Answer **all** the questions.

1 There is concern over the way the oceans are becoming more acidic as more carbon dioxide dissolves in them.

(a) (i) Draw a '*dot-and-cross*' diagram for carbon dioxide.

Show outer electron shells only.

[1]

(ii) Use your diagram to state and explain the shape of a carbon dioxide molecule.

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

(iii) A bond between carbon and oxygen is polar but the molecule of carbon dioxide has no overall dipole.

- Describe and explain the polarity of a carbon–oxygen bond.
- Explain why the molecule of carbon dioxide has no overall dipole.

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

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

(iv) Carbon dioxide forms hydrogen bonds with water.

Draw a diagram to illustrate this.

Include relevant partial charges and lone pairs.

[3]

(v) Carbon dioxide is not very soluble in water.

Suggest an explanation for this in terms of hydrogen bonding.

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

(b) An equilibrium occurring in the oceans is:

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$ **equation 1.1**

(i) Explain why an increase in the concentration of dissolved carbon dioxide leads to an increase in the acidity of the water.

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

Turn over

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$ **equation 1.1**

(ii) The pH of the oceans is buffered by the reaction in **equation 1.1**.

Explain the meaning of *buffered* and give the important condition necessary for this equilibrium to result in buffering.

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

(c) Give the conjugate base of HCO_3^-.

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

(d) Reference books say that the pH of the oceans has changed from 8.179 in pre-industrial times to 8.069 today.

Calculate the percentage increase in $[H^+]$.

percentage increase in $[H^+]$ = ... % **[2]**

(e) **(i)** The shells of some sea creatures are made of calcium carbonate.

Use the equations below to explain a possible effect of increased acidity on the shells of these sea creatures.

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad \textbf{equation 1.2}$$

$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq) \qquad \textbf{equation 1.3}$$

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

(ii) Explain **one** reason why it may be beneficial for the human race if more carbon dioxide dissolves in the oceans.

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

(f) The concentration of a saturated solution of carbon dioxide in water is 3.3×10^{-3} mol per 100 g at room temperature and pressure.

1.0 kg of this saturated solution is boiled, releasing all the CO_2.

Calculate the volume (in **cm^3**) that this CO_2 would occupy at room temperature and pressure.

One mole of gas at room temperature and pressure occupies 24 dm^3.

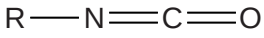
Give your answer to an **appropriate** number of significant figures.

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

[Total: 29]

Turn over

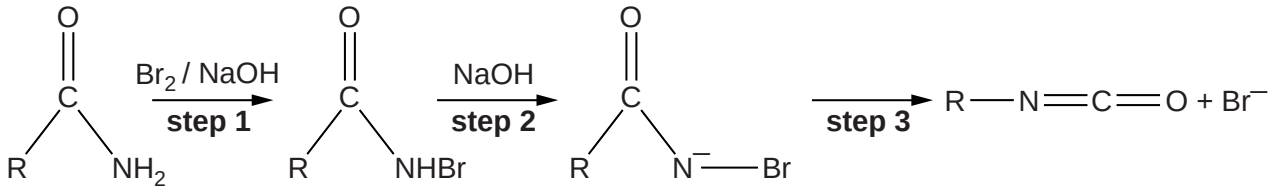
2 Isocyanates are useful organic intermediates as they can be used to make pesticides and polymers.



an isocyanate

(a) Isocyanates can be formed by reacting compound **A** with bromine and alkali.

A textbook shows the steps in the reaction as:



compound A **compound B**

(i) Name the functional group in compound **A**.

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

(ii) Name the **type** of reaction occurring in **step 2**.

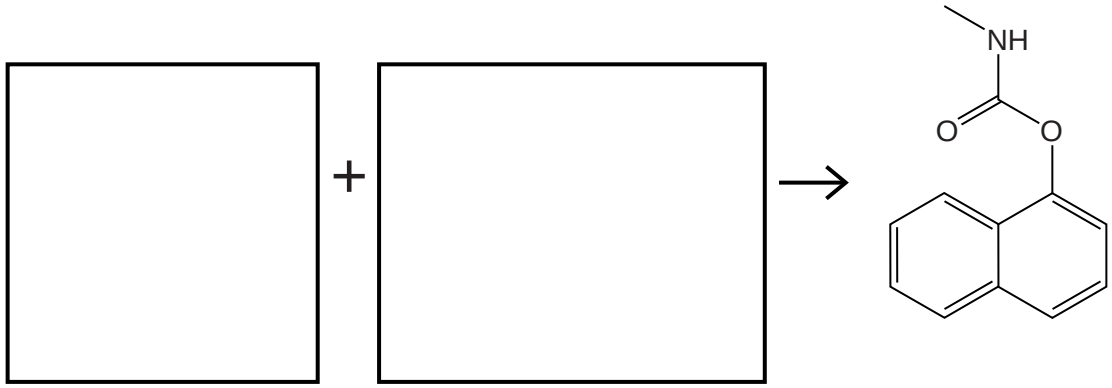
..... **[1]**

(iii) Draw 'curly arrows' on compound **B** to suggest the movement of electrons in **step 3**. **[3]**

(b) Isocyanates (R–N=C=O) form carbamates by reacting with compounds with an –OH group.

