

Answer **all** the questions.

1 'Nitrous oxide' gas, N_2O , is formed in the soil by denitrifying bacteria.

(a) (i) Give the systematic name for nitrous oxide.

..... [1]

(ii) One model of the bonding in nitrous oxide includes a dative covalent bond between the oxygen atom and the central nitrogen atom. Complete the 'dot-and-cross' diagram for a molecule of nitrous oxide based on this model.

Suggest a shape for the molecule.



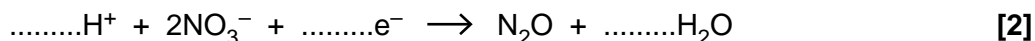
shape [3]

(b) Nitrate ions, NO_3^- , in soil undergo denitrification to nitrous oxide.

(i) Give the oxidation state of nitrogen in:

nitrate, NO_3^- nitrous oxide [2]

(ii) Balance the half-equation below by writing numbers on the dotted lines.



(iii) Give **two** reasons why this process can be referred to as **reduction**.

1

2 [2]

(iv) Suggest **one** reason why denitrification is a problem for crop production.

.....

..... [1]

- (c) When an electric spark is passed through a sample of another oxide of nitrogen it decomposes completely to nitrogen and oxygen. When the oxygen is removed from the mixture, the volume decreases by 67%.

Calculate the formula of the oxide of nitrogen, showing your working.

formula = [2]

- (d) Nitrous oxide is used as a propellant in aerosol cans. It is especially useful as an aerosol propellant for whipped dairy cream because the gas dissolves in fat. Most fats are triglycerides (esters of propane-1,2,3-triol).
- (i) Draw the **full** structural formula of a triester of propane-1,2,3-triol. Represent the hydrocarbon chains of the carboxylic acids by 'R'.

[2]

- (ii) Suggest, in terms of intermolecular bonds, why nitrous oxide is readily soluble in fat.

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..... [2]

Turn over

- (e) Nitrous oxide is a co-product in the two-stage synthesis of hexanedioic acid from cyclohexane. Hexanedioic acid is used in the production of nylon.

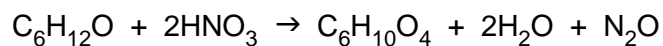


- (i) Draw the **skeletal** formulae for cyclohexane, cyclohexanol and hexanedioic acid.

cyclohexane	cyclohexanol	hexanedioic acid

[3]

- (ii) The equation for the oxidation of cyclohexanol to hexanedioic acid is shown below.



The hexanedioic acid is used in the production of nylon and the nitrous oxide is used as an aerosol propellant.

Calculate the atom economy of this reaction.

(M_r : $\text{C}_6\text{H}_{12}\text{O}$, 100; HNO_3 , 63; $\text{C}_6\text{H}_{10}\text{O}_4$, 146; H_2O , 18; N_2O , 44)

atom economy =% [2]

[Total: 22]

- 2 There are four isomeric alcohols with formula C_4H_9OH . One of the isomers is 't-butanol', $(CH_3)_3COH$, which is sometimes included as an additive to ethanol to make it undrinkable. It has the lowest boiling point of all the C_4H_9OH isomers.

(a) Draw the **skeletal** formula for t-butanol and give its systematic name.

name [2]

(b) The isomer t-butanol is **not** readily oxidised because it is a tertiary alcohol.

(i) Explain why t-butanol is classed as a *tertiary* alcohol.

.....
 [1]

(ii) Primary and secondary alcohols are readily oxidised by acidified potassium dichromate(VI).

For the reaction of **butan-2-ol** with acidified potassium dichromate(VI), give:

the colour change of the reagent, from
 to.....

the **name** of the organic product [3]

(c) t-Butanol is soluble in ethanol because the two molecules form hydrogen bonds together.

Draw a diagram of a molecule of t-butanol and a molecule of ethanol linked by **one** hydrogen bond.

Show the relevant partial charges and lone pair.

[3]

(d) t-Butanol has a lower boiling point than butan-1-ol.

