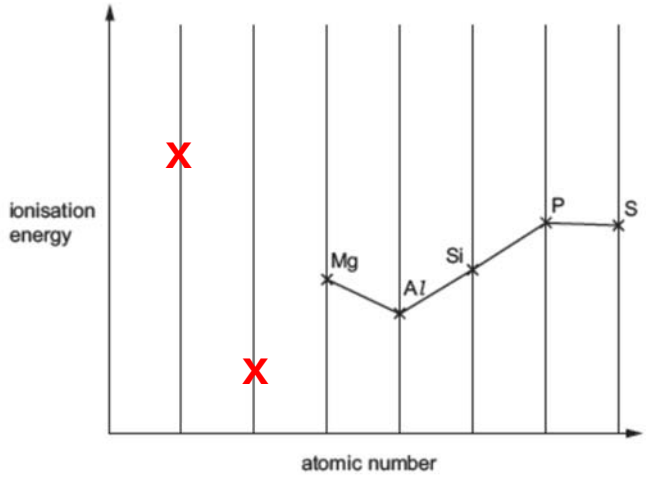
NJC SH2 H2 Chemistry P2 Solutions

1 The properties of elements and their compounds show similarities, differences and trends depending on the positions of the elements.

(a) The elements in the third period, and their compounds, show trends in their physical and chemical properties.
A sketch graph of the first ionisation energies of five successive elements in the third period is shown.



(i) Sketch on the graph, the position of the ionisation energy of the two elements that come before Mg in this sequence.

Cross shown on first vertical line from the y-axis (group 0/Ne) is clearly higher than all shown.
Cross shown on second vertical line from the y-axis (group 1/Na) is clearly lower than all shown.

[1]

(ii) Explain, with reference to electronic arrangements, the decreases in first ionisation energy between Mg and A*l* and between P and S.

Mg and A*l*:
The most loosely held electron in A*l* is in the **higher energy 3p subshell** while that of Mg is in the **lower energy 3s subshell.**
This **outweighs the effect of the increase in nuclear charge** from Mg to A*l*.
Hence **nuclear attraction for the most loosely held electron in A*l* is weaker**, i.e. A*l* has a lower 1st IE. [1]

P and S:
The most loosely held electron in S is one of the **paired electrons in 3p** orbital while that of P is in the **singly filled 3p** orbital.
Inter-electronic repulsion between the paired electrons in the same p orbital **outweighs the effect of an increase in nuclear charge**.
Hence, **nuclear attraction for the most loosely held electrons is weaker in S**, i.e. S has a lower first IE. [1]

[2]

(b) The chlorides of the elements in the third period behave in different ways when added to water, depending on their structure and bonding.

L is a chloride of an element in Period 3. A student investigated **L** and the results are as given below.

- **L** is a white crystalline solid with a melting point of 987 K.
- **L** dissolves in water to form a weakly acidic solution.
- Addition of NaOH(aq) to an aqueous solution of **L** produces a white precipitate, **M** .

(i) Identify **L** and **M.**

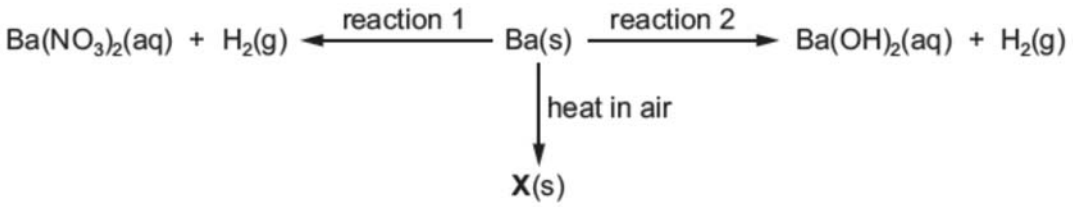
L: $MgCl_2$ **M:** $Mg(OH)_2$

[1]

(ii) Write an equation to illustrate the formation of the weakly acidic solution.

$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$ [1]
(state symbols not necessary)

(c) Some reactions based on the Group 2 metal barium, Ba, are shown below.



