Section A

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

1(a) Samples of three different oxides were added to water separately.

(i) State the Arrhenius theory of acids and bases. [1]

(ii) The pH value of the solution formed when sodium oxide is shaken with water is greater than the pH value of the solution formed when magnesium oxide is shaken with water. The pH of the solution formed when sulfur trioxide is shaken with water is less than both of these solutions.

Explain these observations using the Arrhenius theory. Write equations for all the reactions described. [3]

(b) 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. At the end of the reaction, 60 cm^3 of nitrogen gas was collected. The experiment results are plotted in Fig. 1.1 below.

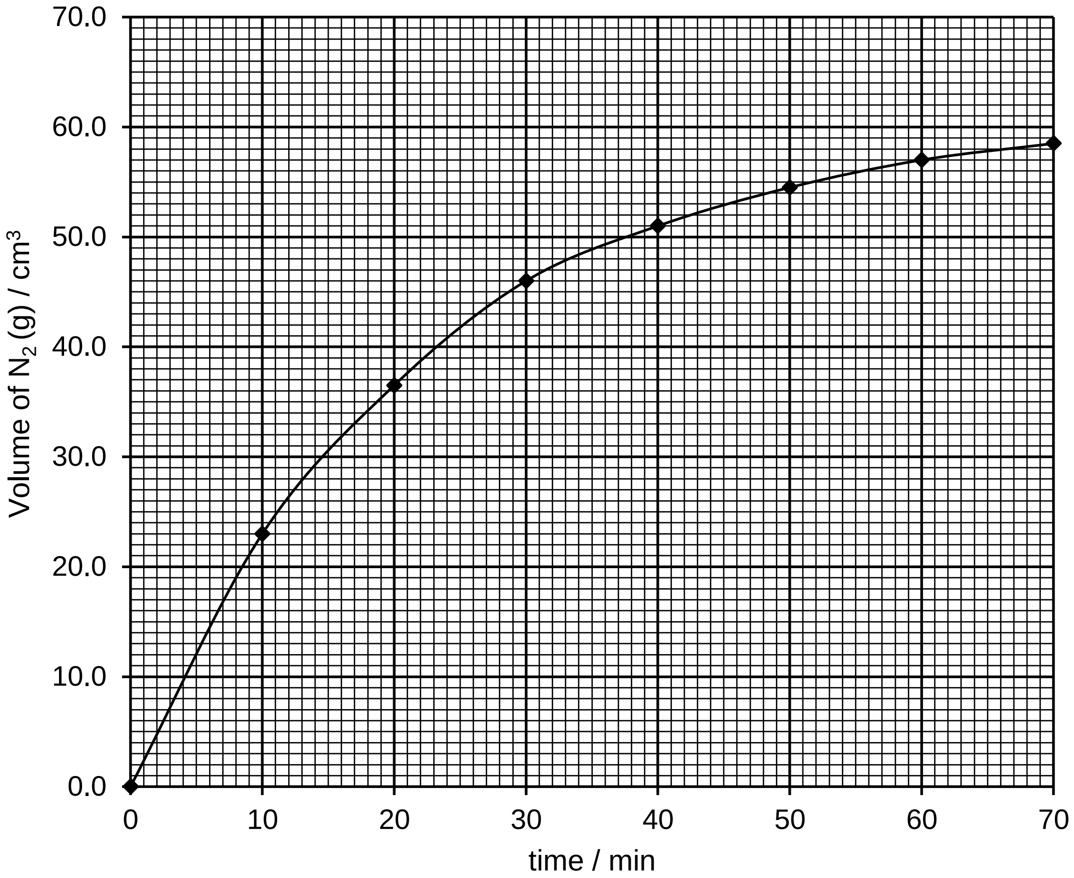

Fig. 1.1

(i) Use Fig. 1.1 and the information given to show that the order of reaction with respect to $[CH_2N_2]$ is 1. [2]

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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 1.1.