Explain this in terms of intermolecular bonds.

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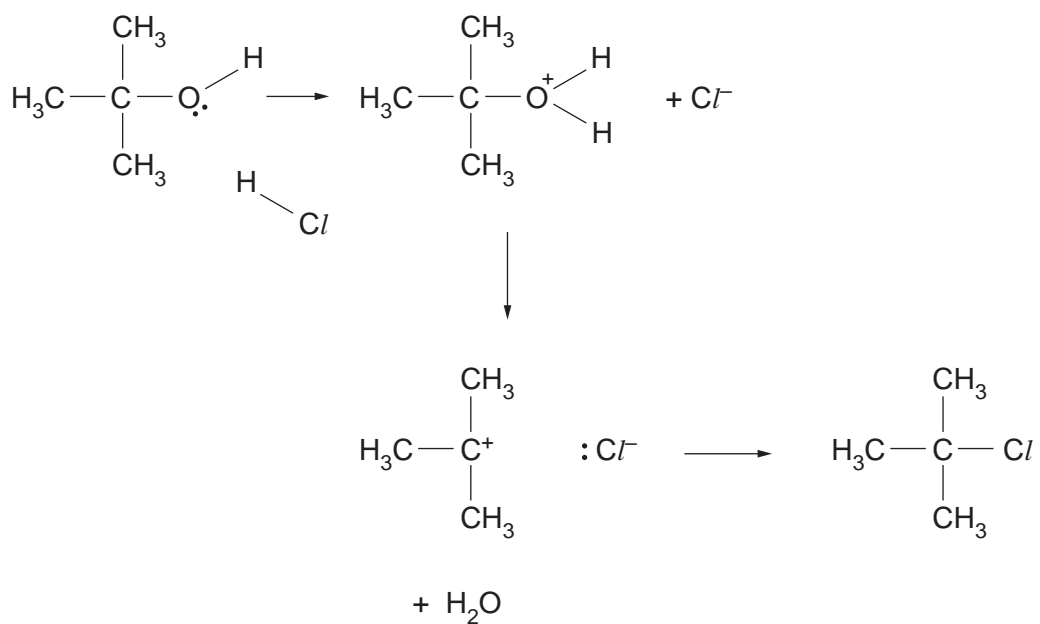
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..... [3]

(e) t-Butanol reacts with concentrated hydrochloric acid to form 2-chloro-2-methylpropane. Part of the mechanism for this reaction is shown below.

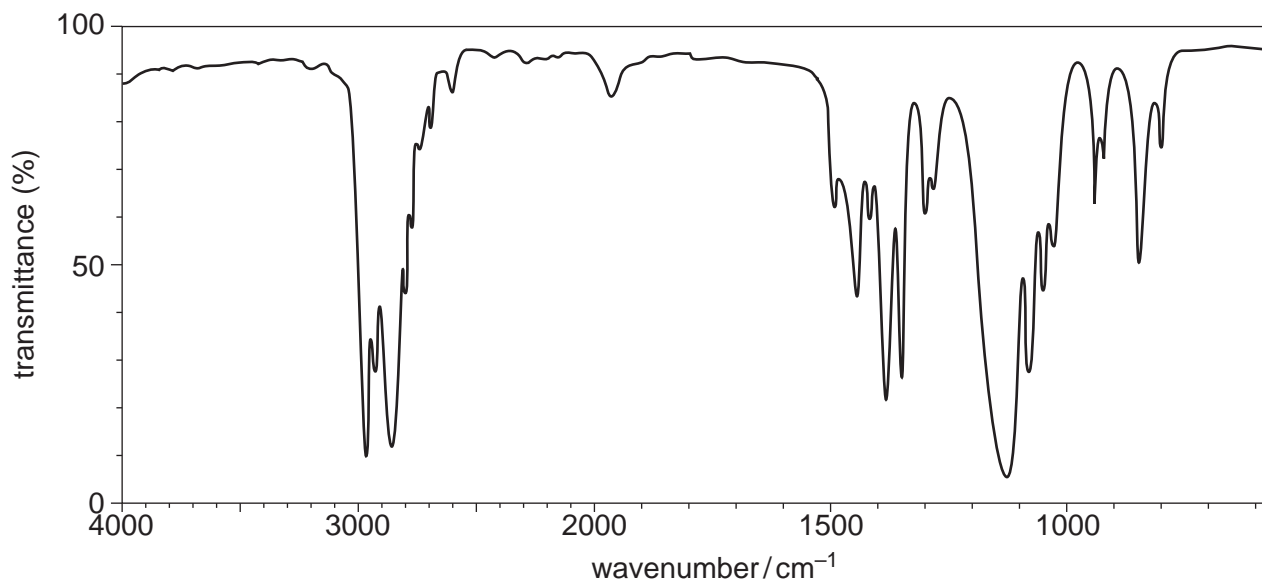
Complete the mechanism by inserting four 'curly arrows'.



