Answer all questions in the spaces provided.

1 The Periodic Table currently used is derived from that proposed in 1869 by Mendeleev who had noticed patterns in the physical and chemical properties of the elements he had studied.

(a) (i) The atomic radius of the Period 3 elements decreases from Na to C*l*. Explain why this is so.

- There is an increasing nuclear charge due to increase in number of protons.
- There is an approximately constant shielding effect as additional electrons are added to the same valence shell and provides negligible shielding effect.
- Effective nuclear charge increases

- Valence electrons thus experiences stronger nuclear attraction.
  OR
  Therefore, electrons are pulled closer to the nucleus.

(ii) Write the electronic configurations of the sodium atom and its ion

Na $1s^2$……

Na^+ $1s^2$……

[1]

Na: $1s^2 2s^2 2p^6 3s^1$
Na^+: $1s^2 2s^2 2p^6$

(iii) Explain the difference in the radius of the sodium atom and the radius of its ion, Na^+.

……[1]

- Na^+ has one less shell of electrons than Na, hence Na^+ is smaller.

(b) (i) Complete Table 1.1 by describing the acid/base behaviour of Al_2O_3 and SO_3. Provide equation(s) to illustrate the behaviour of each oxide.

Table 1.1

oxide	acid/base behaviour	equation(s) illustrating behaviour of each oxide
Al_2O_3	amphoteric	$\mathbf{Al_2O_3} + 6\mathbf{HCl} \rightarrow 2AlCl_3 + 3H_2O$ $\mathbf{Al_2O_3} + 2\mathbf{NaOH} + 3H_2O \rightarrow 2Na^+[Al(OH)_4]^-$

SO_3	acidic	$SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$

[4]

(ii) State **one** source of SO_2 pollution.

……[1]

- Sulfur compounds in fuels / fossil fuels / biomass
  OR
  sulfide ores
  OR
  volcanoes

(iii) State an environmental consequence of SO_2.

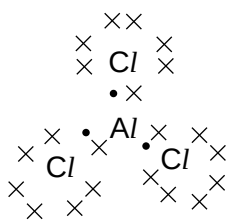
……[1]

- Formation of acid rain
  OR
  its consequences e.g. damage to buildings / crops / plants / marine life / deforestation

(c) A diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third Periods. The elements and their compounds in these pairs are observed to share similar properties.

An example of such a pair is beryllium and aluminium.

(i) Draw the dot-and-cross diagram for $AlCl_3$ and state the $Cl{-}Al{-}Cl$ bond angle.



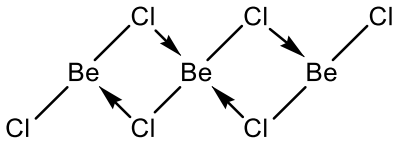
Dot-and-cross diagram of $AlCl_3$

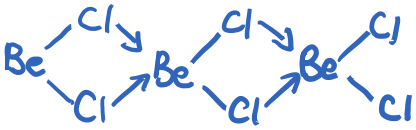
[1]

Bond angle: …… [1]

(ii) Unlike $AlCl_3$ which dimerises to form Al_2Cl_6, $BeCl_2$ polymerises and exists as long chains in the solid state.

Draw a section of one chain with three $BeCl_2$ monomers, showing clearly the bonding within the chain. [1]





(iii) With a small amount of water, $BeCl_2$ hydrolyses in the same manner as $AlCl_3$.

Write an equation for the hydrolysis of $BeCl_2$.

……[1]

- $BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$

[Total: 14]

2 This question concerns the chemistry of the halogens and hydrogen halides.

(a) F_2 and Cl_2 are halogens that exist as gases under room temperature and pressure.

(i) With reference to their structures and bonding, explain why Cl_2 has a higher boiling point than F_2.