Table 1.1

Experiment	$[CH_2N_2]$ / mol dm^{-3}	pH	Relative rate
1	1.00×10^{-3}	1.00	1
2	4.00×10^{-3}	1.30	2

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

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

[Turn over

(c) Pure magnesium needed for making alloys can be obtained by the electrolysis of molten magnesium chloride as shown in Fig. 1.2.

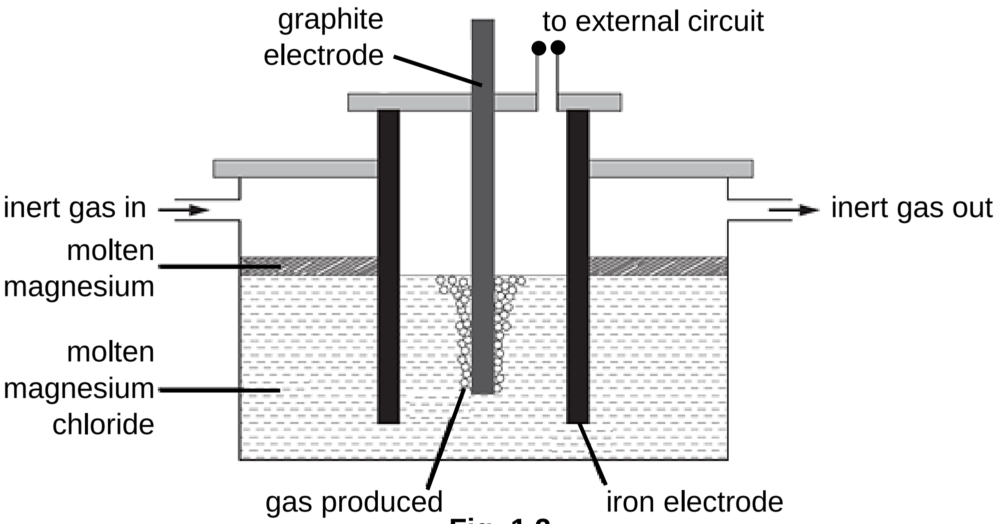

Fig. 1.2

(i) Write the half-equations, including state symbols, for the reactions occurring at the graphite and iron electrodes. Label your equations clearly to indicate the reaction occurring at the graphite and iron electrode respectively. [2]

(ii) Draw and label the direction of electron flow in the cell on Fig. 1.2. [1]

(iii) Calculate the mass of magnesium obtained if a current of 3.00 A is supplied for 10.0 h. [2]

(iv) A gas is continuously passed over the molten magnesium in the electrolytic cell to provide an inert environment. Suggest a gas that can be used for this. [1]

(v) Molten magnesium chloride in the cell is being replaced with aqueous magnesium chloride. Using relevant data from the *Data Booklet*, state and explain the reactions taking place at both electrodes when this change is made. [2]

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[Total: 17]

[Turn over

2 Chromium is a steely-grey, hard and dense transition element. Its name came from the Greek word 'chrȭma', which means colour, because many of its compounds are coloured.

(a) Define *transition element*. [1]

(b) Transition elements have significantly higher density and melting point compared to main group metals.

(i) Briefly explain why transition elements exhibit higher density. [1]

(ii) Explain why the melting point of chromium is significantly higher than the melting point of calcium. [1]

(c) Anhydrous chromium(III) chloride may be prepared by the chlorination of chromium metal.

$$Cr(s) + \frac{3}{2}Cl_2(g) \rightarrow CrCl_3(s)$$

The thermodynamic data at 298 K are given in the table below.

