Answer **all** the questions.

1 Methanol is added to ethanol to make the ethanol unfit to drink.

Methanol can be made by the following reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -91\,kJ\,mol^{-1} \qquad \textbf{equation 1.1}$$

(a) A pressure of between 50 and 100 atmospheres is used for this reaction.

(i) Raising the pressure increases both the **rate** of the reaction and the **yield** of methanol.

Give the reasons for this.

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..... **[4]**

(ii) Give **one** reason why the use of high pressures is expensive.

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..... **[1]**

(iii) Describe and explain how the **yield** of methanol at equilibrium would change with increasing temperature.

In your answer you should make it clear how the points you make link together.

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..... **[3]**

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\Delta H = -91\,kJ\,mol^{-1}$ **equation 1.1**

(iv) Write the expression for the equilibrium constant, K_c, for the reaction in **equation 1.1**.

K_c =

[1]

(v) The composition of an equilibrium mixture of the gases shown in **equation 1.1** was determined at 500 K.

gas	**concentration / mol dm^{-3}**
CO(g)	0.10
H_2(g)	0.10
CH_3OH(g)	1.03

Calculate the value of K_c at 500 K and give its units.

K_c = ...units ..... **[2]**

Turn over

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\Delta H = -91\,kJ\,mol^{-1}$ **equation 1.1**

(b) Entropy data for the substances in **equation 1.1** are given in the table.

gas	$S^{\ominus}$ / J K^{-1} mol^{-1}
CO(g)	+198
H_2(g)	+131
CH_3OH(g)	+240

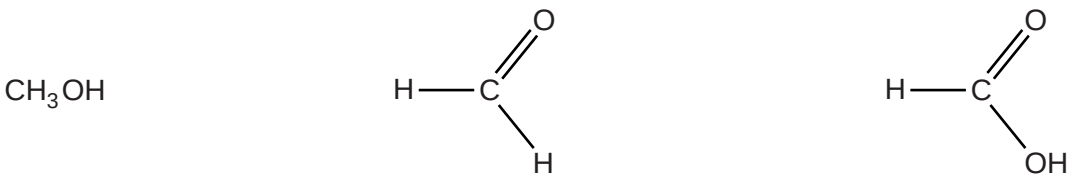
(i) Calculate $\Delta S^{\ominus}_{sys}$ for the forward reaction shown in **equation 1.1**.

$\Delta S^{\ominus}_{sys}$ = ... J K^{-1} mol^{-1} **[2]**

(ii) Calculate the temperature at which $\Delta S^{\ominus}_{tot}$ is zero for the reaction shown in **equation 1.1**.

T = ... K **[2]**

(c) Methanol is toxic. It is oxidised in the body to methanal and then to methanoic acid. Methanal and methanoic acid cause nerve damage.



methanol **methanal** **methanoic acid**

(i) Give the reagents and conditions for the laboratory oxidation of an alcohol to an aldehyde.

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..... **[2]**

(ii) Methanol, methanal and methanoic acid can be distinguished by their infrared spectra.

Describe how you could use the infrared spectra of these three compounds to distinguish between them.

For all peaks you refer to, give the wavenumber range **and** the bond responsible.

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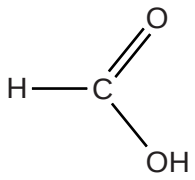
..... **[5]**

(iii) Predict the proton NMR spectrum for **methanol** by completing the table below.

type of proton	chemical shift	relative number of protons	splitting

[4]



methanoic acid

(iv) 46 g of methanoic acid vapour are found to occupy 16 dm^3 at 120 °C and room pressure.

Suggest an explanation for these data. Include a **full** structural formula in your answer.

One mole of molecules of a gas at 120 °C and room pressure occupies 32 dm^3.

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[3]

(d) Methanol is also used to make esters that are used as volatile solvents. In one process, methanol is reacted with methanoic acid to produce an ester.

(i) Draw the **full** structural formula of this ester and name it.

formula:

name ..... **[2]**

(ii) The ester in **(d)(i)** has a boiling point of 32 °C. Methanol has a boiling point of 65 °C. Explain this difference in the boiling points.

