1 Butane and propanal are compounds with M_r = 58.0, calculated using data from your Periodic Table.

(a) A mass spectrometer can be used to distinguish between samples of butane and propanal.

The table shows some precise relative atomic mass values.

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

(i) Use data from the table to show that, to 3 significant figures, a more accurate value for the M_r of butane is 58.1

.....

.....

.....

.....

(1)

(ii) State why the precise relative atomic mass quoted in the table for the ^{12}C isotope is exactly 12.00000

.....

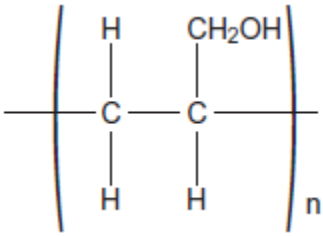
.....

(1)

(b) Draw a **displayed formula** for the organic product that is formed when propanal is oxidised by warm Tollens' reagent.

(1)

(c) Prop−2−en−1−ol is an isomer of propanal and can be polymerised to form a polymer represented by the following structure.



(i) Draw the structure of prop−2−en−1−ol.

(1)

(ii) Deduce the type of polymerisation that results in the formation of this polymer from prop−2−en−1−ol.

.....

(1)

(iii) There are two functional groups in prop−2−en−1−ol. Each of these functional groups contains a bond with a characteristic absorption range in the infrared spectrum.

Use **Table A** on the Data Sheet to suggest a bond and its absorption range for each of the two functional groups.

Bond 1 ..... Absorption range .....

Bond 2 ..... Absorption range .....

(2)

(d) Compound **X** is another isomer of propanal. The infrared spectrum of **X** shows an absorption in the range 1680−1750 cm^{-1}.

(i) Draw the structure of **X**.

(ii) Which of the following, **A**, **B**, **C** or **D**, represents the type of isomerism shown by **X** and propanal?

Write the correct letter, **A**, **B**, **C** or **D**, in the box.

A chain isomerism
B E−Z isomerism
C functional group isomerism
D position isomerism

(1)
(Total 9 marks)

2 Glucose can decompose in the presence of microorganisms to form a range of products. One of these is a carboxylic acid (M_r = 88.0) containing 40.9% carbon and 4.5% hydrogen by mass.

(a) Deduce the empirical and molecular formulas of the carboxylic acid formed.

Empirical formula = ... Molecular formula = ...

(4)

(b) Ethanol is formed by the fermentation of glucose.
A student carried out this fermentation reaction in a beaker using an aqueous solution of glucose at a temperature of 25 °C in the presence of yeast.

Write an equation for the reaction occurring during fermentation.

.....

(1)

(c) In industry, this fermentation reaction is carried out at 35 °C rather than 25 °C.

Suggest **one** advantage and **one** disadvantage for industry of carrying out the fermentation at this higher temperature.

Advantage .....

.....

Disadvantage .....

.....

(2)

(d) The method used by the student in part (b) would result in the ethanol being contaminated by ethanoic acid.

How does this contamination occur?

.....

.....

(1)

(e) Give **two** differences between the infrared spectrum of a carboxylic acid and that of an alcohol other than in their fingerprint regions.
Use **Table A** on the Data Sheet.

Difference 1 .....

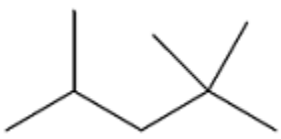
.....

Difference 2 .....

.....

(2)
(Total 10 marks)

3 Isooctane (C_8H_{18}) is the common name for the branched-chain hydrocarbon that burns smoothly in car engines. The skeletal formula of isooctane is shown below.



(a) Give the IUPAC name for isooctane.

.....

(1)

(b) Deduce the number of peaks in the ^{13}C NMR spectrum of isooctane.

5 ⬭

6 ⬭

7 ⬭

8 ⬭

(1)

(c) Isooctane can be formed, together with propene and ethene, in a reaction in which one molecule of an alkane that contains 20 carbon atoms is cracked.

Using molecular formulas, write an equation for this reaction.