Substance	$\Delta S_f^\ominus$ / J mol^{-1} K^{-1}	$\Delta H_f^\ominus$ / kJ mol^{-1}
$CrCl_3$	–236.0	–556.6

(i) Explain the significance of the sign of $\Delta S_f^\ominus$. [1]

(ii) Using the information above, calculate $\Delta G^\ominus$ for the formation of $CrCl_3$(s). [1]

(iii) Using your answer from **(c)(ii),** suggest whether the ratio of [product] / [reactants] at equilibrium for the formation of $CrCl_3$ at 298 K will be less than, equal to or greater than 1. Give a reason for your answer. [1]

(iv) Comment on the effect of increasing temperature on the spontaneity of the reaction. [2]

(d) The following sequence of reactions in Fig. 2.1 involves chromium.

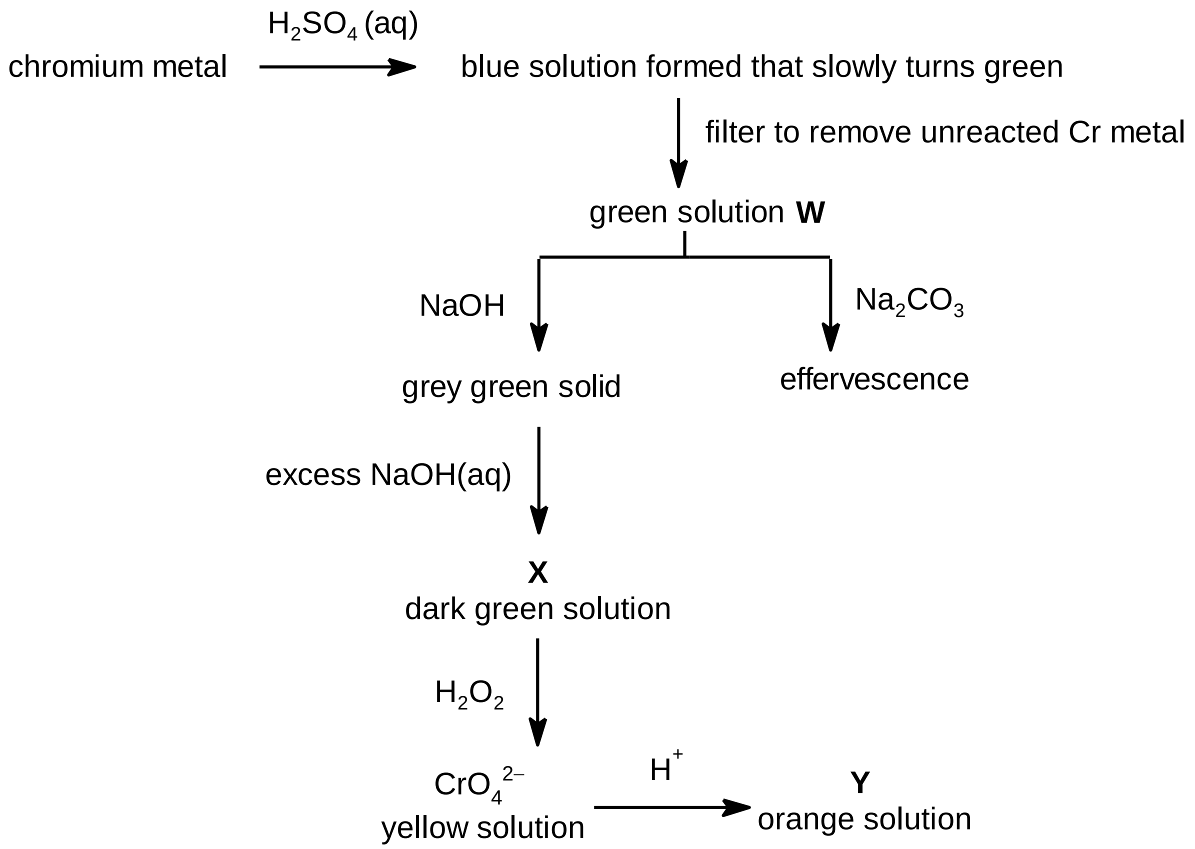


Fig. 2.1

(i) Using relevant $E^\ominus$ values from the *Data Booklet*, explain why the blue solution slowly turns green in air. [2]