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..... **[3]**

(iii) The ester from **(d)(i)** is heated under reflux with sodium hydroxide solution.

Methanol is one of the products.

Give the systematic **name** of the other product.

..... **[1]**

[Total: 35]

2 Borane, BH_3, and diborane, B_2H_6, are reactive compounds that have been used as rocket propellants.

(a) **(i)** Give the electron configuration for a boron atom.

[1]

(ii) Draw a '*dot-and-cross*' diagram for borane, BH_3.

Show outer shell electrons only.

[1]

(iii) Use your '*dot-and-cross*' diagram to predict the shape of a molecule of BH_3.

Give reasons for your answer.

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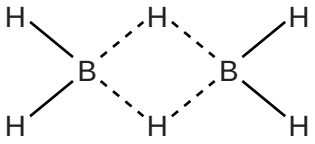
..... **[3]**

(b) The structure of diborane can be represented as shown below.



The B---H---B arrangement is unusual and is known as a 'three centre bond'.

(i) How many electrons are present in each 'three centre bond'?

..... **[1]**

(ii) A '*dot-and-cross*' model cannot be used to describe the bonding in diborane.

Suggest why chemists continue to use the '*dot-and-cross*' model, even though it cannot account for structures such as B_2H_6.

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..... **[1]**

(c) Diborane reacts with water as shown below.

$$B_2H_6 + 6H_2O \rightarrow 6H_2 + 2B(OH)_3$$

Boron is slightly less electronegative than hydrogen, so it is given the positive oxidation state in B_2H_6.

(i) Explain the meaning of the term *electronegativity*.

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..... **[2]**

(ii) Write, on the dotted lines, the oxidation states of each **hydrogen** atom in the substances below.

$$B_2H_6 + 6H_2O \rightarrow 6H_2 + 2B(OH)_3$$

....

[3]

(d) Diborane can be made industrially by reacting boron trifluoride with sodium hydride.

$$2BF_3 + 6NaH \rightarrow B_2H_6 + 6NaF$$

Some data for the compounds in this equation are given below.

substance	M_r	melting point / K
BF_3	67.8	129
NaH	24.0	1073
B_2H_6	27.6	108
NaF	42.0	1266

(i) Calculate the atom economy for the production of diborane by the reaction shown.

Comment on the implications of this value for an industrial process.

atom economy = ... %

comment .....

..... **[2]**

(ii) Use the data to suggest the type of bonding in NaH and draw a '*dot-and-cross*' diagram for NaH.

Show outer electrons only.

type of bonding .....

'*dot-and-cross*' diagram:

[3]

(e) Diborane reacts vigorously and exothermically with oxygen difluoride, OF_2. This mixture has been investigated as a rocket propellant.

The possible products of the reaction are boron(III) oxide and hydrogen fluoride.

(i) Write an equation for the above reaction.

[2]

(ii) Use your equation in **(i)** to calculate the maximum mass of OF_2 that could react with 25 g of diborane in this reaction.

Give your answer to an **appropriate** number of significant figures.

mass = ... g **[3]**

(iii) Suggest the **formula** of another possible product of the reaction of diborane and oxygen difluoride.

..... **[1]**

[Total: 23]

3 The pigment *smalt* was used by painters in the sixteenth century. It is a glass pigment made by melting cobalt(II) arsenate(V) with sand (silicon dioxide) and potassium carbonate.

(a) (i) The arsenate(V) ion can be written as $(AsO_4)^{n-}$.

Work out the value of *n* and give the formula of cobalt(II) arsenate(V).

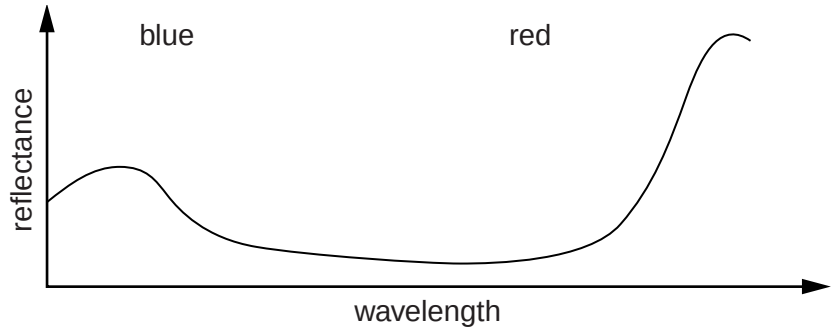
n = ... formula = ... **[2]**

(ii) Complete the electron configuration for the cobalt(II) ion.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **[1]**

(b) (i) The reflectance spectrum of smalt is shown below.