(i) State the reagent needed for each of reactions 1 and 2.

Reaction 1: HNO_3 [1]

Reaction 2: H_2O [1]

(ii) Write an equation for the formation of **X**.

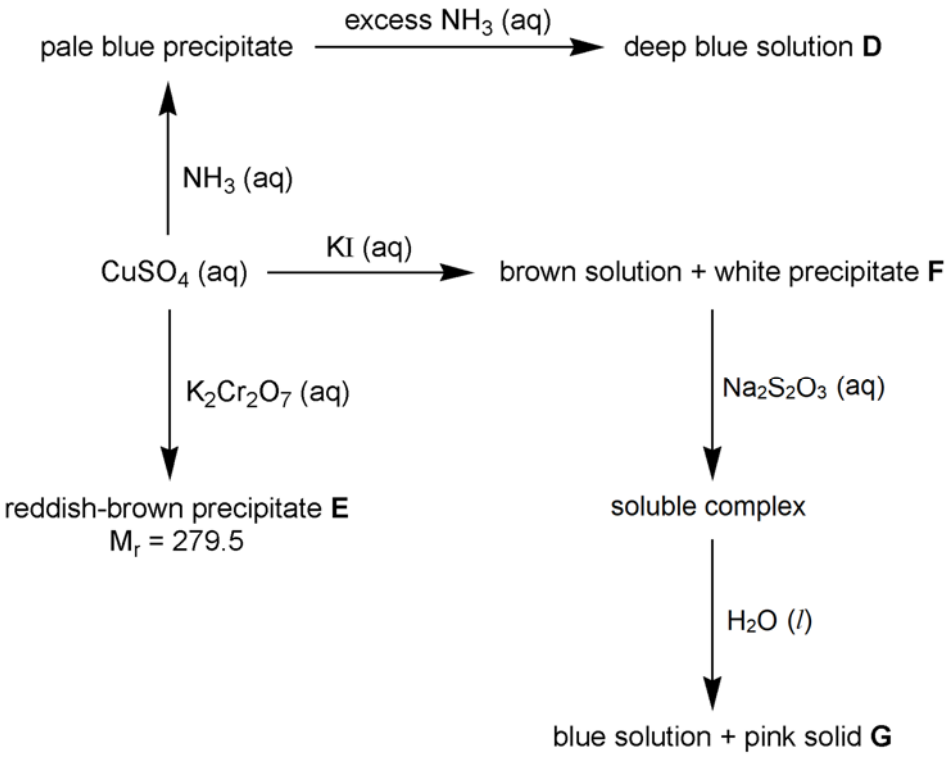
$2Ba + O_2 \rightarrow 2BaO$

[1]

[Total: 8]

2 The use of *Data Booklet* is relevant to this question.

(a) Copper(II) sulfate, an inorganic compound that has wide uses in organic syntheses and in engraving of zinc plates for intaglio printmaking, can undergo a series of reactions as shown below.



(i) Identify **D**, **E**, **F** and **G**.

D: $[Cu(NH_3)_4(H_2O)_2]^{2+}$ or $[Cu(NH_3)_4]^{2+}$ E: $CuCr_2O_7$

F: CuI G: Cu

(ii) With the aid of relevant equations, account for the formation of the deep blue solution **D** from the pale blue precipitate.

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$ ---(1)

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$ ---(2)

Formation of $[Cu(NH_3)_4]^{2+}$ complex lowers $[Cu^{2+}]$. This causes the ionic product of $Cu(OH)_2$ to become less than K_{sp} of $Cu(OH)_2$, and hence the pale blue $Cu(OH)_2$ precipitate dissolves to form the deep blue solution.

OR

Formation of $[Cu(NH_3)_4]^{2+}$ complex lowers $[Cu^{2+}]$. By Le Chatelier's Principle, the position of equilibrium (2) shifts to the right to partially increase $[Cu^{2+}]$. Hence the pale blue $Cu(OH)_2$ precipitate dissolves to form the deep blue solution.

[2]

(b) **(i)** By quoting relevant data, account for the trend in the thermal stabilities from HC*l* to HI.