(ii) State the type of reaction and write a balanced equation to account for the observation when a small amount of aqueous sodium hydroxide was added to a solution **W**. [2]

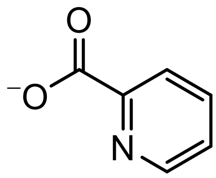
(iii) Suggest the formula of the chromium containing species in **X** and **Y**. [2]

(iv) State, with reasoning, the role of hydrogen peroxide in Fig. 2.1. [1]

[Turn over

(e) Chromium(III) picolinate is a chemical compound with the formula $Cr(C_5H_4N(CO_2))_3$, commonly abbreviated as $CrPic_3$. It is sold as a nutritional supplement to treat type-2 diabetes and promote weight loss.

The structure of the bidentate ligand picolinate is shown below.



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Draw the structure of chromium(III) picolinate. [1]

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(f) Aluminium hydroxide, $Al(OH)_3$, was used as white pigment for paints. $Al(OH)_3$ has a solubility of 2.90×10^{-9} mol dm^{-3} in pure water.

(i) Write the expression for the solubility product, K_{sp}, of $Al(OH)_3$ and calculate its solubility product in pure water. [3]

(ii) How would you expect the solubility of $Al(OH)_3$ in excess NaOH(aq) to compare with that in pure water? Briefly explain your answer with an equation with state symbols. [2]

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[Total: 21]

[Turn over

3(a) Outline the mechanism of the reaction between hydrogen cyanide, HCN and propanal, CH_3CH_2CHO, to form 2-hydroxybutanenitrile, $CH_3CH_2CH(OH)CN$.

Include all the necessary charges, dipoles, lone pairs and curly arrows. [3]

(b) Compound **P** is an isomer of propanal and it forms a yellow precipitate when reacted with alkaline aqueous iodine.

P can be converted to compound **S** as shown in Fig. 3.1.

$$\mathbf{P} \xrightarrow{\text{I}} \mathbf{Q} \xrightarrow{\text{II}} \mathbf{R} \xrightarrow{\text{III}} (CH_3)_2C(OH)CO_2CH_2CH_3$$

compound **S**

Fig. 3.1

(i) Suggest structures for the compounds **P**, **Q** and **R**. [3]

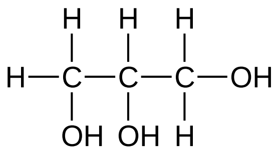
(ii) Suggest reagents and conditions for each of the steps **I**, **II** and **III**. [3]

(iii) Suggest a suitable carbonyl compound which can be used to form $CH_3CH_2CH_2CH(OH)CO_2CH_2CH_3$ using the three-step synthesis shown in Fig. 3.1. [1]

[Turn over

(c) Compound **T** is another isomer of propanal and it contains two different functional groups.

T reacts with cold alkaline $KMnO_4$ to form propane-1,2,3-triol.



propane-1,2,3-triol

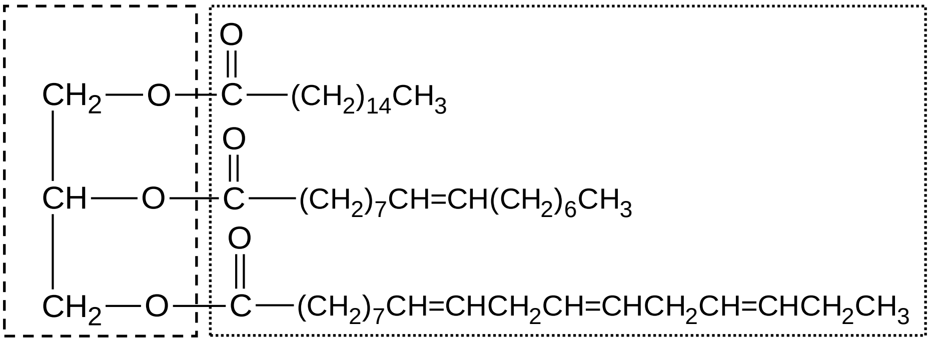
(i) Give the **displayed** formula of **T**. [1]