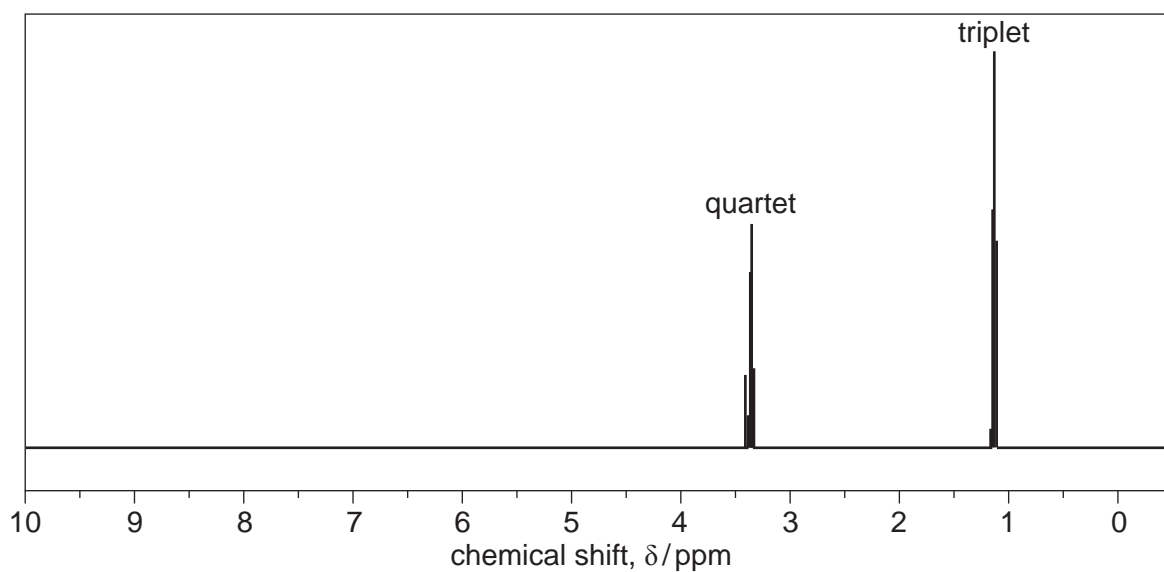
[4]

Turn over

- (f) **Compound A**, an isomer of t-butanol, $C_4H_{10}O$ is added to diesel fuel to improve its performance. The infrared and proton NMR spectra for this compound are shown below.

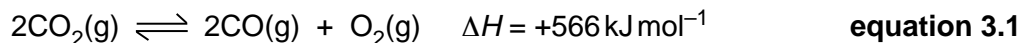


infrared spectrum of **compound A**



proton NMR spectrum of **compound A**

- 3 A novel way of removing carbon dioxide from the atmosphere has been reported. This method involves converting carbon dioxide to carbon monoxide, using the reaction shown in **equation 3.1**. The carbon monoxide can be used as a fuel or converted into hydrocarbons.



