OCR
RECOGNISING ACHIEVEMENT

**ADVANCED GCE** **2854/01**

**CHEMISTRY (SALTERS)**

Chemistry by Design

**THURSDAY 24 JANUARY 2008** Afternoon

Time: 2 hours

Candidates answer on the question paper.
**Additional materials:** Scientific calculator
*Data Sheet for Chemistry (Salters)* (Inserted)

*CUP/T45134*

| Candidate Forename | | Candidate Surname | |
|---|---|---|---|

| Centre Number | | | | | | Candidate Number | | | | |
|---|---|---|---|---|---|---|---|---|---|---|

**INSTRUCTIONS TO CANDIDATES**

- Write your name in capital letters, your Centre Number and Candidate Number in the boxes above.
- Use blue or black ink. Pencil may be used for graphs and diagrams only.
- Read each question carefully and make sure that you know what you have to do before starting your answer.
- Answer **all** the questions.
- Do **not** write in the bar codes.
- Do **not** write outside the box bordering each page.
- Write your answer to each question in the space provided.

**INFORMATION FOR CANDIDATES**

- The number of marks for each question is given in brackets [ ] at the end of each question or part question.
- The total number of marks for this paper is **120**.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry (Salters)*.
- You are advised to show all the steps in any calculations.

| FOR EXAMINER'S USE | | |
|---|---|---|
| **Qu.** | **Max.** | **Mark** |
| **1** | **16** | |
| **2** | **30** | |
| **3** | **28** | |
| **4** | **25** | |
| **5** | **21** | |
| **TOTAL** | **120** | |

This document consists of **20** printed pages and a *Data Sheet for Chemistry (Salters)*.



**[Turn over**

Answer **all** the questions.

**1** Methanol, $CH_3OH$, can be oxidised to methanal, HCHO, by a variety of methods.

One method involves the catalytic oxidation of methanol over a platinum catalyst. This method is used in model aircraft engines to avoid the use of a sparking plug.

**(a) (i)** Write an equation for the oxidation of methanol to methanal by the oxygen in the air.

[1]

**(ii)** Draw a full structural formula for **methanal**.

[1]

Another method of converting methanol to methanal involves the dehydrogenation of methanol by heating its vapour over copper at 300 °C to produce an equilibrium mixture.

$$CH_3OH(g) \rightleftharpoons HCHO(g) + H_2(g) \qquad \Delta H = +80\,kJ\,mol^{-1} \qquad \textbf{equation 1.1}$$

**(b) (i)** What would be the effect of raising the temperature on the **yield** of methanal?

Explain your answer.

.....

.....

.....

..... [2]

**(ii)** What would be the effect of raising the pressure on the **yield** of methanal?

Explain your answer.

.....

.....

.....

..... [2]

**(c)** **(i)** Write the equation for $K_p$ for the equilibrium in **equation 1.1** and give its units when pressures are measured in atmospheres.

$K_p$ =

units ..... [2]

**(ii)** Calculate the partial pressure of methanal in an equilibrium mixture at 300 °C, given the following data.

| | |
|---|---|
| numerical value of $K_p$ at 300 °C | $4.1 \times 10^{-5}$ |
| partial pressure of $CH_3OH$ | 1.1 atm |
| partial pressure of $H_2$ | $7.0 \times 10^{-3}$ atm |

partial pressure of methanal = ..... atm [2]