(ii) Draw the structure of the compound **U** formed when propane-1,2,3-triol reacts with hot acidified $K_2Cr_2O_7$. [1]

(iii) How would you expect the acidity of compound **U** to compare with that of propane-1,2,3-triol? Briefly explain your answer. [2]

(d) Triglycerides are triesters formed from a glycerol (propane-1,2,3-triol) and three fatty acid (carboxylic acid) molecules.

A natural triglyceride with three different fatty acid chains is shown below.



part from glycerol   part from fatty acid molecules

A particular triglyceride, **J**, in castor oil produces glycerol (1 mol) and compound **K**, $C_{18}H_{34}O_3$ (3 mol) when heated with dilute sulfuric acid.

K decolourises bromine in an organic solvent. On gentle oxidation, **K** gives **L**, $C_{18}H_{32}O_3$, which gives an orange precipitate with 2,4-dinitrophenylhydrazine.

Warming **K** with concentrated sulfuric acid gives a compound **M**, $C_{18}H_{32}O_2$. On treating **M** with hot concentrated $KMnO_4$, $CH_3(CH_2)_5COOH$, $HO_2C(CH_2)_7CO_2H$ and CO_2 are produced.

Suggest structures for **K, M** and **J**. For each reaction, state the type of reaction described and the functional group present in each compound.. [8]

[Turn over

[Total: 22]

Section B

Answer **one** question from this section.

4(a) Carbon dioxide is the most significant greenhouse gas in Earth's atmosphere. The volume of 0.30 mol of carbon dioxide gas was measured at a temperature of 25 °C when various pressures were applied. The following results were obtained.

Table 4.1

pressure, *p* / atm	volume, V / dm^3	pressure x volume, *p*V / atm dm^3
5.00	1.436	7.18
10.0	0.7015	7.02
15.0	0.4566	6.85

(i) Calculate the volume, in dm^3, of 0.30 mol of an ideal gas at a temperature of 25 °C and at a pressure of 12.0 atm. [1]

(ii) Based on the data given in Table 4.1, estimate the value of *p*V when *p* = 12.0 atm. Hence, calculate the value of V when *p* = 12.0 atm. [1]

(iii) Compare the values of V you have obtained in **(a)(i)** and **(a)(ii)**. Account for the difference in the values by taking into consideration the properties of CO_2 molecules. [1]

[Turn over

(b) Dry ice is the solid form of carbon dioxide. Dry ice sublimes readily and is commonly used to preserve ice cream where mechanical cooling is unavailable.

Table 4.2 shows the standard enthalpy changes of sublimation for several substances. Enthalpy change of sublimation is the energy required to change one mole of a substance from solid state to gaseous state.

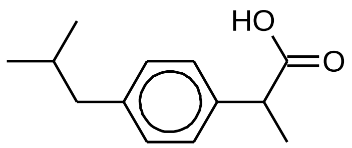
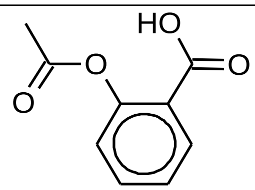
Table 4.2

	$\Delta H^{\ominus}_{sub}$ / kJ mol^{-1}
standard enthalpy change of sublimation of C(s)	+715
standard enthalpy change of sublimation of Si(s)	+456
standard enthalpy change of sublimation of CO_2(s)	+25.0

Explain the relative standard enthalpy change of sublimation for these three substances. [2]

(c) Ibuprofen and aspirin are nonsteroidal anti-inflammatory drugs that are commonly used as painkiller and for fever reduction. Some data of ibuprofen and aspirin are shown below in Table 4.3.

