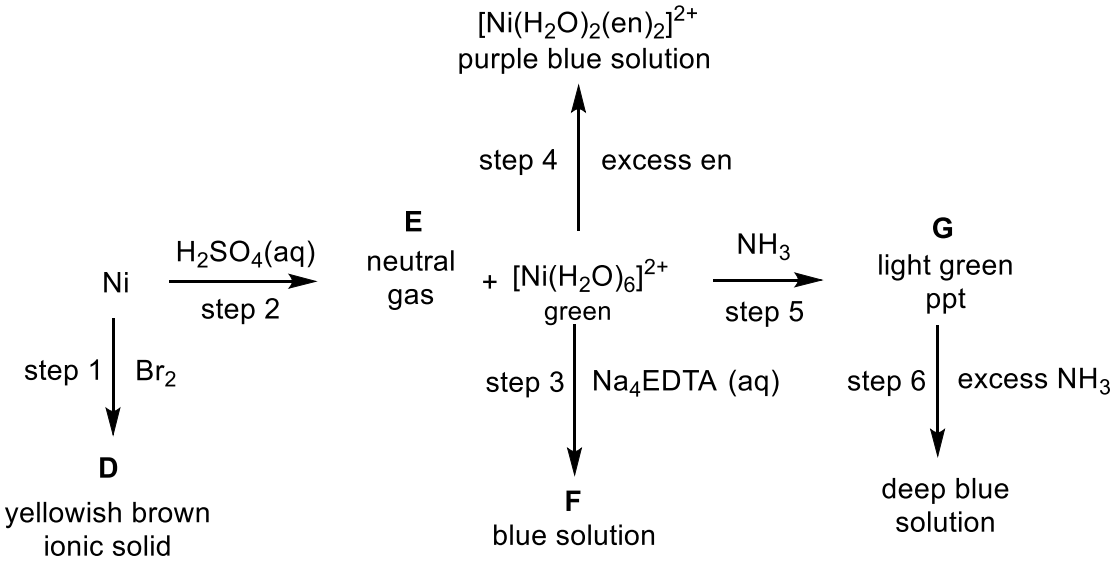


Fig 5.2

(i) Identify compounds **E** and **G**.

compound **E**:.....

compound **G**: ..... [2]

(ii) Write an ionic equation for the formation of **F** from $[Ni(H_2O)_6]^{2+}$.

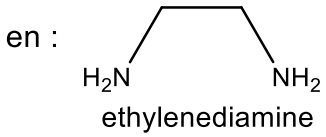
.....[1]

(iii) State the type of reaction that occurred in steps 1 and 6.

step 1: .....

step 6: ..... [2]

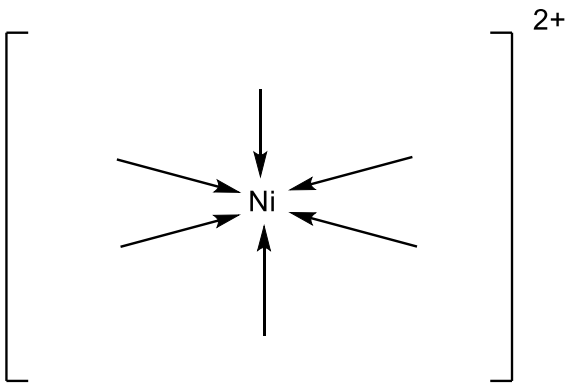
(iv) The "en" refers to ethylenediamine, which is a bidentate ligand as it has two nitrogen atoms that can form coordination bonds with a metal ion.



ethylenediamine

$[Ni(H_2O)_6]^{2+}$ reacts with excess ethylenediamine to form a purple-blue solution of $[Ni(H_2O)_2(en)_2]^{2}$.

$[Ni(H_2O)_2(en)_2]^{2+}$ can exist in both cis and trans isomeric forms due to the placement of the ligands around nickel cation. Given that the cis form is non-symmetrical, suggest a 3-dimensional structure of cis-$[Ni(H_2O)_2(en)_2]^{2+}$.



[1]

(v) Ni^{2+} undergoes a reaction with an excess of chloride ions to yield $[NiCl_4]^{2-}$ instead of $[NiCl_6]^{4-}$. Suggest a reason.

.....

.....

..... [1]

(vi) Ethylenediamine is a versatile organic compound used as a starting material in organic synthesis due to its ability to form stable complexes and its amine properties.

Fig. 5.3 illustrates a synthesis pathway that utilises ethylenediamine as a starting material to produce compound **Z** through a series of chemical transformations.

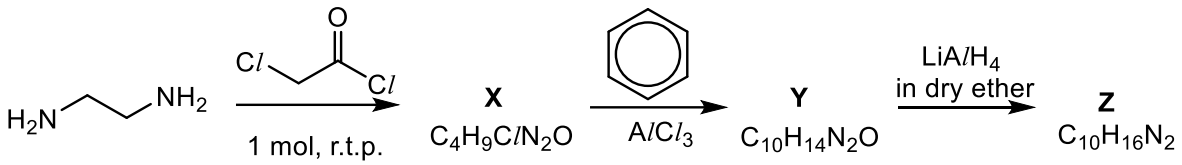


Fig. 5.3

Draw the structure of the compounds **X**, **Y** and **Z** in the spaces provided.

X

Y

Z

[3]

[Total: 17]