One example of a carbamate, called 'carbaryl', is an insecticide. The structure of carbaryl is shown below.

(i) Complete the equation below for the formation of carbaryl by drawing structural formulae in the boxes. **[2]**



isocyanate **compound with an –OH group** **carbaryl**

(ii) Explain, in terms of atom economy, why reactions such as that shown in the equation in **(b)(i)** could be regarded as 'environmentally friendly'.

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

(c) Carbaryl is an effective insecticide that works by reversibly inhibiting an enzyme vital to insect and mammalian metabolism. The use of carbaryl is now forbidden in the UK.

(i) Suggest **one** reason why the use of carbaryl is forbidden.

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

(ii) Suggest how carbaryl inhibits the enzyme.

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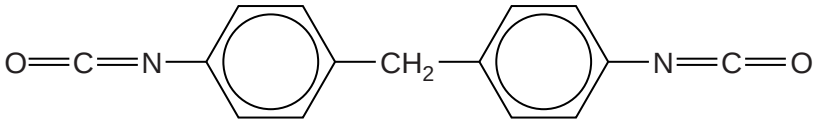
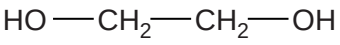
..... **[3]**

(d) Di-isocyanates are used to make polyurethane polymers.

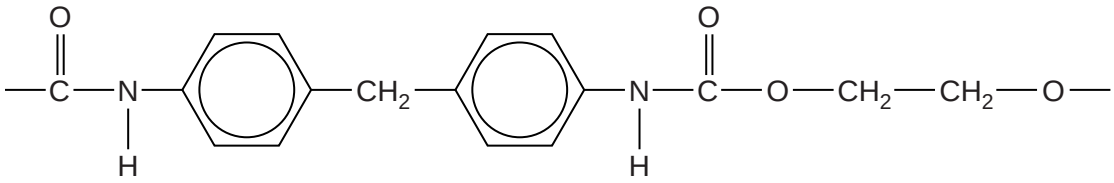
For example, the di-isocyanate MDI can react with ethane-1,2-diol to form the polyurethane shown below.



MDI



ethane-1,2-diol



polyurethane

Name the **type** of polymerisation that is described above and explain your answer.

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

(e) Polyurethane polymers can be 'blown' to produce foams.

Water vapour can be used to produce a blowing agent as it reacts with unreacted isocyanate groups to form carbon dioxide.

Suggest an equation for the reaction, representing the isocyanate as RNCO.

[1]

(f) A chemist wishes to substitute methyl groups on to the benzene rings in MDI to vary the properties of the polymer.

Give the reagents and conditions needed to substitute a methyl group on to benzene.

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

[Total: 18]

3 Methanoic acid, CH_2O_2, is used in solution as a limescale remover.

(a) Draw the **full** structural formula for methanoic acid.

[1]

(b) **(i)** Complete the equation for the ionisation of methanoic acid in aqueous solution.

$CH_2O_2 \rightleftharpoons$

[1]

(ii) Write the expression for K_a for methanoic acid.

K_a =

[1]

(iii) The pK_a of methanoic acid is 3.77.

Show that $K_a = 1.70 \times 10^{-4}$ mol dm^{-3}.

[1]

(iv) Calculate the pH of a 0.0040 mol dm^{-3} solution of methanoic acid.

Give your answer to **two** decimal places.

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

(v) You used two approximations in **(iv)**. One of these is not a very good approximation when used for acids as strong as methanoic acid.

- Give the approximation.
- Explain, with reference to numbers in your calculation, why it is not a very good approximation.

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

(c) Limescale is mainly calcium carbonate. Write an equation for the reaction of methanoic acid with calcium carbonate.

[2]

(d) Methanoic acid and methanoates together form buffer solutions.

(i) Calculate the pH of a solution containing equal amounts of methanoic acid and sodium methanoate.

$K_a = 1.70 \times 10^{-4}\,\text{mol}\,\text{dm}^{-3}$.