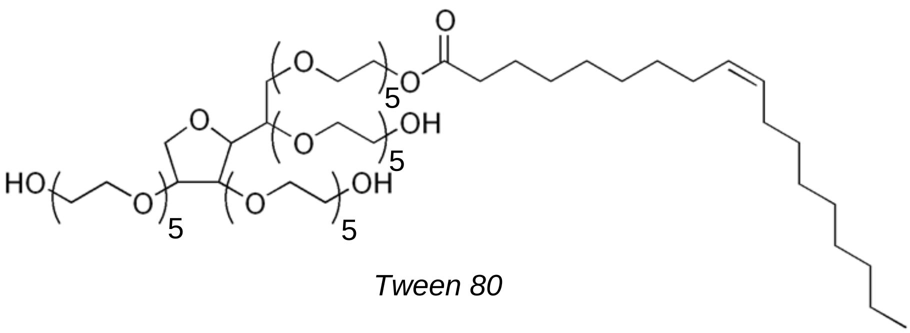
Table 4.3

	ibuprofen	aspirin
Structural formula		
Molecular formula	$C_{13}H_{18}O_2$	$C_9H_8O_4$
pK_a value	4.45	3.49

(i) Ibuprofen exhibits stereoisomerism. Explain how this stereoisomerism arises. Draw the structures of these stereoisomers. [2]

(ii) Compare and explain the relative acidity of ibuprofen and aspirin. [1]

(iii) Young children often find it difficult to swallow tablets. Thus, ibuprofen can also be supplied in the form of an emulsion. Given that ibuprofen is insoluble in water, an emulsifier such as *Tween 80* is used to create a homogenous mixture.



Tween 80

Using your knowledge from chemical bonding and the above information on the role of an emulsifier, explain clearly in terms of intermolecular forces, how *Tween 80* can create a homogenous mixture of ibuprofen in water. [2]

[Turn over

(d) A student proposed using 2-methylpropylbenzene to synthesise ibuprofen. The reaction scheme is shown in Fig. 4.1 below.

