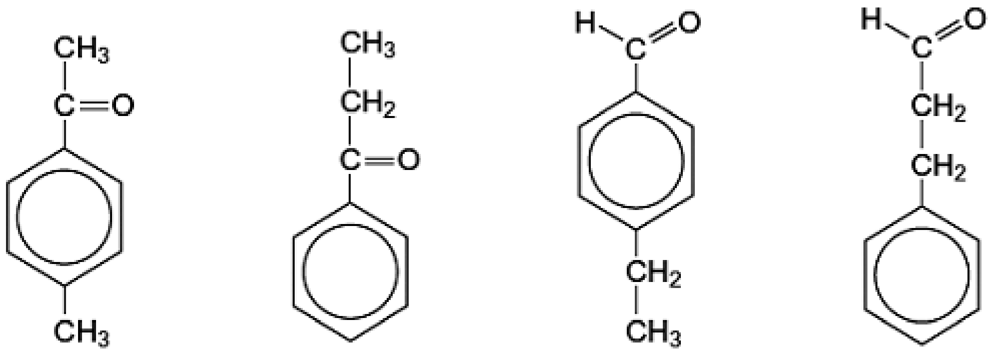
Q9.

Mass spectrometry is used by organic chemists to help distinguish between different compounds.

Four isomers of $C_9H_{10}O$, shown below, were analysed by mass spectrometry.



A **B** **C** **D**

The mass spectra obtained from these four isomers were labelled in random order as I, II, III and IV.

Each spectrum contained a molecular ion peak at *m/z* = 134

The data in the table below show the *m/z* values greater than 100 for the major peaks in each spectrum due to fragmentation of the molecular ion. The table also shows where no major peaks occurred.

Spectrum	*m/z* values for major peaks	No major peak at *m/z*
I	119	133, 105
II	133, 119 and 105	
III	133, 105	119
IV	105	133, 119

(a) Two of the molecular ions fragmented to form an ion with *m/z* = 133 by losing a radical. Identify the radical that was lost.

____

(1)

(b) Two of the molecular ions fragmented to form an ion with *m/z* = 119 by losing a radical. Identify the radical that was lost.

____

(1)

(c) Three of the molecular ions fragmented to form ions with m/z = 105 by losing a radical with M_r = 29

Identify **two** different radicals with M_r = 29 that could have been lost.

Radical 1 ____

Radical 2 ____

(2)

(d) Consider the structures of the four isomers and the fragmentations indicated in parts (a) to (c).
Write the letter **A**, **B**, **C** or **D**, in the appropriate box below, to identify the compound that produces each spectrum.

Spectrum I ☐

Spectrum II ☐

Spectrum III ☐

Spectrum IV ☐

(4)
(Total 8 marks)

Q10.

(a) Some scientists thought that the waste water from a waste disposal factory contained **two** sodium halides.

They tested a sample of the waste water.

They added three reagents, one after the other, to the same test tube containing the waste water.

The table below shows their results.

Reagent added	Observations
1. Silver nitrate solution (acidified with dilute nitric acid)	A cream precipitate formed
2. Dilute ammonia solution	A yellow precipitate remained
3. Concentrated ammonia solution	The yellow precipitate did not dissolve

(i) Identify the yellow precipitate that did **not** dissolve in concentrated ammonia solution.
Write the **simplest** ionic equation for the formation of this precipitate from silver ions and the correct halide ion.
Identify the other sodium halide that must be present in this mixture of two sodium halides.

____

____

____

____

(3)

(ii) Give **one** reason why the silver nitrate solution was acidified before it was used in this test.

____

____

____

(1)

(iii) The method that the scientists used could **not** detect one type of halide ion. Identify this halide ion.
Give **one** reason for your answer.

___

___

___

___

(2)

(b) The scientists thought that the waste water also contained dissolved barium ions. An aqueous solution of sodium sulfate can be used to test for the presence of dissolved barium ions.

