Q1. This question is about halogenoalkanes.

(a) Chlorine atoms are formed in the upper atmosphere when ultraviolet radiation causes C–Cl bonds in chlorofluorocarbons (CFCs) to break.

Write **two** equations to show how chlorine atoms catalyse the decomposition of ozone.

1. ____

____

2. ____

____

(2)

(b) Chloroethane reacts with potassium hydroxide in the presence of propan-1-ol to form ethene.

State the role of potassium hydroxide and the role of propan-1-ol in the reaction.

Role of potassium hydroxide ____

Role of propan-1-ol ____

(2)

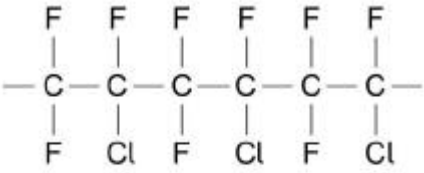
(c) Name and outline a mechanism for the reaction in part **(b)** between chloroethane and potassium hydroxide to produce ethene.

Name of mechanism ____

Mechanism

(4)

(d) The structure of polymer **A** is shown.



Draw the structure of the monomer used to form polymer **A**.

(1)

(e) Chemical analysis shows that a chlorofluoroalkane, **B**, contains by mass 51.6% fluorine, 32.1% chlorine and no hydrogen.

Chlorine exists as two isotopes, ^{35}Cl and $3^{37}Cl$, in the ratio 3:1
Fluorine only exists as one isotope, ^{19}F.

A mass spectrum of **B** is obtained using electron impact ionisation. The mass spectrum shows three molecular ion peaks at *m/z* = 220, 222 and 224.

Determine the formula of each of the three molecular ions of **B**.

Predict and explain the ratio of the relative abundancies of each of the three molecular ion peaks at *m/z* = 220, 222 and 224.

To gain full marks you must show all your working.

(6)
(Total 15 marks)

Q2. Haloalkanes are used as refrigerants, solvents and anaesthetics.

(a) Trichloromethane ($CHCl_3$) is a haloalkane that can be formed by heating a mixture of chloromethane (CH_3Cl) and chlorine.

(i) Write an overall equation for the formation of trichloromethane by the reaction of chloromethane with chlorine.

____

(1)

(ii) Name the mechanism for this formation of trichloromethane.

____

(1)

(iii) Dichloromethane (CH_2Cl_2) is an intermediate in this formation of trichloromethane.

Write an equation for each of the following steps in the mechanism for the reaction of dichloromethane with chlorine.

Initiation step

____

First propagation step

____

Second propagation step

____

A termination step leading to the formation of a compound with formula $C_2H_2Cl_4$

____

(4)

(b) Chlorotrifluoromethane ($CClF_3$) is used as a refrigerant, but is being phased out due to concerns about ozone depletion in the upper atmosphere.
In the upper atmosphere, $CClF_3$ decomposes in the presence of UV light forming a reactive intermediate that catalyses the decomposition of ozone.

(i) Write an equation to show how $CClF_3$ decomposes to form the reactive intermediate.

____

(1)

(ii) Write two equations to show how this reactive intermediate is involved in catalysing the decomposition of ozone.

1. ____

2. ____

(2)

Q3. There are many uses of halogenated organic compounds despite environmental concerns.

(a) Bromotrifluoromethane is used in fire extinguishers in aircraft.
Bromotrifluoromethane is formed when trifluoromethane reacts with bromine.

$$CHF_3 + Br_2 \longrightarrow CBrF_3 + HBr$$

The reaction is a free-radical substitution reaction similar to the reaction of methane with chlorine.

(i) Write an equation for each of the following steps in the mechanism for the reaction of CHF_3 with Br_2

Initiation step

____

First propagation step

____

Second propagation step

____

A termination step

____

(4)

(ii) State **one** condition necessary for the initiation of this reaction.

____

(1)

(b) Bromine-containing and chlorine-containing organic compounds may have a role in the decomposition of ozone in the upper atmosphere.