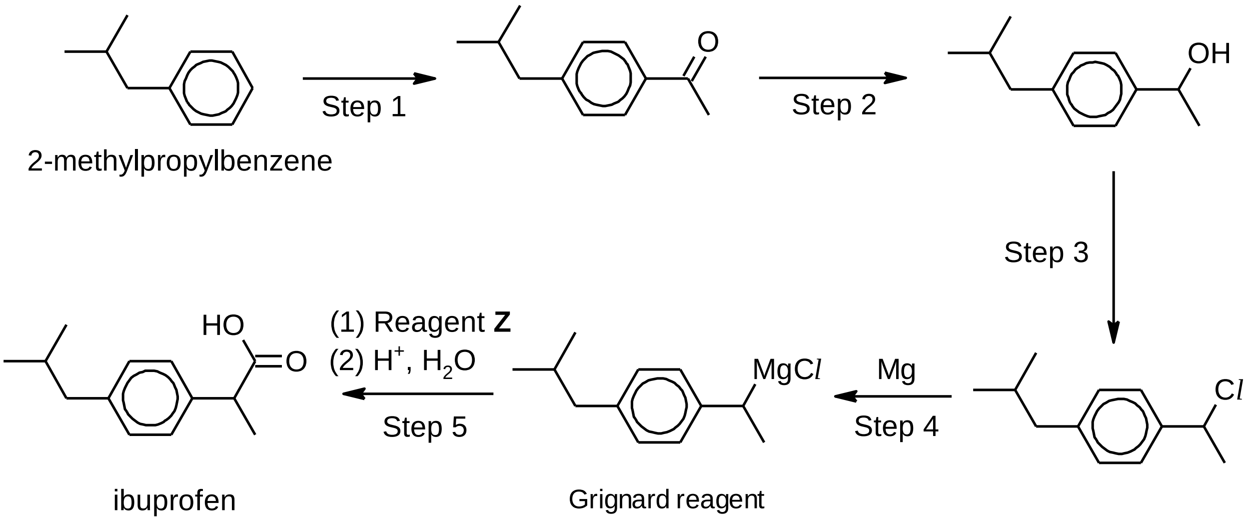


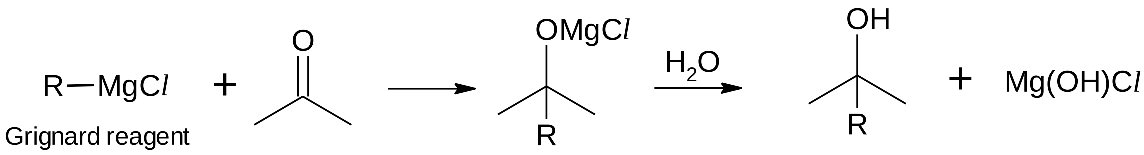
Fig. 4.1

(i) Name the type of reaction that occurs in steps 1 and 3. [2]

(ii) Suggest the reagents and conditions for steps 1 and 2. [2]

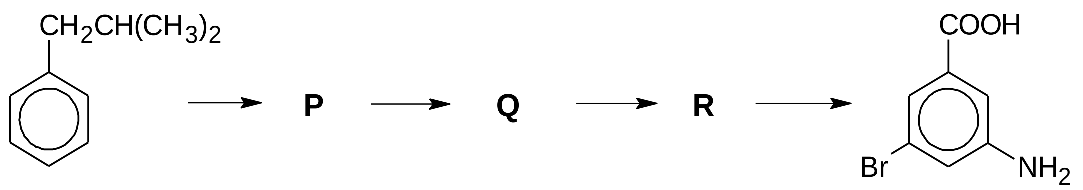
(iii) Describe a simple chemical test that can be carried out to indicate that Step 3 of the reaction scheme is complete. [2]

Step 4 in the reaction scheme involves the formation of a Grignard reagent. A Grignard reagent is useful to form new carbon-carbon bonds. The alkyl group in R−MgC*l* behaves like an anion, R^-. The Grignard reagent adds to a reagent via a nucleophilic addition reaction as shown below.



(iv) Suggest the identity for Reagent **Z** in Step 5. [1]

(e) 2-methylpropylbenzene undergoes a four-step reaction as shown below.



Suggest the structures of intermediates **P**, **Q** and **R** [3]

[Total: 20]

5(a) The halogens (chlorine, bromine and iodine) are found in Group 17 of the Periodic Table.

(i) Copy and complete the electronic configuration for a bromine atom, Br. [1]

$1s^2$ ……………………………….

(ii) Hence, sketch and label all occupied valence orbitals of the bromine atom. [2]

(iii) State and explain the trend in first ionisation energy down Group 17. [2]

(iv) By considering the relative positions of iodine, $_{53}I$, and lead, $_{82}Pb$, in the Periodic Table, and their first ionisation energies given in the *Data Booklet*, suggest a value for the first ionisation energy of astatine, $_{85}At$. Explain your answer. [2]

(b) The Period 3 elements sodium, aluminium and silicon, react with chlorine gas to produce chlorides with varying chemical properties.

Describe what would be observed when water is added to separate samples of $NaCl$, $AlCl_3$ and $SiCl_4$. Suggest the pH of the resulting solutions and write equations where appropriate. [3]

(c) At 450 K, phosphorus pentachloride, PCl_5(g), decomposes to form phosphorus trichloride, PCl_3(g), and chlorine, Cl_2(g). A *dynamic equilibrium* is established as shown.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H = +124 \text{ kJ mol}^{-1}$$

(i) Explain what is meant by the term *dynamic equilibrium*. [1]

(ii) Suggest, with reasoning, the effect of increasing temperature on the percentage of PCl_5(g) that decomposes. [1]

When 2.00 mol of PCl_5(g) are decomposed at 450 K and 1.00×10^5 Pa, the resulting equilibrium mixture contains 0.900 mol of Cl_2(g).