- (a) A reaction temperature of 2000K is quoted, and this is obtained by focussing sunlight on to the reaction chamber.

- (i) Describe and explain, in terms of equilibrium, the effect on the yield of carbon monoxide of increasing temperature and increasing pressure.

.....

 [4]

- (ii) Suggest why it is important that the energy for **this** reaction comes from the Sun rather than from burning fossil fuels.

.....

 [1]

- (b) (i) Write the equation for K_c for the reaction in **equation 3.1**.

$K_c =$

[1]

(ii) Use the data below to calculate the value for K_c at 2000 K. Give the units of K_c .

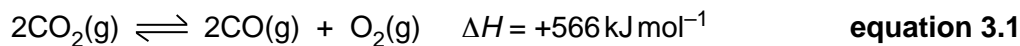
Give your answer to an **appropriate** number of significant figures.

substance	equilibrium concentration at 2000 K/mol dm ⁻³
CO ₂	1 × 10 ⁻²
CO	2 × 10 ⁻⁸
O ₂	1 × 10 ⁻⁸

$K_c = \dots\dots\dots$ units $\dots\dots\dots$ [3]

(c) (i) Calculate the entropy change of the system in **equation 3.1** from the data below.

substance	S [°] /J mol ⁻¹ K ⁻¹
CO ₂	+214
CO	+198
O ₂	+204



$\Delta S_{\text{sys}}^{\ominus} = \dots\dots\dots$ J mol⁻¹ K⁻¹ [2]

(ii) Calculate the temperature at which ΔS_{tot} is zero.

$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ $\Delta S_{\text{surr}} = -\Delta H/T$

temperature = $\dots\dots\dots$ [2]

Turn over

(d) A method of capturing carbon dioxide from power station chimneys is to react it with substances such as calcium hydroxide.

(i) Write a chemical equation for the reaction of carbon dioxide with calcium hydroxide.

[1]

(ii) Classify this reaction by underlining one term from those below.

acid–base ligand exchange precipitation redox

[1]

(iii) Suggest **one** disadvantage of using this method of capturing carbon dioxide.

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..... [1]

[Total: 16]

4 In the nineteenth century, chemists had problems determining the structure of benzene.

- (a) (i) The empirical formula was discovered by burning a known mass of benzene in air. The masses of carbon dioxide and water formed were measured. Calculations showed the empirical formula of benzene to be CH.

Calculate the mass of carbon dioxide that would be formed by burning 1.00g of benzene.

mass of carbon dioxide = g [2]

- (ii) Determinations of the M_r of benzene showed its molecular formula to be C_6H_6 .

How can the M_r of benzene be found today from its mass spectrum?

.....

 [1]

- (b) An early structure suggested for benzene was $CH_2=CH-C\equiv C-CH=CH_2$.

- (i) Draw a **full** structural formula for this structure.

Show on the diagram the values of **two different** bond angles.

[3]

- (ii) Benzene was found **not** to react with HBr at room temperature and pressure.

Explain why this cast doubt on the structure given in (i).

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 [1]

Turn over

(f) Benzene reacts with bromine to give C_6H_5Br .

(i) Give the systematic name for C_6H_5Br .

..... [1]

(ii) Write an equation for the reaction of benzene with bromine.

[1]

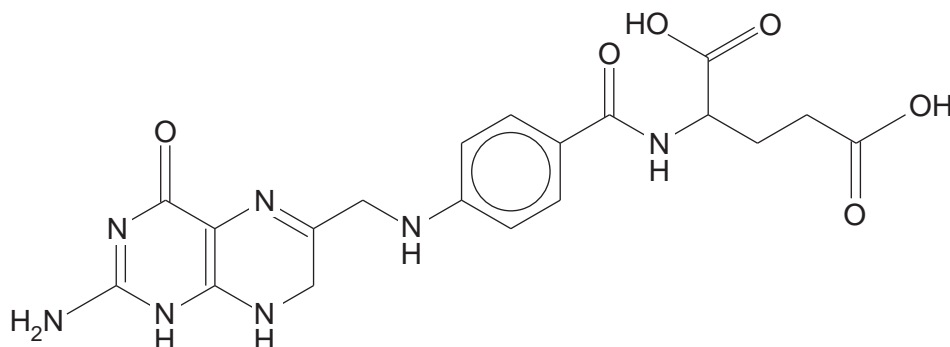
(iii) This reaction is described as *electrophilic substitution*.