**(d)** Methanal can be reduced back to methanol in the laboratory.

**(i)** Use your *Data Sheet* to write down the formula of the reagent that is used in this reduction.

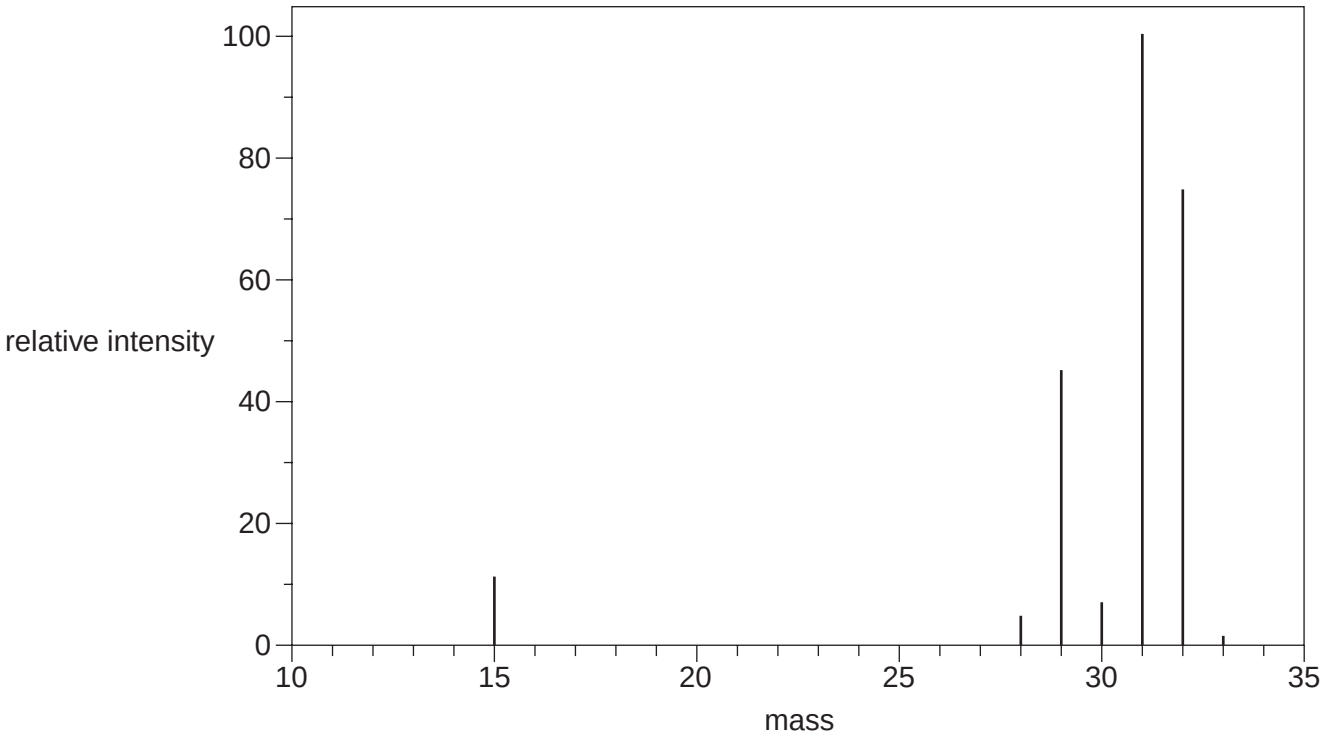
..... [1]

**(ii)** This reagent can be regarded as a source of hydride, $H^-$, ions. $H^-$ ions react with methanal by the same mechanism as $CN^-$ ions.

Name this mechanism.

..... [2]

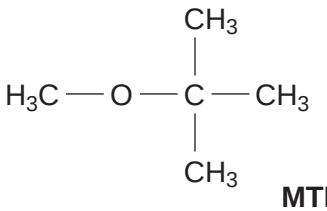
**(e)** The presence of methanol can be confirmed by its mass spectrum, shown below.




Choose **two** peaks in the spectrum and label each with the formula of the ion that gives rise to that peak. [3]

[Total: 16]

**2** MTBE is added to car petrol as an oxygenate. There has been concern over the leakage of MTBE into water supplies, mainly because of the foul taste it gives to the water.



**MTBE**

**(a)** **(i)** Suggest why oxygenates are added to car petrol.

.....

..... [1]

**(ii)** Name the functional group in MTBE.

..... [1]

**(b)** The solubility of MTBE in water has been measured as $0.5\,\text{mol}\,\text{dm}^{-3}$ at 20 °C. An estimate of the lowest detectable concentration of MTBE in drinking water is $4 \times 10^{-6}\,\text{g}\,\text{dm}^{-3}$.