Write the **simplest** ionic equation for the reaction between barium ions and sulfate ions to form barium sulfate.

State what is observed in this reaction.

Give a use for barium sulfate in medicine and explain why this use is possible, given that solutions containing barium ions are poisonous.

___

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___

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___

___

___

___

(4)

(c) The scientists also analysed the exhaust gases from an incinerator used to destroy waste poly(ethene).
Mass spectrometry showed that there was a trace gas with a precise M_r = 28.03176 in the exhaust gases from the incinerator.

The table below contains some precise relative atomic mass data.

Atom	**Precise relative atomic mass**
^{12}C	12.00000
^{1}H	1.00794
^{16}O	15.99491

Use the data to show that the trace gas is ethene. Show your working.

Suggest why both ethene and carbon monoxide might have been identified as the trace gas if the scientists had used relative atomic masses to a precision of only one decimal place.

Write an equation for the incomplete combustion of ethene to form carbon monoxide and water only.

Ethene is used to make poly(ethene).
Draw the displayed formula for the repeating unit of poly(ethene).
Name this type of polymer.

____

____

____

____

____

____

____

____

____

____

(5)

(Total 15 marks)

Q11.

A scientist used mass spectrometry to analyse a sample of the air near a fertiliser factory. The sample of air included traces of a gas which was shown by its molecular ion to have a precise M_r = 44.00105

(a) State the meaning of the term *molecular ion*.

___

___

(1)

(b) (i) Use the following data to show that the trace gas was dinitrogen oxide (N_2O).

Show your working.

Atom	**Precise relative atomic mass**
^{12}C	12.00000
^{14}N	14.00307
^{16}O	15.99491

___

___

(1)

(ii) Propane is used as a fuel in the fertiliser factory. State why both propane and its combustion product, carbon dioxide, might have been identified as the trace gas if the scientist had used relative molecular masses calculated to one decimal place.

___

___

(1)

(iii) State why the precise relative atomic mass for the ^{12}C isotope is exactly 12.00000

___

(1)

(c) Dinitrogen oxide is formed when ammonia is oxidised according to the following equation.

$$2NH_3(g) + 2O_2(g) \rightarrow N_2O(g) + 3H_2O(l)$$

(i) Use the standard enthalpies of formation in the table below to calculate a value for the standard enthalpy change of this reaction.

	$NH_3(g)$	$O_2(g)$	$N_2O(g)$	$H_2O(l)$
ΔH_f^o/ kJ mol^{-1}	–46	0	+82	–286

____

____

____

____

(3)

(ii) State **one** condition necessary for enthalpies of formation to be quoted as standard values at a specified temperature of 298 K.

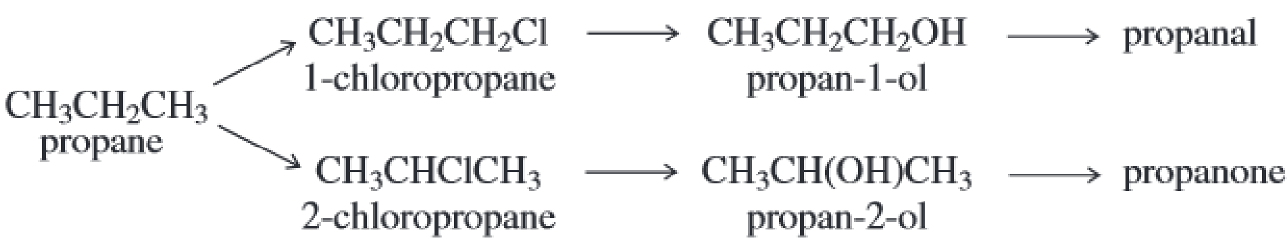
____

(1)

(Total 8 marks)

Q12.

Consider the following scheme of reactions.



(a) State the type of structural isomerism shown by propanal and propanone.

____

(1)

(b) A chemical test can be used to distinguish between separate samples of propanal and propanone.