(i) Draw an appropriate **displayed formula** in the space provided to complete the following equation to show how $CBrF_3$ may produce bromine atoms in the upper atmosphere.

$$CBrF_3 \longrightarrow \underline{\qquad\qquad} + Br^{\bullet}$$

(1)

(ii) In the upper atmosphere, it is more likely for $CBrF_3$ to produce bromine atoms than it is for $CClF_3$ to produce chlorine atoms.

Suggest **one** reason for this.

____

____

(1)

(iii) Bromine atoms have a similar role to chlorine atoms in the decomposition of ozone. The overall equation for the decomposition of ozone is

$$2O_3 \longrightarrow 3O_2$$

Write **two** equations to show how bromine atoms (Br•) act as a catalyst in the decomposition of ozone.

Explain how these two decomposition equations show that bromine atoms behave as a catalyst.

Equation 1

____

Equation 2

____

Explanation ____

____

(3)

(Total 10 marks)

Q4. Trifluoromethane (CHF_3) can be used to make the refrigerant chlorotrifluoromethane($CClF_3$).

(a) Chlorotrifluoromethane is formed when trifluoromethane reacts with chlorine.

$$CHF_3 + Cl_2 \longrightarrow CClF_3 + HCl$$

The reaction is a free-radical substitution reaction similar to the reaction of methane with chlorine.

(i) Write an equation for each of the following steps in the mechanism for the reaction of CHF_3 with Cl_2

Initiation step

____

First propagation step

____

Second propagation step

____

Termination step to form hexafluoroethane

____

(4)

(ii) Give **one** essential condition for this reaction.

____

(1)

(b) In some refrigeration systems, CHF_3 has replaced $CClF_3$ because of concerns about ozone depletion.

(i) Identify the species formed from $CClF_3$ that is responsible for the catalytic decomposition of ozone in the upper atmosphere.

____

(1)

(ii) Write an overall equation to represent the decomposition of ozone into oxygen.

____

(1)

(Total 7 marks)

Q1.

(a) $Cl\bullet + O_3 \longrightarrow ClO\bullet + O_2$

Allow dot in free-radical on either O or Cl.

1

$ClO\bullet + O_3 \longrightarrow 2O_2 + Cl\bullet$

1

(b) (KOH acts as a) base

1

(propan-1-ol acts as a) solvent.

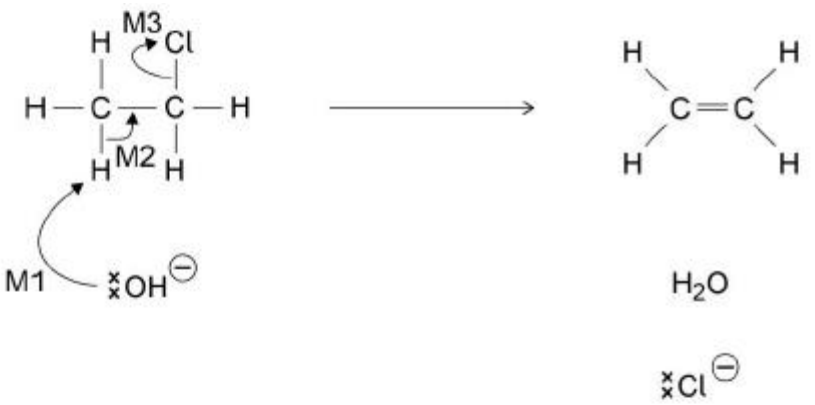
Allow product of reaction between KOH and propan-1-ol / $CH_3CH_2CH_2O^-$ acts as base.

1

(c) (Name of mechanism) Elimination

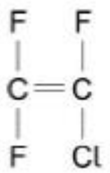
1

mechanism: 3 arrows (1 mark each).