BE(H–C*l*) = 431 kJ mol^{-1} BE(H–Br) = 366 kJ mol^{-1}
BE(H–I) = 299 kJ mol^{-1}

Down the group, less energy is needed to break the weaker H–X bond, resulting in decreasing thermal stability of HX.

[2]

(ii) Identify a transition metal cation that can be used to differentiate the oxidising abilities of Br_2 and I_2. Explain your answer with appropriate workings.

[3]

The transition metal cation is Fe^{2+}.

From Data Booklet	$E^{\ominus}$ / V
$Br_2 + 2e \rightleftharpoons 2Br^-$	+1.07
$I_2 + 2e \rightleftharpoons 2I^-$	+0.54
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.77

$Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$ $E^{\ominus}_{cell} = +0.30\ V > 0$

Br_2 can oxidise Fe^{2+} to Fe^{3+} since the reaction is spontaneous.

$I_2 + 2Fe^{2+} \rightarrow 2I^- + 2Fe^{3+}$ $E^{\ominus}_{cell} = -0.23\ V < 0$

I_2 cannot oxidise Fe^{2+} to Fe^{3+} since the reaction is non-spontaneous.

(iii) Suggest a series of steps to verify the presence of chloride and iodide ions in a mixture, given the following reagents:

- Aqueous silver nitrate
- Aqueous ammonia
- Aqueous nitric acid
- Filter paper
- Filter funnel

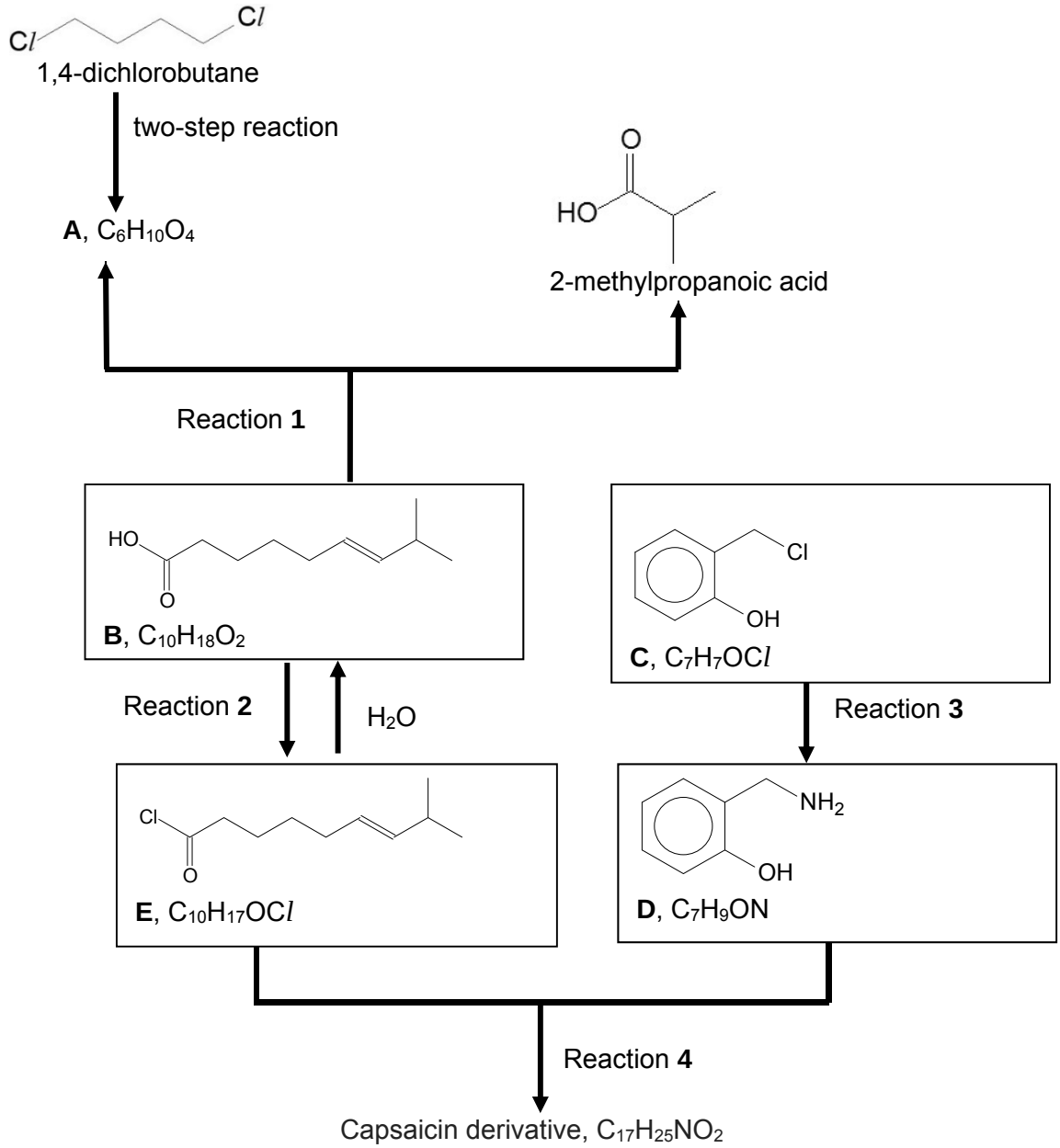
1. Add excess aqueous silver nitrate to the mixture. Yellowish-white precipitate is formed.
2. Next, add excess aqueous ammonia. Some of the precipitate will dissolve and only a yellow precipitate remains.
3. Filter the mixture with filter paper and filter funnel. Yellow residue indicates the presence of iodide ions.
4. To the colourless filtrate, add excess aqueous nitric acid. White precipitate formed indicates the presence of chloride ions.