- Both have simple molecular structures
- Cl_2 has a larger, more polarisable electron cloud
- Stronger instantaneous dipole-induced dipole (id – id) interactions between Cl_2 molecules
- Requires more energy to overcome these interactions

(iii) Use data from the *Data Booklet* to compare the oxidising strength of F_2 and Cl_2.

……[2]

The electrode potential of +2.87V ($F_2 + 2e^- \rightleftharpoons 2F^-$) is more positive than +1.36V ($Cl_2 + 2e^- \rightleftharpoons 2Cl^-$), showing F_2 is a stronger oxidising agent than Cl_2 as it has a greater tendency for reduction.

(b) Chlorine gas was bubbled through an aqueous solution of potassium iodide. Hexane was subsequently added and the mixture was shaken in a test − tube. Table 2.1 gives the density of water and hexane.

Table 2.1

compound	density / g cm^{-3}
water	1.00
hexane	0.655

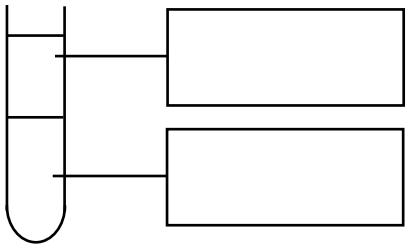
(i) Write an equation for the reaction that occurs between chlorine gas and potassium iodide solution.

……[1]

$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$

(ii) Complete Fig. 2.1 by stating the colours observed in the test – tube.

Fig. 2.1



- Purple layer above the brown layer

(c) Vapour pressure is defined as the pressure exerted by a vapour in equilibrium with its liquid in a closed system. Table 2.2 shows the vapour pressure of HF and HC*l* measured at 25 °C.

Table 2.2

compound	vapour pressure / kPa
HF	122
HC*l*	4660

Give a reason for the higher vapour pressure of HC*l*.

……..……..

……..……..

……..…[1]

- HF molecules experiences stronger hydrogen bonding, compared to HCl's weaker permanent dipole – permanent dipole interactions, resulting in higher vapour pressure for HCl as there is more gaseous HCl than HF.

[Total: 7]

3 The Sabatier reaction describes the *reversible reaction* between carbon dioxide and hydrogen in the following equation:

$$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) \qquad \Delta H = -126 \text{ kJ mol}^{-1}$$

The reactants are passed through a solid support coated with ruthenium metal as a catalyst, where the reaction occurs.

(a) **(i)** Define the term *reversible reaction*.

……..…..

……..…[1]

- It is a reaction that proceeds in both the forward and backward directions in a closed system
  OR
  A reaction that proceeds in either direction.

(ii) Write the K_p expression for this reaction.

[1]

$$K_p = \frac{P_{CH_4} P_{H_2O}^{\ 2}}{P_{CO_2} P_{H_2}^{\ 4}}$$

(iii) State the type of catalyst used in this reaction.

……..…[1]

Heterogeneous

(b) 0.05 mol of carbon dioxide and 0.05 mol of hydrogen were introduced in a 1 dm^3 evacuated vessel at 353 °C.

The Sabatier reaction occurred and an equilibrium was established. The equilibrium partial pressure of methane was measured to be 20 kPa.

(i) Calculate the initial partial pressure, in kPa, of carbon dioxide in the vessel.

[2]

$$P = \frac{0.05 \times 8.31 \times (353 + 273)}{1 \times 10^{-3}} = 260.1$$

= 260 kPa

(ii) Determine the equilibrium partial pressures, in kPa, of:

- carbon dioxide
- hydrogen
- water

[2]

	CO_2	$+ 4H_2$	$\rightleftharpoons$	CH_4	$+ 2H_2O$
Initial / kPa	260	260		0	0
Change / kPa	-20	-80		+20	+40
Eqm / kPa	240	180		20	40

P_{CO_2} = 240 kPa

P_{H_2} = 180 kPa

P_{H_2O} = 40 kPa

(c) **(i)** Describe and explain how the position of equilibrium will change when the volume of the vessel is decreased from 1 dm^3 to 0.5 dm^3.