Identify a suitable reagent for the test.
State what you would observe with propanal and with propanone.

Test reagent ____

Observation with propanal ______________________________________

Observation with propanone ______________________________________

(3)

(c) State the structural feature of propanal and propanone which can be identified from their infrared spectra by absorptions at approximately 1720 cm^{-1}.

____

(1)

(d) The reaction of chlorine with propane is similar to the reaction of chlorine with methane.

(i) Name the type of mechanism in the reaction of chlorine with methane.

____

(1)

(ii) Write an equation for each of the following steps in the mechanism for the reaction of chlorine with propane to form l-chloropropane ($CH_3CH_2CH_2Cl$).

Initiation step

____

First propagation step

____

Second propagation step

____

A termination step to form a molecule with the empirical formula C_3H_7

____

(4)

(e) High resolution mass spectrometry of a sample of propane indicated that it was contaminated with traces of carbon dioxide.

Use the data in the table to show how precise M_r values can be used to prove that thesample contains both of these gases.

Atom	Precise relative atomic mass
^{12}C	12.00000
^{1}H	1.00794
^{16}O	15.99491

(2)

(Total 12 marks)

Q13.

It is necessary to use several analytical techniques to determine the structure of an unknown compound.

An analytical chemist was asked to determine the structure of compound **Q** which was found in a waste tank in a mixture of volatile liquids.

Compound **Q** has the molecular formula C_4H_7ClO. It is a volatile liquid which does not produce misty fumes when added to water.

(a) Suggest how the chemist could obtain a sample of **Q** for analysis from the mixture of volatile liquids.

(1)

(b) The infra-red spectrum of Q contains a major absorption at 1724 cm^{-1}. Identify the bond which causes this absorption.

(1)

(c) The mass spectrum of Q contains two molecular ion peaks at *m/z* = 106 and *m/z* = 108. It also has a major peak at *m/z* = 43.

(i) Suggest why there are two molecular ion peaks.

____

(ii) A fragment ion produced from **Q** has *m/z* = 43 and contains atoms of **three** different elements. Identify this fragment ion and write an equation showing its formation from the molecular ion of **Q**.

Fragment ion ____

Equation ____

(3)

(d) The proton n.m.r. spectrum of **Q** was recorded.

(i) Suggest a suitable solvent for use in recording this spectrum of **Q**.

____

(ii) Give the formula of the standard reference compound used in recording proton n.m.r. spectra.

____

(2)

(e) The proton n.m.r. spectrum of Q shows 3 peaks. Complete the table below to show the number of adjacent, non-equivalent protons responsible for the splitting patterns.

	Peak 1	Peak 2	Peak 3
Integration value	3	3	1
Splitting pattern	doublet	singlet	quartet
Number of adjacent, non-equivalent protons	1		

(1)

(f) Using the information in parts (a), (b) and (d) deduce the structure of compound **Q**.

(1)

(g) A structural isomer of **Q** reacts with cold water to produce misty fumes. Suggest a structure for this isomer.

(1)
(Total 10 marks)

Q9.

(a) H ***OR*** hydrogen ***OR*** $H^{\bullet}$

Ignore brackets ignore dot

penalise + or – charge

1

(b) CH_3 ***OR*** methyl ***OR*** $CH_3^{\bullet}$ ***OR*** $^{\bullet}CH_3$

Ignore brackets ignore dot

penalise + or – charge

1

(c) Either order

C_2H_5 ***OR*** ethyl ***OR*** $CH_3CH_2^{\bullet}$ ***OR*** $C_2H_5^{\bullet}$

Ignore brackets ignore dot

penalise + or – charge

1

CHO ***OR*** HCO ***OR*** COH ***OR*** H—C=O

1

(d) I A

1

II C

1

III D

1

IV B

1

[8]

Q10.