[3]

[Total: 14]

3 Capsaicin is an active component of chili peppers. The reaction scheme involving the formation of a derivative of Capsaicin, $C_{17}H_{25}NO_2$, is shown below.

Information on compounds **A** to **D** are given on pages 6 and 7.



Compounds **A** to **D** react with sodium metal.
Compounds **A** and **B** react with aqueous sodium carbonate.
Compound **C**, Compound **D** and the capsaicin derivative reacts with aqueous sodium hydroxide but does not react with aqueous sodium carbonate.
Compounds **B** and **E** also react with cold acidified $KMnO_4$.

(a) Name the functional group common to compounds **A** and **B**.

Carboxylic acid

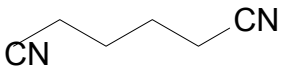
[1]

(b) Compound **A** can be synthesised from 1,4-dichlorobutane in two steps.
Suggest reagents and conditions for the synthesis, and the intermediate product for the reaction.

Step 1: ethanolic NaCN, heat

Step 2: dil H_2SO_4, heat

Intermediate product:



[3]

(c) There are two functional groups in compound **B**. Suggest the identity of the functional group in **B** that reacts with cold acidified $KMnO_4$.

Functional group that reacts with cold acidified $KMnO_4$: alkene

[1]

(d) Hence, draw the structure of compound **B** in the box on pg 6 and state the reagents and conditions for reaction **1**.

Reagents and conditions for reaction **1**: $KMnO_4$, dil H_2SO_4, heat

[2]

(e) Compound **C** reacts with hot ethanolic silver nitrate to produce a white ppt.
Draw the structure of Compounds **C** and **D** in the box on pg 6.
Name the type of reaction for reaction **3**.

Type of reaction for reaction **3**: nucleophilic substitution

[3]

(f) Compound **E** readily hydrolyses in water to produce Compound **B**.

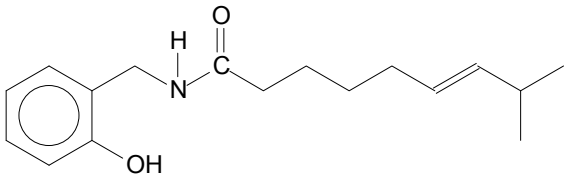
Draw the structure of compound **E** in the box on pg 6, and hence state the reagents and conditions for reaction **2**.

Reagents and conditions for reaction **2**: PCl_5 (s), anhydrous

[2]

(g) Compounds **D** and **E** react to produce the Capsaicin derivative.