Suggest the colour of smalt and give your reasons.



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..... **[2]**

(ii) Name the element in smalt that is likely to be responsible for the colour of the pigment. Explain how the colour arises in terms of electron energy levels.

In your answer you should make it clear how the points you make link together.

name of element .....

explanation of colour .....

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..... **[5]**

(c) Cobalt in smalt can be identified by the presence of bright lines in its atomic emission spectrum.

Explain how these bright lines arise and why they are at different frequencies from the lines of other elements.

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..... **[3]**

Turn over

(d) Smalt is not used today, partly because arsenic compounds are very toxic. Their poisonous effect on the body occurs because they bind with –SH groups on the structure of a metabolic enzyme. This changes the shape of the active site.

(i) Explain the meaning of the term *active site*.

Explain how changing the shape of the active site stops the enzyme functioning.

In your answer, you should use appropriate technical terms spelled correctly.

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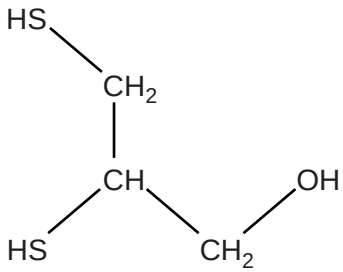
..... **[3]**

(ii) An antidote to arsenic poisoning is 'dimercaprol'.



dimercaprol

Suggest how dimercaprol counteracts the effects of arsenic poisoning.

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..... **[2]**

(iii) Dimercaprol is itself toxic. Suggest **one** of the tests that chemists had to do before allowing the use of dimercaprol as an antidote for arsenic poisoning.

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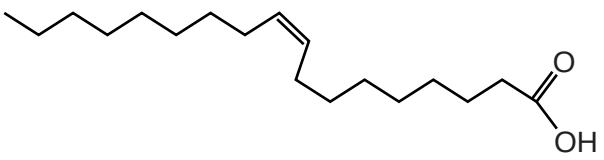
..... **[1]**

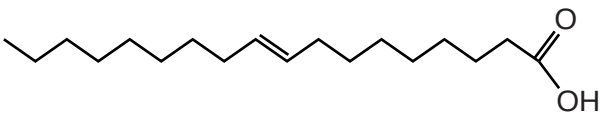
[Total: 19]

4 'Oleic acid' and 'elaidic acid' are *E/Z* isomers of $C_{17}H_{33}COOH$, both of which are found as esters in the fats that we eat.

Oleic acid is present in '*cis* fats' and elaidic acid in '*trans* fats'. '*Trans* fats' are thought to be harmful to the body but manufacturers use them because of the crispness they give to baked products. This is related to the fact that '*trans* fats' have higher melting points than '*cis* fats'.



oleic acid
melting point 13 °C



elaidic acid
melting point 46 °C

(a) Classify oleic acid as *E* or *Z*. Give a reason for your answer.

.....

..... **[1]**

(b) **(i)** Name the intermolecular bonds between the hydrocarbon chains of these acids.

..... **[1]**

(ii) Explain why elaidic acid has a higher melting point than oleic acid.

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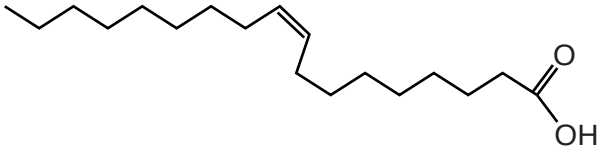
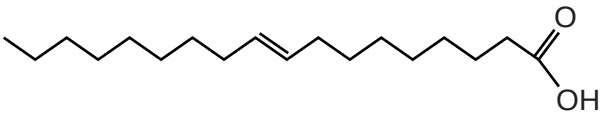
..... **[3]**



oleic acid



elaidic acid

(c) The 'iodine number' of an unsaturated carboxylic acid is the mass of iodine in grams that reacts with 100 g of the acid.