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

(ii) Enough sodium hydroxide is added to react with half the methanoic acid in the mixture of methanoic acid and sodium methanoate in **(i)**.

Calculate the pH of the resulting solution.

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

Turn over

(e) Methanoic acid can be made in the laboratory by the oxidation of methanol. A chemist attempts to oxidise methanol and purifies an organic product from this reaction.

(i) The product has just one peak in its proton NMR spectrum.

Identify the product and explain why it gives the NMR spectrum described.

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

(ii) The chemist runs an infrared spectrum of this product.

Give the wavenumber ranges of the peaks (above 1500 cm^{-1}) and the bonds responsible for these peaks that you would expect to find in the infrared spectrum.

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

(f) Methanoic acid vapour (CH_2O_2) decomposes in the presence of certain catalysts to give carbon dioxide and hydrogen.

(i) Suggest an industrial use for the hydrogen produced by this reaction.

.....

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

(ii) Write the equation for the equilibrium reaction for the decomposition of methanoic acid.

Complete the expression for K_c for this equilibrium.

equation:

K_c =

[1]

(iii) Give the **sign** of the ΔS_{sys} for the forward reaction in **(ii)** and give your reasons.

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

(iv) The value of K_c at 298 K for the reaction in **(f)(ii)** is 4.8×10^6 mol dm^{-3}.
Methanoic acid vapour is allowed to reach equilibrium at 298 K.
The concentration of methanoic acid vapour in the equilibrium mixture is found to be 2.5×10^{-9} mol dm^{-3}.

Calculate the equilibrium concentrations of CO_2 and H_2.

concentration of CO_2 = ... mol dm^{-3}

concentration of H_2 = ... mol dm^{-3} **[2]**

(v) A student suggests that the reaction in **(f)(ii)** should be carried out at low pressure.

Give the chemical reasoning behind this suggestion.

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

(vi) The enthalpy change for the forward reaction in **(f)(ii)** is +6 kJ mol^{-1}. The student suggests that the reaction should be carried out at high temperature because of the effect of temperature on the equilibrium yield of products.

Give the chemical reasoning behind this suggestion.

Suggest why it might not be economical to use a high temperature in this case.

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

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

[Total: 29]

Turn over

4 In 2014, it is hoped that a European spacecraft called Rosetta will send a landing craft to a distant comet. One of the many measuring instruments on the landing craft will be a gas–liquid chromatograph linked to a mass spectrometer.

(a) A gas–liquid chromatograph uses a carrier gas moving through a column.

(i) Give an important feature of the carrier gas.

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

(ii) What is inside the column?

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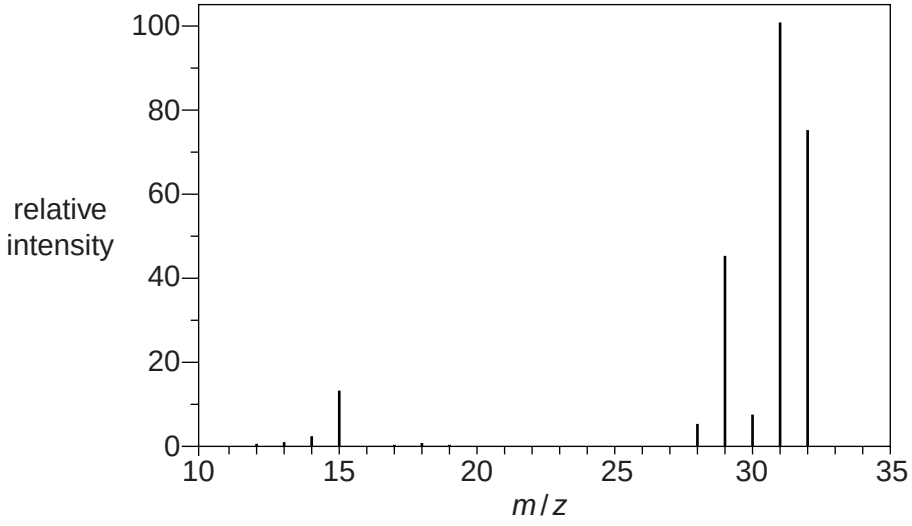
..... **[1]**

(iii) What measurement is used to distinguish the compounds separated by the gas–liquid chromatograph?

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

(b) The compounds emerging from the gas–liquid chromatograph are passed through a mass spectrometer. This is used to determine the M_r of the substances and to give more detailed information about their structure.

The mass spectrum of a simple **organic** compound, containing C, H and O only, is shown below.



(i) What is the M_r of the compound?

Explain how you arrived at your answer.

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

(ii) Suggest the formula of the ion that gives rise to the peak at m/z 15.