Draw the structure of the Capsaicin derivative.



[1]

[Total: 13]

4 On 11 May 2018, Mount Merapi on Central Java, Indonesia erupted, causing the local airport to be closed. The eruption was reported to be caused by accumulation of volcanic gases. The volcanic ash and gases spewed can be dangerous to planes passing through the plume. The most abundant volcanic gas is harmless water vapour. However, significant amounts of carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen halides are also emitted.

When carbon dioxide is emitted from volcanoes, it typically becomes diluted to low concentrations very quickly and is not life threatening. However, cold carbon dioxide gas can flow into low-lying areas where it can reach much higher concentrations. Breathing air with more than 3% CO_2 can quickly lead to headaches, dizziness, increased heart rate and difficulty breathing. At about 15%, unconsciousness and death can result quickly.

Table 1.1: Volcanic gas composition in area **A**

Gas	Volume Percentage
Water vapour, H_2O	87.1
Carbon dioxide, CO_2	unknown
Sulfur dioxide, SO_2	0.5
Hydrogen, H_2	0.7
Carbon monoxide, CO	0.01
Hydrogen sulfide, H_2S	0.23
Hydrochloric acid, HCl	2.89
Hydrofluoric acid, HF	2.55

Composition of the volcanic gases are typically expressed in terms of volume percentage, which can be calculated as follows

$$volume\ percentage = \frac{volume\ of\ gas}{Total\ volume} \times 100\%$$

However, percentages are only additive for ideal gases.

(a) (i) State **two** assumptions of the kinetic theory of gases.

1) Negligible attractive or repulsive forces between gas particles
2) Negligible volume of gas particles compared to the volume they are moving in/ volume of the container they are in.

[2]

(ii) Under what conditions of temperature and pressure would you expect the behaviour of carbon dioxide to be most like that of an ideal gas?

Low pressure and high temperature.

[1]

(iii) Suggest a reason why at low temperature, carbon dioxide would sink rapidly and accumulate to high concentrations.

At low temperatures, there is insufficient energy to overcome the strong temporary dipole induced dipole (tdid) interactions between CO_2 molecules. Hence CO_2 would aggregate together/ more CO_2 molecules in a smaller volume and have a higher density thus sink down.

[2]

(iv) People living in area A were evacuated as the level of carbon dioxide and temperature of surroundings were increasing rapidly.

Given that 0.30 mg of CO_2 was present in 10 cm^3 of gas mixture at 43 ^oC and 11.2 kPa, determine the volume percentage of carbon dioxide present.

Hence comment on the possible danger if people remained in the area.

Amt of CO_2 = $\frac{0.30 \times 0.001}{44.0} = 6.818 \times 10^{-6} mol$

pV = nRT

$(11200)(V) = (6.818 \times 10^{-6})(8.31)(273 + 43)$

$V = 1.598 \times 10^{-6}\ m^3$

volume percentage of $CO_2 = \frac{1.598 \times 10^{-6}}{10 \times 10^{-6}} \times 100\% = 16.0\%$

Ans: 16.0% unconsciousness and death can result quickly.

[3]

(b) Hydrogen sulfide can react with methane in the following equation.

$$CH_4(g) + 2\ H_2S(g) \rightleftharpoons CS_2(g) + \mathbf{4\ H_2(g)}$$

1 mol of CH_4, 2 mol of H_2S, 1 mol of CS_2 and 1 mol of H_2 was allowed to reach equilibrium at a constant temperature and pressure of 960^{o}C and 2 atm.

Given that partial pressure of CS_2 was found to be 0.5 atm at equilibrium, determine the value of K_p, giving its units.

[3]

Q says to reach equilibrium at 960°C and 2 atm, i.e. Total P initially and Total P at eqm is same, 2 atm.