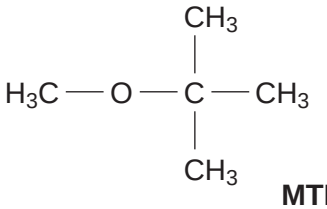
Calculate the ratio of the solubility to the lowest detectable concentration.

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

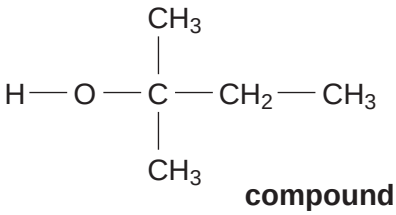
$A_r$: C,12; H, 1.0; O, 16

answer = ..... [3]

**(c)** MTBE has several isomers that have been investigated as oxygenates. One of these isomers, **compound A**, is shown below.



**MTBE**



**compound A**

**(i)** Name the **type** of isomerism by which MTBE and **compound A** are related.

..... [1]

**(ii)** Give the systematic name of **compound A**.

..... [2]

**(iii)** **Compound A** has a higher boiling point than MTBE.

Explain why this is so.

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..... [4]

**(iv)** Alcohols like **compound A** cannot easily be oxidised to carbonyl compounds.

- What reagents and conditions would normally be used in a laboratory to oxidise alcohols to carbonyl compounds?
- What would you see during this oxidation?
- What feature of **compound A** indicates that it cannot easily be oxidised?

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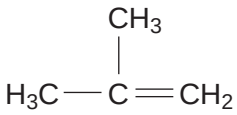
..... [4]

**(d)** MTBE can be made by reacting **compound B** with methanol in the presence of an acid catalyst.



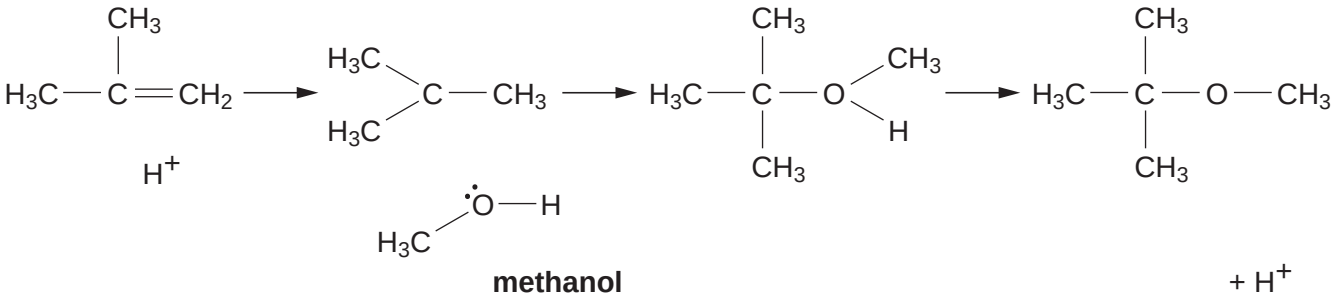
**compound B**

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

..... [1]

**(ii)** Complete the mechanism below by inserting 'curly arrows' to show the movement of pairs of electrons and by inserting charges.

**compound B** **MTBE**




[4]

**(iii)** Circle **two** words in the list below that describe the mechanism of this reaction.

| | | |
|---|---|---|
| **addition** | **electrophilic** | **elimination** |
| **nucleophilic** | **radical** | **substitution** |

[2]

**(iv)** Explain how the mechanism shows that the reaction is catalysed by acid.

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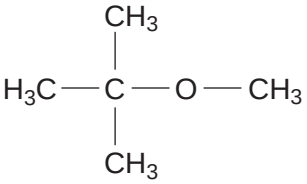
.....

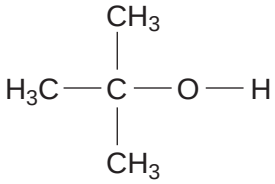
..... [2]

**(e)** Compounds **C** and **D**, shown below, are also oxygenates.

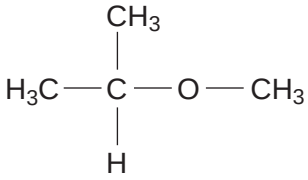
The infrared and proton n.m.r. spectra of **one** of the following compounds are shown below and on the next page.