……

……

……[2]

An decrease in volume will lead to a rise in pressure of the system.
This favours the forward reaction where the number of gaseous particles is fewer. The position of equilibrium shifts to the right.

Fig. 3.1 shows how the forward and backward rates of the Sabatier reaction change with time at 353 °C.

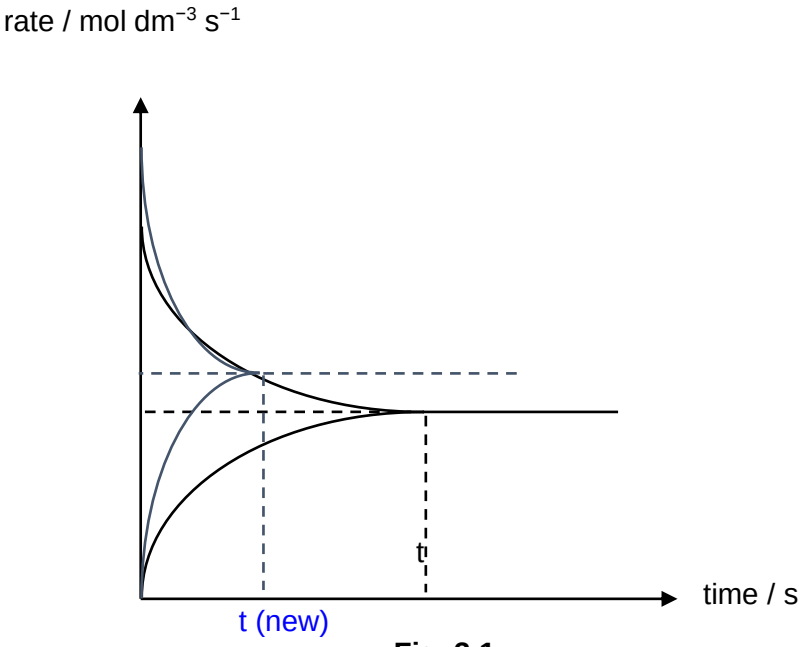


Fig. 3.1

[2]

Accept for pencil for curve drawing

(ii) Sketch, in Fig. 3.1, showing how:

- the time at which equilibrium is reached and
- forward and backward rates of the Sabatier reaction

will change when the temperature is increased from 353 °C to 400 °C.

(iii) State and explain how the K_c value for the Sabatier reaction changes when the temperature is increased from 353 °C to 400°C.

……

……

……

……[2]

- K_c value decreases
- Endothermic reaction which is backward reaction
- To absorb the heat present.

OR

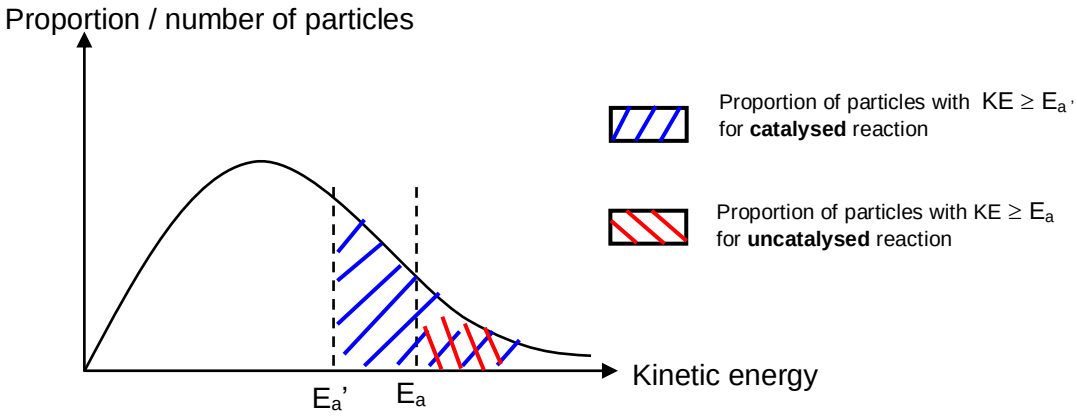
Rate constant of backward reaction increases more than rate constant of forward reaction, thus K_c value decreases.