(a) (i) **M1** (yellow precipitate is) silver iodide OR AgI (which may be awarded from the equation)

M2 $Ag^+ + I^- \longrightarrow AgI$ (Also scores M1 unless contradicted)

M3 sodium chloride OR NaCl

For M2

Accept multiples

Ignore state symbols

Allow crossed out nitrate ions, but penalise if not crossed out

3

(ii) The silver nitrate is acidified to

- react with / remove ions that would interfere with the test
- prevent the formation of other silver precipitates / insoluble silver compounds that would interfere with the test

- remove (other) ions that react with the silver nitrate
- react with / remove carbonate / hydroxide / sulfite (ions)

  Ignore reference to "false positive"

1

(iii) **M1 and M2 in either order**

M1 Fluoride (ion) OR F^-

M2
- Silver fluoride / AgF is soluble / dissolves (in water)
- no precipitate would form / no visible /observable change

Do not penalise the spelling "fluoride",
Penalise "fluride" once only
Mark M1 and M2 independently

2

(b) **M1** $Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4$

(or the ions together)

M2 white precipitate / white solid / white suspension

M3 Barium meal or (internal) X-ray or to block X-rays

M4 $BaSO_4$ / barium sulfate is insoluble (and therefore not toxic)

For M1, ignore state symbols
Allow crossed out sodium ions, but penalise if not crossed out
For M2, ignore "milky"
If $BaSO_3$ OR BaS used in M1 and M4, penalise once only
For M3 Ignore radio-tracing
For M4 NOT barium ions
NOT barium
NOT barium meal
NOT "It" unless clearly $BaSO_4$

4

(c) **M1** **2**(12.00000) + **4**(1.00794) = 28.03176

M2 Ethene and CO or "they" have an imprecise M_r of 28.0 / 28

OR

Ethene and CO or "they" have the same M_r to one d.p.

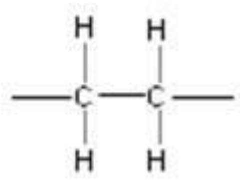
OR

These may be shown by two clear, simple sums identifying both compounds

M3 $C_2H_4 + 2O_2 \longrightarrow 2CO + 2H_2O$

($H_2C{=}CH_2$)

M4 Displayed formula



M5 Type of polymer = Addition (polymer)

M1 must show working using 5 d.p.for hydrogen

Penalise "similar" or "close to", if this refers to the imprecise value in M2, since this does not mean "the same"

For M3, accept $CH_2{=}CH_2$ OR CH_2CH_2

For M4, all bonds must be drawn out including those on either side of the unit.

Penalise "sticks"

*Ignore brackets around **correct** repeating unit but penalise "n"*

Penalise "additional"

5

[15]

Q11.

(a) The molecular ion is

- The molecule with one/an electron knocked off/lost

  Ignore the highest or biggest m/z peak

OR

- The molecule with a (single) positive charge

OR

- the ion with/it has the largest/highest/biggest m/z (value/ratio)

  Ignore "the peak to the right"

OR

- the ion with/it has an m/z equal to the M_r

  Ignore "compound"

1

(b) (i) 2(14.00307) + 15.99491 = 44.00105

A sum is needed to show this

1

(ii) Propane/C_3H_8 and carbon dioxide/CO_2 (and N_2O) or they or both the gases/molecules or all three gases/molecules have an (imprecise) M_r of 44.0 (OR 44)

OR

they have the same $\boldsymbol{M_r}$ or molecular mass (to one d.p)

This could be shown in a calculation of relative masses for propane <u>and</u> carbon dioxide

1

(iii) <u>By definition</u>

OR

The <u>standard</u>/<u>reference</u> (value/isotope)

Ignore "element"

Ignore "atom"

1

(c) (i) **M1 (could be scored by a correct mathematical expression)**

<u>$\Delta H = \Sigma\Delta H_{products} - \Sigma\Delta H_{reactants}$</u>

OR a <u>correct cycle of balanced equations</u>

M1 and M2 can be scored with correct moles as follows

ΔH + 2(– 46) = +82 + 3(– 286)

ΔH – 92 = – 776

ΔH = 92 – 776 OR 92 + 82 – 858

M3

ΔH = <u>– 684</u> (kJ mol^{-1}) (This is worth 3 marks)

Award 1 mark ONLY for + 684

Full marks for correct answer.