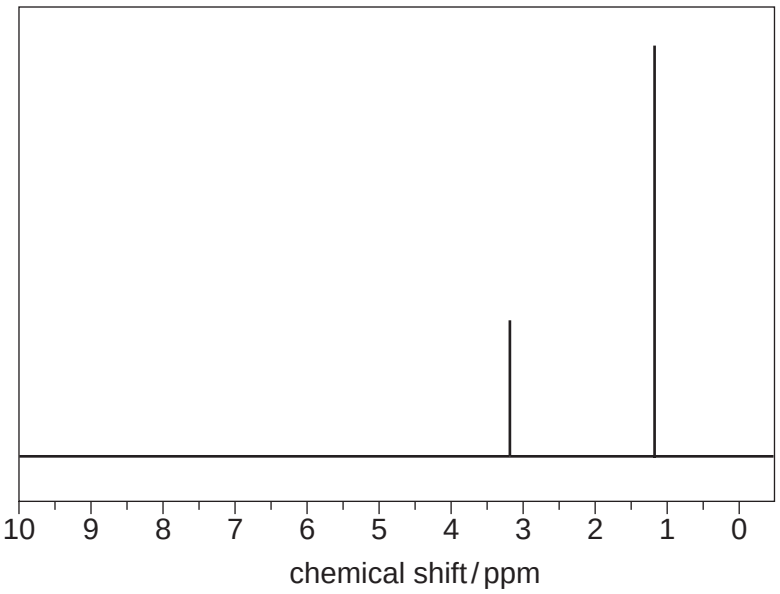
**MTBE**



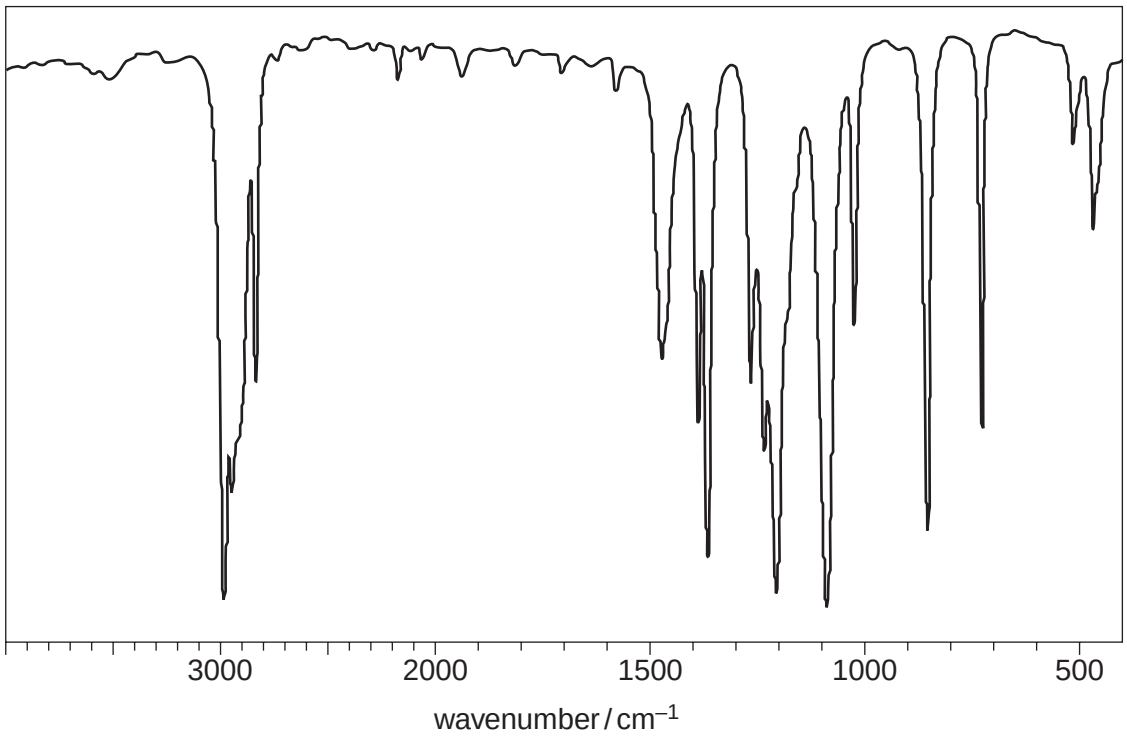
**compound C**



**compound D**




**n.m.r. spectrum**




**i.r. spectrum**

Explain what you can deduce about the identity of the compound from **each** spectrum. Then make a final identification of the compound.

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..... [5]

[Total: 30]

**3** Ammonium nitrate, $NH_4NO_3$, is a very common fertiliser. It is made by reacting ammonia with nitric acid.

**(a) (i)** Name the three **raw materials** that are used to make ammonia on an industrial scale.

1 .....

2 .....

3 ..... [3]

**(ii)** Write an equation for the formation of ammonium nitrate from ammonia and nitric acid, $HNO_3$.

[1]

**(iii)** Nitric acid is a strong acid.

Write an equation for the ionisation of nitric acid in water.

[1]

**(b) (i)** Draw a dot-cross diagram to show the bonding in the ammonium ion, $NH_4^+$.

[2]

**(ii)** Give the bond angle in the ammonium ion and explain your reasoning.

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.....

.....

..... [3]

**(iii)** In this question, one mark is available for the quality of spelling, punctuation and grammar.

Ammonium nitrate has a giant ionic structure but decomposes before it melts.

Predict **two** other properties of ammonium nitrate, based on its structure and bonding. Explain the reasons for your predictions.