(d) Suggest a reagent to remove carbon dioxide from the equilibrium reaction mixture.

……[1]

NaOH / CaO
Any group 1 hydroxide (solid / aqueous)
soda lime (mixture of $Ca(OH)_2$ and NaOH)

(e) With the aid of a labelled Boltzmann distribution, explain how the addition of ruthenium metal increases the rate of the reaction.



Ru catalyst provides the reaction with an **alternative pathway of lower activation energy**, the **proportion of molecules with kinetic energy greater than or equals to activation energy rises**. There is a **greater frequency of effective collisions**, resulting in a faster reaction rate.

[Total: 17]

4 In potentiometric titrations, the electrode potential *E* is measured against the volume of a solution added from the burette. To determine the concentration of acidified $FeCl_2$ solution, 25.0 cm^3 of this solution was placed in a beaker and titrated against 0.02 mol dm^{-3} acidified $K_2Cr_2O_7$ in a burette. It was found that 20.80 cm^3 of $K_2Cr_2O_7$ was needed to reach end – point.

The electrode potential *E* was measured using the standard hydrogen electrode as the reference and all measurements were made at 298 K.

Fig. 4.1 shows the setup for this titration.

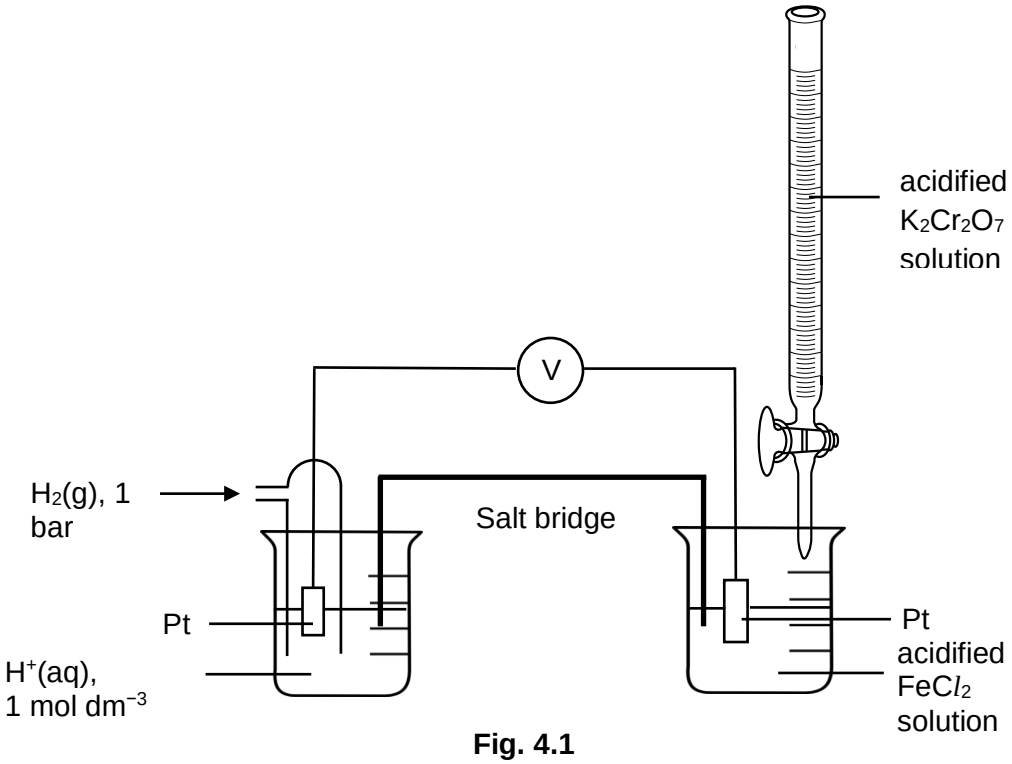


Fig. 4.1

(a) **(i)** State why platinum electrodes are used in this experiment.