.....

(1)

(d) How do the products of the reaction in part (c) show that the reaction is an example of thermal cracking?

.....

(1)

(e) Deduce the number of monochloro isomers formed by isooctane.
Draw the structure of the monochloro isomer that exists as a pair of optical isomers.

Number of monochloro isomers .....

Structure

(2)

(f) An isomer of isooctane reacts with chlorine to form only one monochloro compound.

Draw the **skeletal formula** of this monochloro compound.

(1)

(g) A sample of a monochlorooctane is obtained from a comet. The chlorine in the monochlorooctane contains the isotopes ^{35}Cl and ^{37}Cl in the ratio 1.5 : 1.0
Calculate the M_r of this monochlorooctane.

M_r = ...

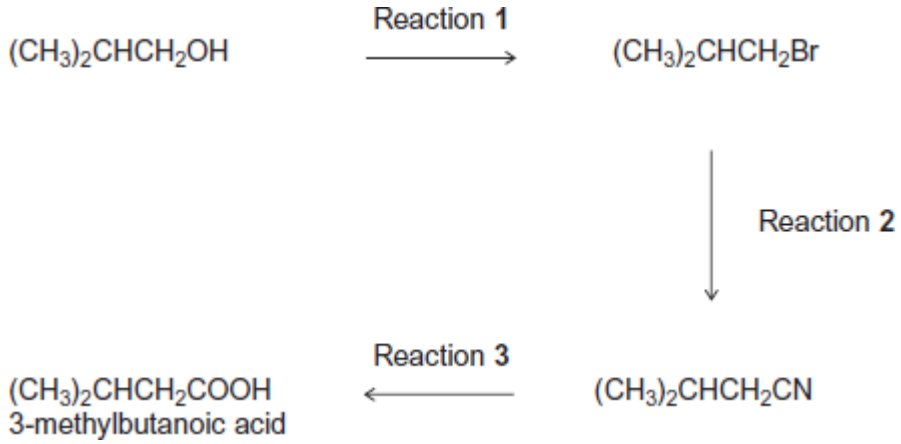
(2)

(h) Isooctane reacts with an excess of chlorine to form a mixture of chlorinated compounds. One of these compounds contains 24.6% carbon and 2.56% hydrogen by mass. Calculate the molecular formula of this compound.

Molecular formula = ...

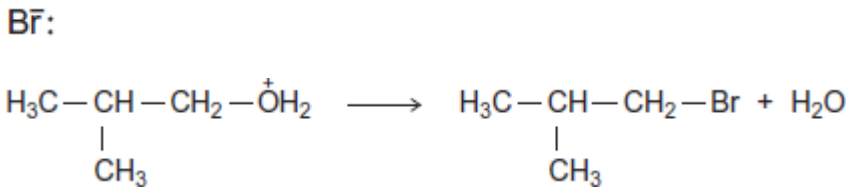
(3)
(Total 12 marks)

4 The carboxylic acid 3-methylbutanoic acid is used to make esters for perfumes.
The following scheme shows some of the reactions in the manufacture of this carboxylic acid.



(a) One of the steps in the mechanism for Reaction **1** involves the replacement of the functional group by bromine.

(i) Use your knowledge of organic reaction mechanisms to complete the mechanism for this step by drawing **two** curly arrows on the following equation.



(2)

(ii) Deduce the name of the mechanism in part (i).

Give the IUPAC name of $(CH_3)_2CHCH_2Br$

.....

.....

.....

(2)

(b) Reaction **3** is an acid-catalysed reaction in which water is used to break chemical bonds when the CN functional group is converted into the COOH functional group.
Infrared spectroscopy can be used to distinguish between the compounds in this reaction.

Deduce the name of the type of reaction that occurs in Reaction **3**.

Identify **one** bond in $(CH_3)_2CHCH_2CN$ and a **different** bond in $(CH_3)_2CHCH_2COOH$ that can be used with infrared spectroscopy to distinguish between each compound.
For each of these bonds, give the range of wavenumbers at which the bond absorbs.
Use **Table A** on the Data Sheet when answering this question.