3

(d)



1

(e) This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

Level 3

All stages are covered & the explanation of each stage is generally correct and virtually complete. Stages 1 and 2 are supported by correct data. Answer communicates the whole process coherently and shows a logical progression from stage 1 to stage 2 and then stage 3.

Steps in stage 3 are in logical order and working is shown. If there is no working for ratio or statement of ratio then full marks cannot be awarded.

If the formulae of the three molecular ions are not correct (2d) then the student can't access Level 3 (any incorrect chemistry drops the student to the bottom mark within the level they have achieved).

5-6 marks

Level 2

Stage 2 is attempted (**2a-2c** do not need to be explicitly stated) but the calculation may contain inaccuracies **OR** the explanation may be incomplete **OR** first two stages are covered and the explanations are generally correct and virtually complete. Answer is mainly coherent and shows a progression through the first two stages. Some steps in each stage may be incomplete.

If percentage of carbon is missing or incorrect (1a) then student can't access Level 2.

3-4 marks

Level 1

Stage 1 needs to be attempted but may contain inaccuracies.

OR

Stage 3 attempted but may contain inaccuracies / molecular formula not determined.

Answer includes some isolated statements, but these are not presented in a logical order or show confused reasoning.

1-2 marks

Level 0

Insufficient correct chemistry to warrant a mark.

0 marks

Indicative Chemistry content

Stage 1 (determines empirical formula)

1a *16.3% carbon*

1b *Divide by* A_r

1c *Divide by smallest (0.904)*

1d *Convert ratio in simplest integer (x 2)*

C	Cl	F
$\frac{16.3}{12.0}$ = 1.358	$\frac{32.1}{35.5}$ = 0.904	$\frac{51.6}{19.0}$ = 2.716
$\frac{1.358}{0.904}$	$\frac{0.904}{0.904}$	$\frac{2.716}{0.904}$
3	2	6

Stage 2 (determines formulae of three molecular ions)

2a *For E.F.* M_r *(corresponds to the molecule) = 221*

2b *since M_r = 221 lies within molecular ion range 220–224*
2c *Thus empirical formula = molecular formula*
2d *Three correct formulae*
2e *Correct M_r for each of three molecules*

$C_3{}^{35}Cl_2F_6{}^{+\bullet}$	$C_3{}^{35}Cl^{37}ClF_6{}^{+\bullet}$	$C_3{}^{37}Cl_2F_6{}^{+\bullet}$
220	222	224

Stage 3 (explains the ratio of 3 molecular ion peaks)
3a *Working*
2b *Correct (simplified) ratio* ***9:6:1***
Note: 9:3:1 will be a common incorrect answer (max 5).

Working:

$C_3{}^{35}Cl_2F_6{}^{+\bullet}$	$C_3{}^{35}Cl^{37}ClF_6{}^{+\bullet}$	$C_3{}^{37}Cl_2F_6{}^{+\bullet}$
220	222	224
${}^{35}Cl_2 = \left(\frac{3}{4}\right)^2 = \frac{9}{16}$	${}^{35}Cl^{37}Cl$ and ${}^{37}Cl^{35} = 2 \times \frac{1}{4} \times \frac{3}{4} = \frac{6}{16}$	${}^{37}Cl_2 = \left(\frac{1}{4}\right)^2 = \frac{1}{16}$

[15]

Q2.

(a) (i) $CH_3Cl + 2Cl_2 \longrightarrow CHCl_3 + 2HCl$

IGNORE *state symbols*
ALLOW *multiples*

1

(ii) (Free-)radical substitution

This answer only

1

(iii) Initiation:

$Cl_2 \longrightarrow 2Cl\bullet$

Penalise absence of dot once only

1

1st Propagation step

$Cl\bullet + CH_2Cl_2 \longrightarrow \bullet CHCl_2 + HCl$

Penalise + and/or – charges every time

1

2nd Propagation step

$\bullet CHCl_2 + Cl_2 \longrightarrow CHCl_3 + Cl\bullet$

ALLOW *• anywhere on •$CHCl_2$ but, if drawn out as a structure, then*
• must be on C