……[1]

- Pt is inert
  OR
  Pt does not take part in the reaction

(ii) Before the addition of any $K_2Cr_2O_7$, suggest what would be observed in the beaker containing $FeCl_2$ if the platinum electrode there was replaced with iron.

……[1]

- Fe electrode will become smaller/dissolves
  OR
  Solution becomes greener

(b) **(i)** The reaction between Fe^{2+} and $Cr_2O_7^{2-}$ can be represented by the **unbalanced** equation:

$$Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + Cr^{3+}$$

Write the balanced equation for this reaction.

……[1]

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

(ii) Determine the concentration of the $FeCl_2$ solution.

[2]

Amount of $Cr_2O_7^{2-} = \frac{0.02}{1000} \times 20.8 = 4.16 \times 10^{-4}$ mol

Amount of $Fe^{2+} = 4.16 \times 10^{-4} \times 6$
$= 2.496 \times 10^{-3}$ mol

Concentration of $Fe^{2+} = \frac{2.496 \times 10^{-3}}{25} \times 1000 = 0.100$ OR 0.0998 mol dm^{-3}

(iii) Calculate the $\Delta G^{\ominus}$ of the reaction in **(b)(i).**

[2]

$E^{\ominus}_{cell} = +1.33 - (+0.77)$
$= +0.56$V

$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$
$= -6 \times 9.65 \times 10^4 \times 0.56$
$= -324$ kJ mol^{-1}

(c) The electrode potential E measured changes during the titration.

The Nernst Equation describes how the relative concentrations of Fe^{2+} and Fe^{3+} change the electrode potential, E from the standard electrode potential, $E^{\ominus}$.

Nernst Equation $\quad E = E^{\ominus} - 0.0592 \lg \frac{[Fe^{2+}]}{[Fe^{3+}]}$

After a certain volume of $K_2Cr_2O_7$ was added, an electrode potential of +0.77 V was recorded on the voltmeter.

(i) State the volume of $K_2Cr_2O_7$ that was added. Explain your answer.

……

……[2]

- $10.4\ cm^3$
- There is equal / same amount / concentration of Fe^{2+} and Fe^{3+}

(ii) On Fig 4.1, indicate the direction of electron flow across the voltmeter. [1]

(From left to right)

(iii) Explain how the electrode potential,*E*, value would change as the titration proceeds up to the end-point.

……

……

……[2]

- $[Fe^{2+}]$ decreases OR $[Fe^{3+}]$ increases during the titration
- There is an increased tendency for Fe^{3+} reduction
  OR
  Position of equilibrium ($Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$) lies towards the right
- Electrode potential becomes more positive / increases.

OR

- $[Fe^{2+}]$ decreases AND $[Fe^{3+}]$ increases / $\frac{[Fe^{2+}]}{[Fe^{3+}]}$ ratio decreases/ $\lg \frac{[Fe^{2+}]}{[Fe^{3+}]}$ decreases/ $-\lg \frac{[Fe^{2+}]}{[Fe^{3+}]}$ increases/$-0.0592 \lg \frac{[Fe^{2+}]}{[Fe^{3+}]}$ increases
- Electrode potential becomes more positive / increases.

(d) **(i)** In another experiment, molten $FeCl_2$ was electrolysed using platinum electrodes. The process was conducted using a current of 0.1 A.

Calculate the time taken to deposit 0.1 g of Fe on the electrode.