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

(iii) Suggest a formula for the compound.

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

(c) The gas chromatograph on the Rosetta landing craft will be able to distinguish between chiral compounds. Scientists will be looking for evidence of amino acids in the comet's tail.

(i) Draw below the structures of the two enantiomers of the amino acid serine, $HOOC–CH(CH_2OH)–NH_2$, to show how they are related.

[2]

(ii) Suggest why scientists are looking for the presence of amino acids in the comet.

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

(d) In 2005, a spacecraft landed on Titan, a moon of Saturn. By gas chromatography, scientists discovered that the atmosphere of Titan contained, among other things, methane, traces of ethane and traces of cyanogen, $(CN)_2$.

(i) High-energy ultraviolet radiation from the Sun breaks down the methane to produce radicals which start a chain reaction. Some of the radicals combine to form ethane.

Write two equations that illustrate the formation of ethane from methane by this method.

Classify each of these equations in terms of the **type** of radical reaction involved.

[4]

(ii) Cyanogen, $(CN)_2$, reacts with ethene in an electrophilic addition where two CN groups are added across the double bond, producing compound **C**.

Compound **C** can be hydrolysed in acid solution to form compound **D**.

Predict the structural formulae of compounds **C** and **D**.

You may need to refer to your *Data Sheet*.

compound C **compound D**

[2]

[Total: 17]

5 'Titanium yellow' is a pigment with formula $NiO•Sb_2O_5•20TiO_2$ that is used for oil painting.

(a) Complete the electron configurations for a titanium atom and for the titanium ion with the oxidation state that titanium shows in TiO_2.

atom $1s^2\ 2s^2\ 2p^6\ 3s^2$ .....

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

(b) Give the oxidation state of antimony in Sb_2O_5 and the systematic name of Sb_2O_5.

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

(c) Calculate the percentage by mass of titanium in $NiO•Sb_2O_5•20TiO_2$ (M_r 1996).

percentage Ti = ... % **[2]**

(d) On a computer screen, the colour of titanium yellow can be represented by mixing 93% red, 90% green and 0% blue.

Sketch the visible reflectance spectrum of titanium yellow on the axes below.

Label the axes. (No scales are necessary.)

[3]

Turn over

(e) Explain, in terms of electron energy levels, why compounds of transition metals are coloured.

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

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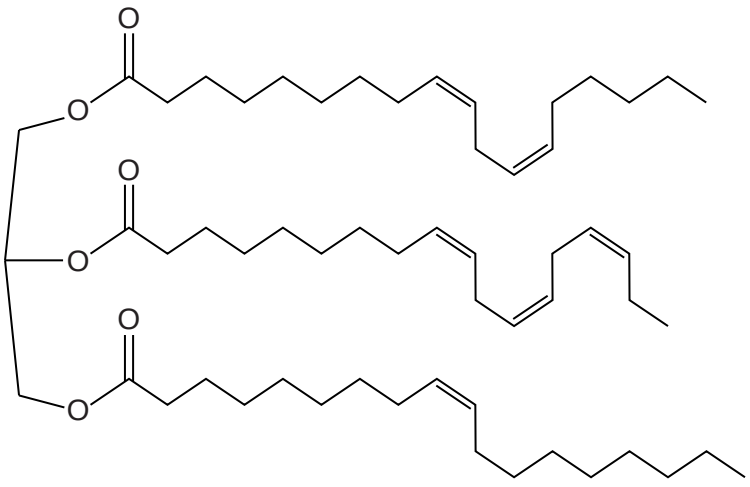
..... **[5]**

(f) An oil is used to suspend the pigment for oil painting. A good oil for this purpose is linseed oil. One of the constituents of linseed oil, compound **E**, is shown below.



compound E

(i) Name the functional group (apart from the C=C group) found in compound **E**.

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

(ii) Classify the arrangements around the C=C double bonds in compound **E** as *cis* or *trans*, giving your reasoning.

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

(iii) Suggest why oils with *trans* groups have higher boiling points than those with *cis* groups.

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

Question 5 continues on page 20

(g) Unsaturated oils react with iodine.

(i) Complete the equation below to show the reaction of iodine with a carbon–carbon double bond in an oil.

[2]

(ii) The 'iodine number' of an oil is the number of grams of iodine that will react with 100 g of the oil.

0.200 g of a sample of linseed oil is reacted with a solution containing 0.00170 mol of I_2 (an excess).

Some iodine remains unreacted.

28.0 cm^3 of 0.0200 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$, are needed to react with the iodine **remaining**.

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Calculate the iodine number of the sample of linseed oil.

iodine number = ... **[5]**

[Total: 27]

END OF QUESTION PAPER