1

Termination

2 •$CHCl_2$ ⟶ $C_2H_2Cl_4$

Mark independently

ALLOW *•CH_2Cl + •CCl_3 ⟶ $C_2H_2Cl_4$*

IGNORE *state symbols throughout*

1

(b) (i) $CClF_3$ ⟶ •CF_3 +Cl•

ALLOW *• anywhere on •CF_3 unless displayed*

1

(ii) Cl• + O_3 ⟶ ClO• + O_2

Equations can be in either order

Penalise absence of • once only

1

ClO• + O_3 ⟶ 2O_2 + Cl•

ALLOW *• anywhere on •ClO*

NOT *•O_3*

1

[9]

Q3.

(a) (i) **Initiation**

Br_2 ⟶ 2Br•

First propagation

Br• + CHF_3 ⟶ •CF_3 + HBr

Second propagation

Br_2 + •CF_3 ⟶ $CBrF_3$ + Br•

Termination

2•CF_3 ⟶ C_2F_6 ***OR*** CF_3CF_3

OR

2Br• ⟶ Br_2

OR

Br• + •CF_3 ⟶ $CBrF_3$

Penalise absence of dot once only

Credit the dot anywhere on the radical

4

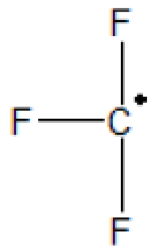
(ii) Ultra-violet / uv / sunlight

OR

T > 100°C OR <u>high</u> temperature

1

(b) (i)



Displayed formula required with the radical dot on carbon

1

(ii) (The) C–Br (bond) breaks more readily / is weaker than (the) C–Cl (bond) (or converse)

OR

The C–Br bond enthalpy / bond strength is less than that for C–Cl (or converse)

*Requires **a comparison** between the two bonds*

Give credit for an answer that suggests that the UV frequency / energy may favour C–Br bond breakage rather than C–Cl bond breakage

Ignore correct references either to size, polarity or electronegativity

Credit correct answers that refer to, for example "the bond between carbon and bromine requires less energy to break than the bond between carbon and chlorine"

1

(iii) **M1**

$Br\bullet + O_3 \longrightarrow BrO\bullet + O_2$

M2

$BrO\bullet + O_3 \longrightarrow Br\bullet + 2O_2$

***M1** and **M2** could be in either order*

Credit the dot anywhere on the radical

Penalise absence of dot once only

Penalise the use of multiples once only

M3 One of the following

They / it / the bromine (atom)

- does not appear in the overall equation
- is regenerated
- is unchanged at the end
- has not been used up
- provides an alternative route / mechanism

3

[10]

Q4.

(a) (i) **M1 Initiation**

$Cl_2 \longrightarrow 2Cl\bullet$

Penalise absence of dot once only.

M2 First propagation

$Cl\bullet + CHF_3 \longrightarrow CF_3\bullet + HCl$

Penalise + or − charges every time.

M3 Second propagation

$Cl_2 + CF_3\bullet \longrightarrow CClF_3 + Cl\bullet$

Credit $CF_3\bullet$ with the radical dot above / below / to either side.

M4 Termination (must make C_2F_6)

$2\ CF_3\bullet \longrightarrow C_2F_6$ or CF_3CF_3

Mark independently.

4

(ii) ultra-violet / uv / sun light

OR (very) high temperature

OR 500 °C ≤ T ≤ 1000 °C

OR 773 K ≤ T ≤ 1273 K

1

(b) (i) Cl• **OR** chlorine atom / chlorine (free−) radical / Cl (atom)

Not 'chlorine' alone.

Credit 'Cl' alone on this occasion.

1

(ii) $\mathbf{2}O_3 \longrightarrow \mathbf{3}O_2$

Or multiples.

Ignore state symbols.

If the correct answer is on the line OR clearly identified below some working, then ignore any working.

1

[7]