	$CH_4(g)$	+ 2 $H_2S(g)$	⇌	$CS_2(g)$	+ 4 $H_2(g)$
Initial/ mol	1	2		1	1
Eqm/ mol	1-x	2-2x		1 + x	1 + 4 x

Total mol at eqm = 5 + 2x

partial pressure of CS_2 =$= 2\left(\frac{1+x}{5+2x}\right) = 0.5$ atm
solve for x , x = 0.5

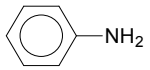
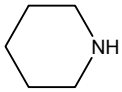
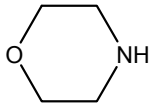
	$CH_4(g)$	+ 2 $H_2S(g)$	⇌	$CS_2(g)$	+ 4 $H_2(g)$
Eqm/ mol	0.5	1		1.5	3
	Total amt of gas at eqm = 6				
Eqm / atm	$\frac{0.5}{6} \times 2 = \frac{1}{6}$	$\frac{1}{6} \times 2 = \frac{1}{3}$		0.5	$\frac{3}{6} \times 2 = 1$

$$K_p = \frac{(P_{H2})^4 . P_{CS2}}{P_{CH4} . (P_{H2S})^2}$$

$$K_p = \frac{1^4(0.5)}{(1/6).(1/3)^2} = 27.0 \text{ atm}^2$$

[Total: 11]

5 **(a)** The following table contains the pK_b values of different nitrogen organic compounds.

Compound	pK_b
$(CH_3)_3CNH_2$ 2-amino-2-methylpropane	3.19
 phenylamine	9.38
 piperidine	2.88
 morpholine	5.17
N_2H_4 hydrazine	5.17, 11.05

(i) Suggest a reason why pK_b of morpholine is higher than piperidine.

Morpholine has an electronegative O that exert ***electron withdrawing effect***, it reduces the availability of lone pair on N to accept H^+, therefore Morpholine is a weaker base hence a higher pK_b value.

(ii) Suggest a reason why pK_b of phenylamine is so much higher than 2-amino-2-methylpropane.

Lone pair on N of phenylamine is delocalised into the benzene ring, making lone pair much less available to receive H^+ than lone pair of N in $(CH_3)_3CNH_2$, phenylamine is a weaker base hence a higher pKb value than $(CH_3)_3CNH_2$.

[2]

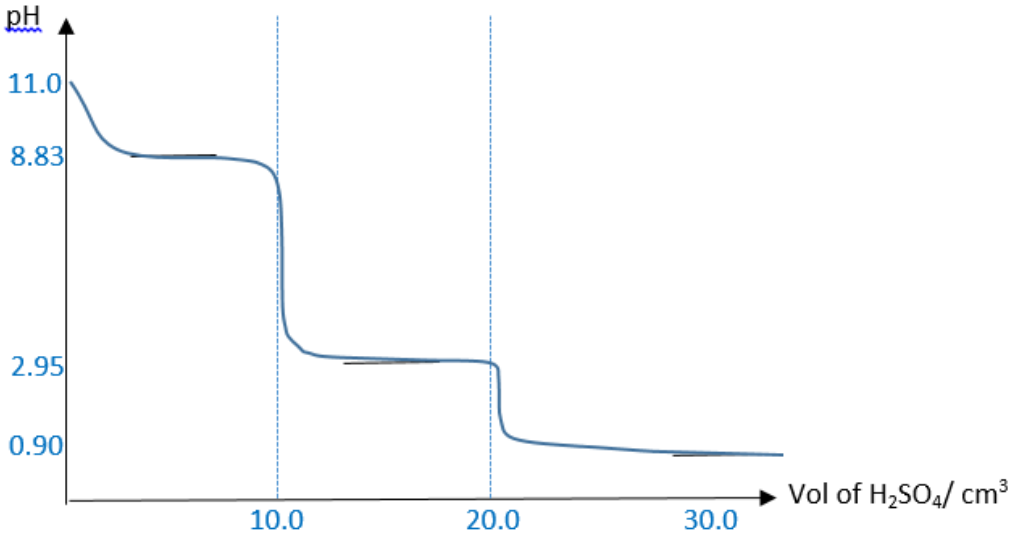
(b) 10.0 cm^3 of an aqueous mixture containing 0.5 mol dm^{-3} of hydrazine was placed in a conical flask and the initial pH was found to be 11.0.