Explain what you understand by the term *electrophile* and describe how bromine behaves as an electrophile in this reaction.

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..... [3]

[Total: 28]

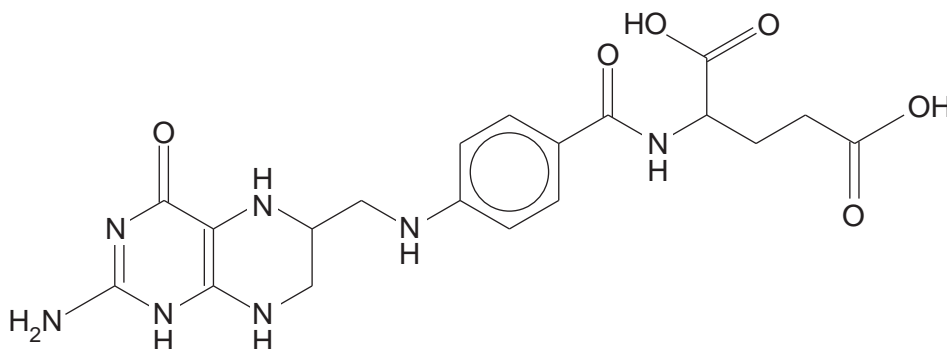
- 5 Folic acid is a vitamin of the B complex. It plays an important part in helping cells multiply. In one series of reactions it is converted to dihydrofolic acid.



dihydrofolic acid

- (a) (i) Draw a ring round a carboxylic acid group in dihydrofolic acid. [1]
- (ii) Name **two** other functional groups (not the arene ring) in dihydrofolic acid.

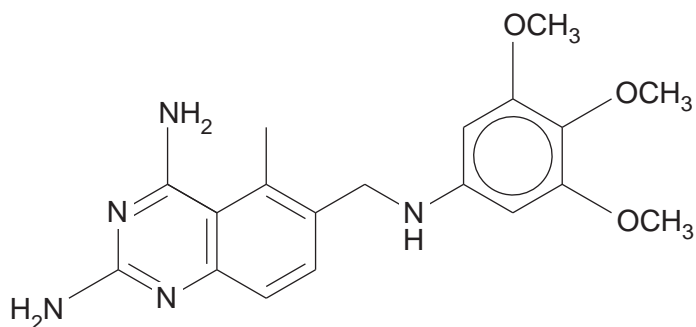
 [2]
- (iii) Indicate with an arrow the chiral carbon on the dihydrofolic acid structure above. [1]
- (b) The dihydrofolic acid is hydrogenated to tetrahydrofolic acid. The structure of tetrahydrofolic acid is shown below.



tetrahydrofolic acid

Indicate with two arrows the positions of the **two** extra hydrogen atoms in this structure, compared with dihydrofolic acid. [2]

- (c) The drug trimetrexate is used in cancer treatment as it inhibits the enzyme that catalyses the conversion of dihydrofolic acid to tetrahydrofolic acid.



trimetrexate

Suggest how trimetrexate inhibits the enzyme but cannot itself be easily hydrogenated.

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..... [3]

- (d) In the synthesis of trimetrexate, it is necessary to place a methyl group on an aromatic ring. Give the reagents and the conditions required to make methylbenzene from benzene.

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..... [3]

Turn over

(e) Folic acid behaves as a weak acid and can be represented as HA.

(i) Write the equation for the ionisation of a weak acid HA in water.

[1]

(ii) Write the terms *conjugate acid* and *conjugate base* under the appropriate formulae for an acid–base pair in your equation. [1]

(iii) Write the expression for the acidity constant, K_a , for this reaction.