[2]

$Q = It$
$= 0.1 \times t$
$= 0.1t$

Amount of Fe = $\frac{0.1}{55.8} = 1.792 \times 10^{-3}$ mol

Amount of $e^- = 1.792 \times 10^{-3} \times 2 = 3.584 \times 10^{-3}$ mol

Charge = $9.65 \times 10^4 \times 3.584 \times 10^{-3} = 345.9$ C

$t = \frac{345.9}{0.1} = 3459$
$= 3460$ s / 57.8 min / 0.960 hr

(ii) The electrolysis was repeated using a dilute aqueous solution of $FeCl_2$ using platinum electrodes.

State the products obtained at the cathode and at the anode.

By quoting relevant electrode potentials from the *Data Booklet*, explain why these products were obtained.

Product at cathode: ……

Explanation: ……..

Product at anode: ……...

Explanation: ……

……..[4]

Explanation: Electrode potential for Fe^{2+}/Fe is less negative / has its equilibrium lying more to the right / shows greater tendency for reduction than that for H_2O/H_2

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ −0.83V
$Fe^{2+} + 2e^- \rightleftharpoons Fe$ −0.44V

Explanation: Electrode potential for O_2/H_2O is less positive/ has its equilibrium lying more to the left / shows greater tendency for oxidation than Cl_2/Cl^-

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ +1.36V
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23V

[Total: 18]

5 Styrene is a precursor of the polystyrene, a commonly used thermoplastic polymer.

Styrene undergoes free radical polymerisation to form long chains of the polymer shown in Fig 5.1. As a thermoplastic polymer, polystyrene becomes moldable when heated to 100 ^{o}C and solidifies at lower temperatures.

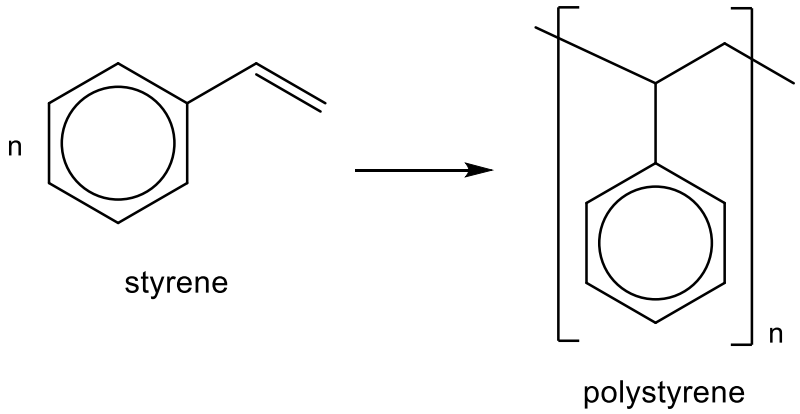


Fig. 5.1

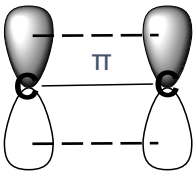
(a) Describe, in terms of orbital overlap, the bonding present in the alkene functional group of styrene. Draw a labelled diagram to illustrate your answer.

……

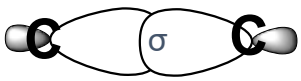
……

……[2]

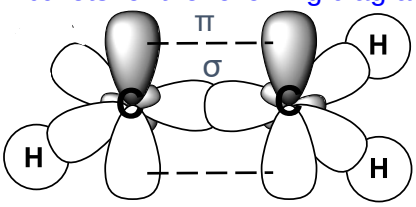
- 1 C-C π (pi) bond formed by sideways/collateral overlap of 2p orbitals



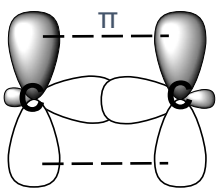
- 1 C-C σ (sigma) bond formed by the head-on/collinear overlap of sp^2 orbitals



2 bullets for the following diagrams (labels are needed)



OR



(b) Styrene can be converted to (1-bromoethyl)benzene and compound **A** through a series of reactions shown in Fig. 5.2.