Sketch the p*H*–volume graph on the axis provided when 10.0 cm^3 of the aqueous mixture was titrated with 0.25 mol dm^{-3} dilute sulfuric acid until a total volume of 30.0 cm^3 of dilute sulfuric acid was added.

Your sketch should include the following points

- Initial pH of hydrazine
- p*H* of the reaction mixture when 30.0 cm^3 of H_2SO_4 is added.

- Maximum buffer points (if any)



Initial pH = 11.0 given in question

volume of H_2SO_4 required for the 1st equiv point = 10.0 cm^3
total vol of H_2SO_4 required for 2nd equiv point = 20.0 cm^3

Max buffer points occur at 5 and 15 cm^3.
pOH = pK_b at max buffer pts
pH = 14- pOH
pH are 14 – 5.17 = 8.83 and 14 – 11.05 = 2.95 respectively.

Final pH
Amt of unreacted H^+ = (2 x 10/1000 x 0.25) = 0.005 mol (since H_2SO_4 is diprotic)
$[H^+]$ = 0.005 x 1000/ 40 = 0.125 $moldm^{-3}$ => pH = 0.90

[3]

(c) Student **M** suggested a 2–step process as shown, to synthesise 2-amino-2-methylpropane from a suitable alkane.

C_4H_{10} **A** —step 1→ C_4H_9Cl **B** —step 2→ $C_4H_{11}N$

(i) Identify the structures of compounds **A** and **B**, and suggest reagents and conditions for each of the two steps.

$(CH_3)_3CH$ Structure of **A**	$(CH_3)_3CCl$ Structure of **B**

Step 1: limited Cl_2, UV. light

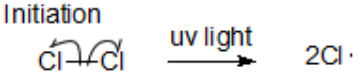
Step 2: excess NH_3 in ethanol, heat in sealed tube

[4]

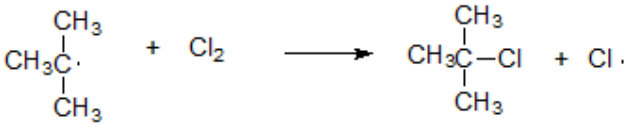
(ii) Outline the mechanism for step 1.

Free radical substitution

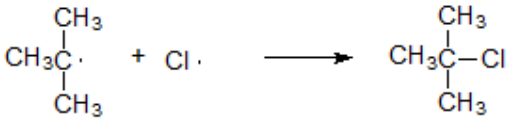
Initiation

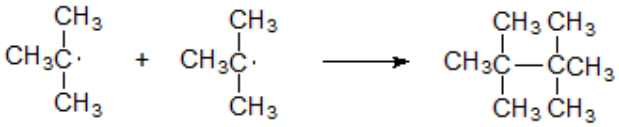


propagation



Termination





[3]

(iii) A student **N** suggested an alternative synthetic route for the synthesis of 2-amino-2-methylpropane, using an alkene as a starting material.

Explain why this synthetic route will give a higher yield as compared to the suggested route in **(c) (ii).**

Electrophilic addition via alkene can only give two possible products and the tertiary carbocation is formed at a greater rate that forms the major product 2-amino-2-methylpropane, while free radical substitution of alkane gives rise to a variety of reactive intermediates that lead to multiple products being formed.

[2]

[Total: 14]

6 1–chloro–1–phenylethane undergoes hydrolysis with hydroxide ions to produce 1–phenylethanol, as shown in the equation below.

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

(a) The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in the solution at a given time after the reaction has been quenched.

(i) Suggest a suitable quenching agent that can be used to stop the reaction effectively.

cold water

[1]

(ii) Using your answer in **(i)**, describe a suitable method for determining the order of reaction with respect to OH^-, given the following.

- Solution **A**, 1.0 mol dm^{-3} 1-chloro-1-phenylethane
- Solution **B**, 0.10 mol dm^{-3} sodium hydroxide
- 0.10 mol dm^{-3} hydrochloric acid
- Quenching agent [as suggested in **(i)**]
- Stopwatch
- Standard laboratory equipment

Specific details of volumes and time is not required.