$K_a =$

[1]

(iv) $K_a = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ for this ionisation of folic acid.

Calculate $\text{p}K_a$.

$\text{p}K_a = \dots\dots\dots$ [1]

(v) Calculate the pH of a 0.10 mol dm^{-3} solution of this acid.

$\text{pH} = \dots\dots\dots$ [2]

- (vi) In this calculation you made two approximations. Give the approximation which leads to the greatest inaccuracy in your answer.

Explain why this approximation causes an inaccuracy.

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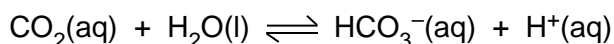
..... [2]

- (f) The folic acid we eat passes into the bloodstream unreacted. The pH of blood is 7.4.

Calculate the value of $\frac{[A^-]}{[HA]}$ for folic acid in the bloodstream.

$$\frac{[A^-]}{[HA]} = \dots\dots\dots [2]$$

- (g) One of the major buffering reactions in the blood is shown below.



- (i) Give the systematic name for HCO_3^- .

..... [1]

- (ii) Use the equilibrium to explain how the pH of the blood is buffered when a small amount of acid is added.

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..... [3]

Turn over

(h) NaHCO_3 is soluble in water. This is because the ions are hydrated in solution.

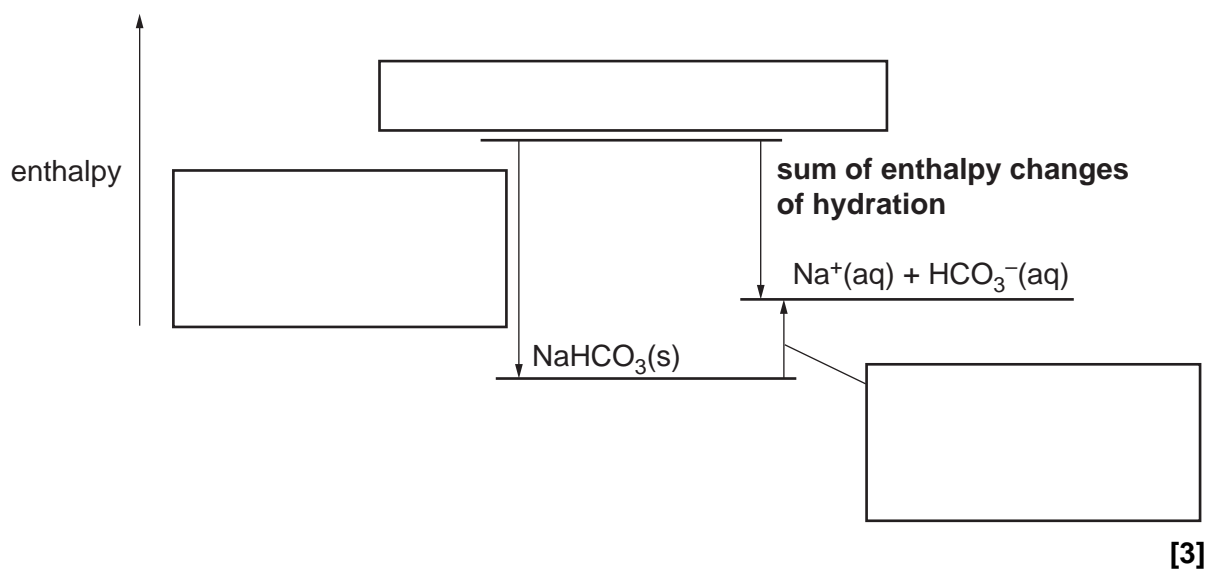
(i) Draw a labelled diagram of a hydrated sodium ion, showing charges and partial charges.

[2]

(ii) Name the interaction between the sodium ions and the water molecules.

..... [1]

(iii) Complete the enthalpy cycle for the dissolving of NaHCO_3 by writing suitable labels in the boxes provided.



[Total: 32]

END OF QUESTION PAPER