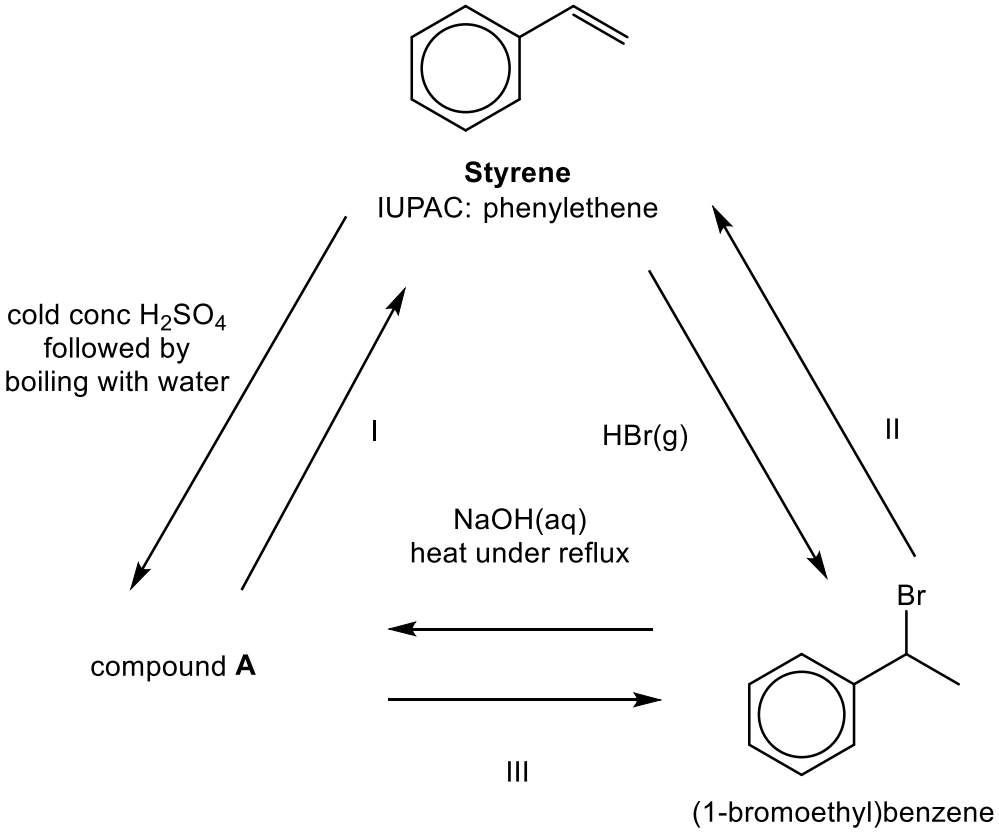
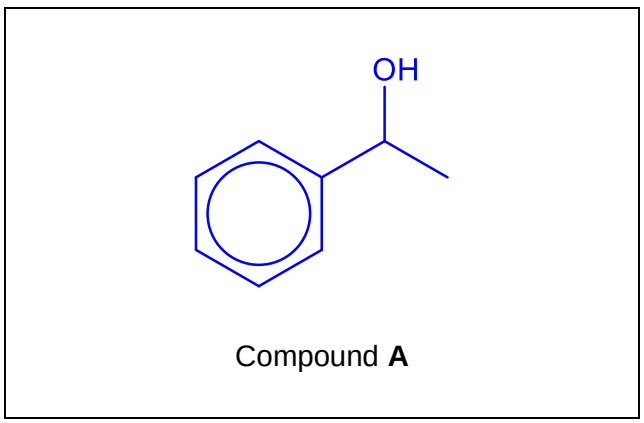


Fig. 5.2

(i) Draw the structure of compound **A** and state the reagents and conditions for steps I, II and III.