Continuous Method:

1. Mix Solution **A** & **B**, swirl the beaker and start the stopwatch.
2. At a certain time, withdraw a fixed volume of mixture into a conical flask, add fixed volume of cold water to the mixture to quench the reaction.
3. Titrate against hydrochloric acid, using phenolphthalein as indicator.
4. Titrate until colour of mixture turns from pink to colourless.
5. Repeat steps 2 - 4 at fixed time intervals (eg, 6 min, 9 min, 12 min)
6. Plot graph of volume of HCl against time.
7. If straight-line graph, it means that reaction is 0 order wrt OH^-
   If constant half-life, it means that reaction is 1st order wrt OH^-
   If increasing half-life, it means that reaction is 2nd order wrt OH^-

(b) The rate of this reaction was measured using different initial concentrations of the two reagents and the results are shown below.

Experiment	$[C_6H_5CHClCH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Relative rate
1	0.05	0.10	1.0
2	0.10	0.20	2.0
3	0.15	0.10	3.0

(i) Deduce the order of reaction with respect to each of the reagents. Explain your reasoning.

Comparing experiment 1 & 3, when [OH^-] is constant, [$C_6H_5CHClCH_3$] is tripled, relative rate is tripled. Hence, reaction is 1st order with respect to $C_6H_5CHClCH_3$. [1]

Comparing experiment 1 & 2, when both [OH^-] and [$C_6H_5CHClCH_3$] are doubled, relative rate is doubled. Since reaction is 1st order with respect to $C_6H_5CHClCH_3$, the doubling of [OH^-] has no effect on rate, so reaction is zero order with respect to OH^-. [1]

* Accept if student write conc / rate increases by 3 times.

Order with respect to $C_6H_5CHClCH_3$ = **first order**

Order with respect to OH^- = **zero order**

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

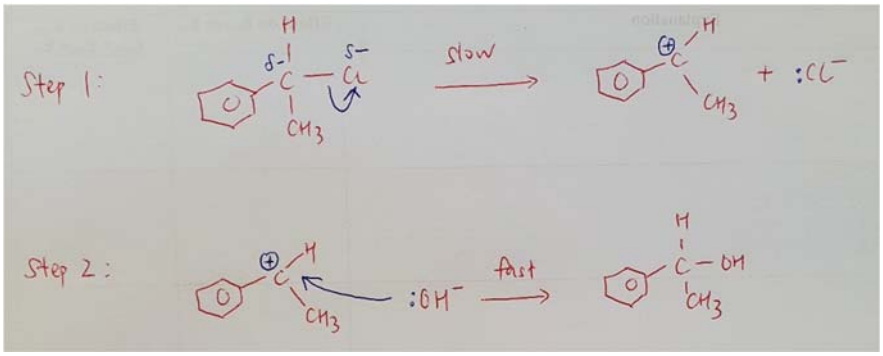
rate = $k[C_6H_5CHClCH_3]$ mol $dm^{-3}s^{-1}$

units of *k* = s^{-1}

[2]

(c) **(i)** By making use of your answer in **(b)(i)**, describe the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions.
In your answer, you should show relevant charges, lone pairs, dipoles and show movement of electrons by curly arrow.

Nucleophilic substitution (S_N1)



(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane. Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

A mixture of 2 optical isomers (racemic mixture) will be formed because the nucleophile can attack the trigonal planar intermediate from top or bottom of the plane with equal probability.

If S_N2 in c(i),
A single optical isomer will be formed as the nucleophile attack the molecule from the opposite side of the leaving chloride, resulting in an inversion of configuration. [2]

(iii) 1-chloro-2-ethyl benzene, $C_6H_4ClCH_2CH_3$, is an isomer of 1-chloro-1-phenylethane, $C_6H_5CHClCH_3$. The ease of hydrolysis for each of the 2 compounds is different. Explain why.

In 1-chloro-2-ethyl benzene, the p-orbital of C*l* overlaps with the π-electron cloud of benzene, resulting in delocalisation of electrons, strengthening the C-C*l* bond, giving it a partial double bond character.

Hence, the C-C*l* bond does not break easily and the ease of hydrolysis will be much lower than that of 1-chloro-1-phenylethane.

[Total: 15]