.....

.....

.....

.....

.....

.....

.....

.....

(3)

(c) When 3-methylbutanoic acid reacts with ethanol in the presence of an acid catalyst, an equilibrium is established. The organic product is a pleasant-smelling ester.

$$(CH_3)_2CHCH_2COOH + CH_3CH_2OH \rightleftharpoons \underset{\text{an ester}}{(CH_3)_2CHCH_2COOCH_2CH_3} + H_2O$$

The carboxylic acid is very expensive and ethanol is inexpensive. In the manufacture of this ester, the mole ratio of carboxylic acid to ethanol used is 1 to 10 rather than 1 to 1.

(i) Use Le Chatelier's principle to explain why a 1 to 10 mole ratio is used. In your explanation, you should **not** refer to cost.

.....

.....

.....

.....

.....

.....

(Extra space) .....

.....

(3)

(ii) Explain how a catalyst increases the rate of a reaction.

.....

.....

.....

.....

(Extra space) .....

.....

(2)

(Total 12 marks)

1

(a) (i) C_4H_{10}

M_r = 4(12.00000) + 10(1.00794)

= <u>58.07940</u> or <u>58.0794</u> or <u>58.079</u> or <u>58.08</u>

<u>and</u> **<u>58.1</u>**

Working is essential, leading to the final value of 58.1 which must be stated in addition to one of the four numbers underlined

1

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

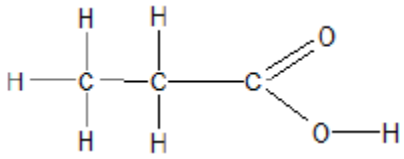
OR

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

Reference to ^{12}C alone is not enough

1

(b)



All bonds and atoms must be drawn

Give credit for the displayed formula for the anion

1

(c) (i) $H_2C = CHCH_2OH$

Any correct representation including correct use of "sticks".

Require the double bond to be shown

1

(ii) <u>Addition</u> (polymerisation)

ONLY this answer

1

(iii) **M1** **<u>C = C</u>** (in range) **<u>1620 to 1680</u>** (cm^{-1})

M2 **<u>O – H</u>** (in range) **<u>3230 to 3550</u>** (cm^{-1})

Award one mark for two correct ranges but a failure to draw out the C = C or O–H bonds

2

(d) (i) CH_3COCH_3

Any correct representation including correct use of "sticks"

1

(ii) C

1

[9]

2 (a) Percentage of oxygen by mass = 100 – 40.9 – 4.5 = 54.6 **1**

	C	H	O
%			
Divide by A_r	$\frac{40.9}{12}$	$\frac{4.5}{1}$	$\frac{54.6}{16}$
	= 3.41	= 4.5	= 3.41

1

Divide by smallest =	$\frac{3.41}{3.41} = 1$	$\frac{4.5}{3.41} = 1.32$	$\frac{3.41}{3.41} = 1$
Nearest whole number ratio =	1 × 3	1.32 × 3	1 × 3

= 3 : 3.96 : 3

Nearest integer ratio = 3 : 4 : 3 **1**

Empirical formula $C_3H_4O_3$

Empirical formula mass = 88 = molecular formula mass

Therefore, molecular formula is same as the empirical formula - $C_3H_4O_3$ **1**

(b) $C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$ **1**

(c) Advantage – ethanol is produced at a faster rate **1**

Disadvantage – more energy is used / required in the reaction **1**

(d) Air gets in / oxidation occurs **1**

(e) Alcohol OH absorption in different place (3230–3550 cm^{-1}) from acid OH absorption (2500–3000 cm^{-1}) **1**

The C=O in acids has an absorption at 1680–1750 cm^{-1} **1**

[10]

3 (a) 2,2,4-trimethylpentane **1**

(b) 5 **1**

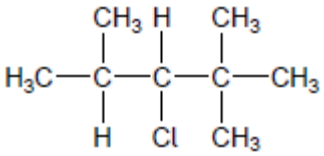
(c) $C_{20}H_{42} \longrightarrow C_8H_{18} + 2C_3H_6 + 3C_2H_4$ **1**