Step I: ……

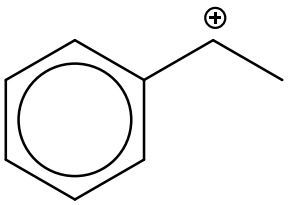
Step II: ……

Step III: ……

[4]

Step I: conc H_2SO_4 heat OR Al_2O_3, heat OR conc H_3PO_4, heat
Step II: NaOH (ethanolic), heat under reflux
Step III: HBr
Red phosphorus, Br_2, heat
OR PBr_3 and heat
OR conc H_2SO_4, NaBr, reflux

(ii) When styrene reacts with HBr(g) to form (1-bromoethyl)benzene, the following intermediate is formed.



Intermediate

State the type of reaction and account for the stability of the intermediate.

Type of reaction: ……

Explanation: ……

……[3]

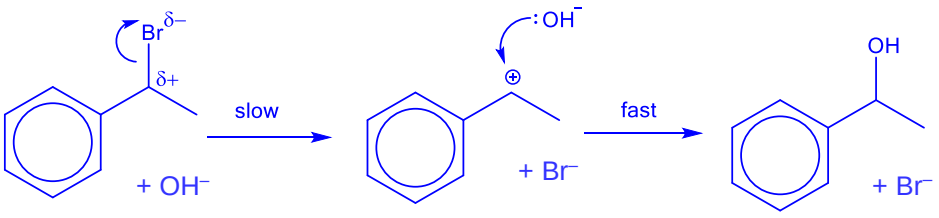
Type of reaction: Electrophilic addition

The empty p orbital of the carbocation overlaps with the pi electron cloud of the phenyl group. The pi electrons / positive charge can be delocalised to the carbon with the positive charge, thus the carbocation is stabilized.

(iii) When enantiomerically pure (1-bromoethyl)benzene is heated under reflux with aqueous NaOH, the same carbocation intermediate as in **(b)(ii)** is formed.
Name and draw the mechanism for this reaction.

[3]

Unimolecular nucleophilic substitution / S_N1



(iv) With reference to your mechanism in **(b)(iii)**, suggest and explain whether the product in **(b)(iii)** is optically active.

……

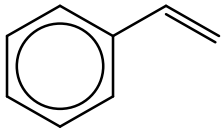
……

……

……[2]

- The product is optically inactive.
- In the mechanism, the nucleophile to attack from either side of the planar intermediate with equal probability.
- Hence a racemic mixture is formed / both enantiomers will form in equal concentration.
  Rotation of plane polarized light by both enantiomers is cancelled out.

(c) Under standard conditions, styrene undergoes combustion according to the following equation.



(l) + 10 $O_2(g)$ ⟶ 8 $CO_2(g)$ + 4 $H_2O(l)$

(i) Use relevant bond energy values in the Data Booklet to calculate the standard enthalpy change of combustion of styrene.

[2]

$\Delta H_c^{\ominus}$ (styrene) = BE(bond breaking) – BE(bond forming)
= [6(520) + (8)(410) + (10)(496) + (350) + 610] – [(8×2)(805) + (4×2)(460)]
= 12320 – 16560
= – 4240 kJ mol^{-1}

(ii) The standard enthalpy changes of formation of styrene, carbon dioxide and water are given in Table 5.1. Use these values to calculate another value for the standard enthalpy change of combustion of styrene.

Table 5.1

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
styrene(*l*)	– 148.3
CO_2(g)	– 393.5
H_2O(*l*)	– 285.8

[2]

$\Delta H_c^{\ominus}$ (styrene) = ΔH_f(pdt) – ΔH_f(rct)
= [8(– 393.5) + 4(– 285.8)] – (–148.3)
= –4142.9
= –4140 kJ mol^{-1}

(iii) Account for the difference between your answers in **(c)(i)** and **(c)(ii)**.

……

……[1]

The answer in c(i) does not take into account $\Delta H_{vapourisation}$ of water and styrene or the bond energies from the Data Booklet are average values.

[Total: 19]