Ignore units.

Deduct one mark for an arithmetic error.

3

(ii) The value is quoted at a pressure of <u>100 kPa</u> OR <u>1 bar</u> or <u>10^5 Pa</u>

OR

<u>All reactants and products</u> are in their <u>standard states/their normal states at 100 kPa or 1 bar</u>

Ignore 1 atmosphere/101 kPa

Ignore "constant pressure"

1

[8]

Q12.

(a) <u>Functional group</u> (isomerism)

1

(b)

M1 Tollens' (reagent)
(*Credit ammoniacal silver nitrate* **OR** *a description of making Tollens'*)
(*Ignore either $AgNO_3$ or $[Ag(NH_3)_2^+]$ or "the silver mirror test" on their own, but mark M2 and M3*)

M2 silver mirror

OR

black solid/precipitate
(NOT silver precipitate)

M3 (stays) colourless
or no change or no reaction

M1 Fehling's (solution) or Benedict's solution
(*Ignore Cu^{2+}(aq) or $CuSO_4$ on their own, but mark on to M2 and M3*)

M2 Red solid/precipitate
(*Credit orange or brown solid*)

M3 (stays) blue
or no change or no reaction

Mark on from an incomplete/incorrect attempt at the correct reagent, penalising M1

No reagent, CE=0

Allow the following alternatives
***M1** (acidified) potassium dichromate(VI) (solution)*
***M2** (turns) green*
***M3** (stays) orange/no change*
OR
***M1** (acidified) potassium manganate(VII) (solution)*
***M2** (turns) colourless*
***M3** (stays) purple/no change*

For M3
Ignore "nothing (happens)"
Ignore "no observation"

3

(c) (Both have) C=O ***OR*** a carbonyl (group)

1

(d) (i) (Free-) radical substitution ONLY

Penalise "(free) radical mechanism"

1

(ii) **Initiation**
$Cl_2 \rightarrow 2Cl\bullet$

Penalise absence of dot once only.

First propagation
$Cl\bullet + CH_3CH_2CH_3 \rightarrow \bullet CH_2CH_2CH_3 + HCl$
OR C_3H_8

Penalise incorrect position of dot on propyl radical once only.

Penalise $C_3H_7\bullet$ once only

Second propagation
$Cl_2 + \bullet CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2Cl + Cl\bullet$

OR

C_3H_7Cl

Accept $CH_3CH_2CH_2$• with the radical dot above/below/to the side of the last carbon.

Termination (must make C_6H_{14})
2 $•CH_2CH_2CH_3 \rightarrow C_6H_{14}$ or $CH_3CH_2CH_2CH_2CH_2CH_3$

Use of the secondary free radical might gain 3 of the four marks

4

(e) M_r = 44.06352 (for propane)
M_r = 43.98982 (for carbon dioxide)

Mark independently

M1 a correct value for both of these M_r values.

M2 a statement or idea that two peaks appear (in the mass spectrum)

OR

two molecular ions are seen (in the mass spectrum).

2

[12]

Q13.

(a) GLC or distillation

1

(b) C=O

1

(c) (i) Cl has two isotopes

1

(ii) $CH_3\overset{+}{C}=O$

1

$C_4H_7ClO^{+•} \rightarrow CH_3\overset{+}{C}=O + C_2H_4Cl^{•}$

1

(d) (i) e.g. $CDCl_3$ or CCl_4

1

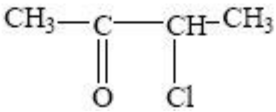
(ii) $Si(CH_3)_4$

1

(e) 0 and 3

1

(f)



1

(g) $CH_3CH_2CH_2COCl$ or $(CH_3)_2CHCOCl$ 1

[10]