(iii) Write the expression for the equilibrium constant, K_p, for the decomposition of PCl_5(g). [1]

(iv) Determine the partial pressures of each of the gases at equilibrium. Hence, calculate the value of K_p and state its units. [3]

[Turn over

(d) Nitrogen mustard gas was stockpiled as a chemical warfare agent in World War II. However, it was not deployed in combat.

It was proposed that the synthesis of nitrogen mustard can be carried out via the following synthetic pathway as shown in Fig. 5.1.

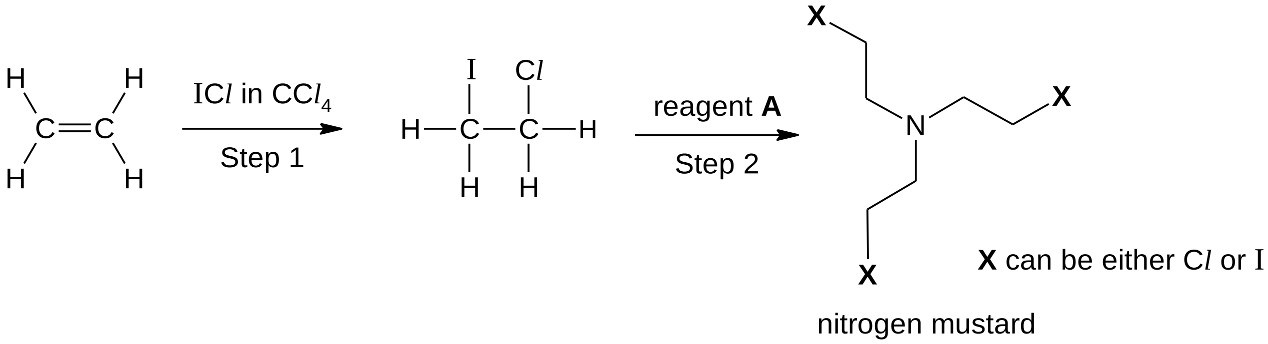


Fig. 5.1

(i) Suggest the reagents and conditions necessary for an optimal yield in Step 2 in Fig. 5.1. [1]

(ii) Is **X** in nitrogen mustard more likely to be C*l* or I? Explain your answer. [1]

Another reaction pathway was suggested for the synthesis of nitrogen mustard, with reagent **A** used in the first step as shown in Fig. 5.2.

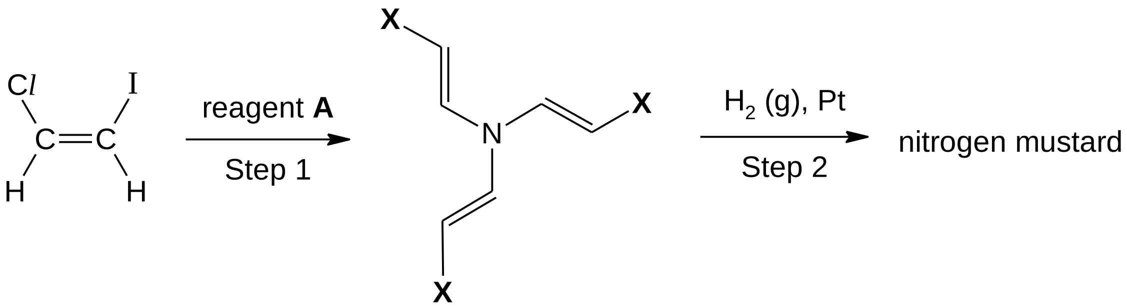


Fig. 5.2

(iii) By considering Step **1** of the reaction pathway in Fig. 5.2, explain why this method of synthesis is not likely to be feasible. [2]

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[Turn over

[Total: 20]