(i) Complete the equation to show an alkene group reacting with iodine:

[2]

(ii) Classify the function of iodine in this reaction by underlining **one** word below.

electrophile **nucleophile** **radical**

[1]

(iii) Calculate the iodine number of elaidic acid, $C_{17}H_{33}COOH$ (M_r = 282).

iodine number = ... g **[2]**

(iv) Write down the iodine numbers of the two other acids shown below:

oleic acid $C_{17}H_{33}COOH$ .....

stearic acid $C_{17}H_{35}COOH$ ..... **[2]**

(d) Oleic acid is insoluble in water.

Explain this insolubility in terms of intermolecular bonds.

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..... **[3]**

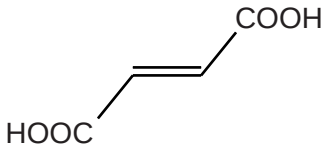
(e) Fats are triglycerides (esters of propane-1,2,3-triol). Triglycerides are hydrolysed in the body to give carboxylic acids.

Write an equation to show the hydrolysis of a triglyceride by water. Show the full structural formula of the ester group. Represent the long carbon chains by 'R'.

[4]

[Total: 19]

5 'Fumaric acid' is used as an 'acidity regulator' in food.



fumaric acid

(a) Give the **empirical** formula of fumaric acid.

..... **[1]**

(b) Maleic acid is the *E/Z* isomer of fumaric acid.

Maleic acid and fumaric acid both lose water on heating to form compound **X**.
Fumaric acid requires much stronger heating than maleic acid.

Draw the structural formula of compound **X**.

Suggest why fumaric acid needs to be strongly heated to lose water.

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..... **[3]**

(c) Fumaric acid reacts with bromine to form the compound CHBr(COOH)CHBr(COOH).

(i) Give the number of chiral centres in CHBr(COOH)CHBr(COOH).

..... **[1]**

(ii) There are three stereoisomers with the formula CHBr(COOH)CHBr(COOH).

Suggest an explanation for this.

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..... **[2]**

QUESTION 5 CONTINUES ON THE NEXT PAGE

(d) Fumaric acid acts as an acid, HA, in aqueous solution.

(i) Write the equilibrium for the ionisation of an acid, HA, in aqueous solution.

[1]

(ii) Write the terms *conjugate acid* and *conjugate base* under the appropriate formulae for an acid–base pair in your equation in **(i)**.

[1]

(iii) Calculate the pH of a 0.10 mol dm^{-3} solution of HA in water.
$K_a = 9.3 \times 10^{-4}$ mol dm^{-3}.

pH = ... **[2]**

(iv) Describe the approximations you used in doing your calculation in **(iii)**.

Explain which approximation is likely to lead to the greater inaccuracy in your answer.

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..... **[4]**

(e) A mixture of fumaric acid and sodium fumarate acts as a buffer solution and hence regulates the acidity of food.

(i) Describe what is meant by the term *buffer solution* and explain how a buffer works based on the equilibrium in part **(d)(i)**.

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..... **[5]**

QUESTION 5 CONTINUES ON THE NEXT PAGE

(ii) Calculate the pH of a buffer solution where the concentration of A^- is twice that of HA.

$K_a = 9.3 \times 10^{-4}\,\text{mol}\,\text{dm}^{-3}$

pH = ... **[2]**

(f) A student sets out to make a buffer solution. The student measures out $27\,\text{cm}^3$ of $0.050\,\text{mol}\,\text{dm}^{-3}$ HA solution and reacts it with one-third of the volume of $0.10\,\text{mol}\,\text{dm}^{-3}$ sodium hydroxide needed for complete neutralisation.

(i) Calculate the volume of sodium hydroxide solution that the student uses.

volume = ... cm^3 **[1]**

(ii) Calculate the pH of the resulting buffer solution.

$K_a = 9.3 \times 10^{-4}\,\text{mol}\,\text{dm}^{-3}$

pH = ... **[1]**

[Total: 24]

END OF QUESTION PAPER