(d) Mainly alkenes formed

1

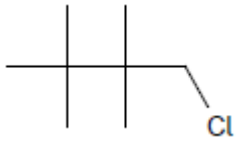
(e) 4 (monochloro isomers)

1



1

(f)



1

(g) $C_8H_{17}{}^{35}Cl = 96.0 + 17.0 + 35.0 = 148.0$
and $C_8H_{17}{}^{37}Cl = 96.0 + 17.0 + 37.0 = 150.0$
Both required

1

M_r of this $C_8H_{17}Cl$ $\frac{(1.5 \times 148.0)}{2.5} + \frac{(1.0 \times 150.0)}{2.5} = 148.8$

1

(h) $\frac{24.6}{12} \quad \frac{2.56}{1} \quad \frac{72.8}{35.5} = 2.05 : 2.56 : 2.05$

Simplest ratio = $\frac{2.05}{2.05} : \frac{2.56}{2.05} : \frac{2.05}{2.05}$

= 1 : 1.25 : 1

1

Whole number ratio (× 4) = 4 : 5 : 4

1

MF = $C_8H_{10}Cl_8$

1

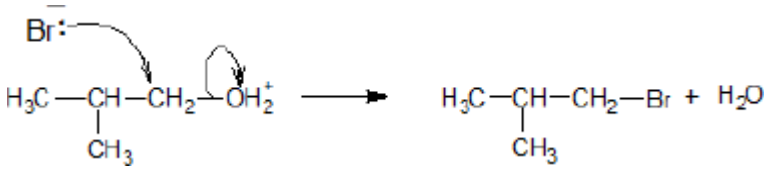
[12]

4 (a) (i) **M1** double-headed curly arrow from the lone pair of the bromide ion to the C atom of the CH_2

Penalise additional arrows.

M2 double-headed arrow from the bond to the O atom

As follows



2

(ii) **M1** nucleophilic substitution

***M1** both words needed (allow phonetic spelling).*

M2 1-bromo(-2-)methylpropane

***M2** Require correct spelling in the name but ignore any hyphens or commas.*

2

(b) **M1** hydrolysis

*For **M1** give credit for 'hydration' on this occasion only.*

M2 C≡N with absorption range 2220–2260 (cm^{-1})

*Credit 1 mark from **M2** and **M3** for identifying C≡N **and** either O–H(acids) **or** C=O **or** C–O without reference to wavenumbers or with incorrect wavenumbers.*

M3 O–H(acids) with absorption range 2500–3000 (cm^{-1})

OR

C=O with absorption range 1680–1750 (cm^{-1})

OR

C–O with absorption range 1000–1300 (cm^{-1})

*Apply the list principle to **M3***

3

(c) (i) **M1** Yield / product **OR** ester increases / goes up / gets more

M2 (By Le Chatelier's principle) the position of equilibrium is driven / shifts / moves to the right / L to R / in the forward direction / to the product(s)

M3 – requires a correct statement in M2

(The position of equilibrium moves)

to oppose the increased concentration of ethanol

to oppose the increased moles of ethanol

to lower the concentration of ethanol

to oppose the change and decrease the ethanol

*If no reference to **M1**, marks **M2** and **M3** can still score BUT if **M1** is incorrect CE=0*

*If there is reference to 'pressure' award **M1** ONLY.*

3

(ii) **M1**

Catalysts provide an alternative route / pathway / mechanism

OR

surface adsorption / surface reaction occurs

*For **M1**, not simply 'provides a surface' as the only statement.*

***M1** may be scored by reference to a specific example.*

M2

that has a lower / reduced activation energy

OR

lowers / reduces the activation energy

*Penalise **M2** for reference to an increase in the energy of the molecules.*

*For **M2**, the student may use a definition of activation energy without referring to the term.*

*Reference to an increase in successful collisions in unit time alone is not sufficient for **M2** since it does not explain why this has occurred.*

2

[12]