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..... [4]

Quality of Written Communication [1]

**(c)** Calculate the percentage of nitrogen by mass in ammonium nitrate, $NH_4NO_3$.

$A_r$: N, 14; H, 1.0; O, 16

answer = ..... % [2]

**(d)** Suggest **two** reasons why ammonium nitrate is an effective fertiliser.

reason 1 .....

.....

reason 2 .....

..... [2]

**(e)** The ammonium ion is acidic in aqueous solution.

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \qquad \textbf{equation 3.1}$$

**(i)** Which feature of this equation tells you that the ammonium ion is a *weak* acid?

..... [1]

**(ii)** Write the expression for $K_a$ for **equation 3.1**.

[1]

**(iii)** Calculate the $H^+$ ion concentration in a 0.010 mol dm$^{-3}$ solution of ammonium ions, given that $K_a = 5.6 \times 10^{-10}$ mol dm$^{-3}$.

$[H^+]$ = ..... mol dm$^{-3}$ [2]

**(iv)** Calculate the pH of this solution.

pH = ..... [1]

**(f)** $$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \qquad \textbf{equation 3.1}$$

The reaction in **equation 3.1** can form the basis of a buffer solution.

**(i)** Name two suitable solutions to mix to give a buffer solution based on **equation 3.1**.

.....

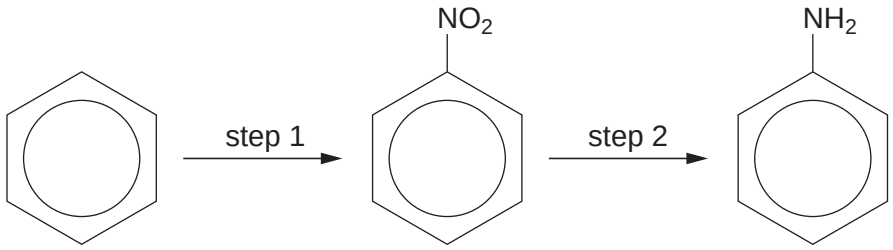
..... [2]

**(ii)** Equal volumes of equal concentrations of these two solutions are mixed. Calculate the pH of the resulting buffer solution.

pH = ..... [2]

[Total: 28]

**4** Azo dyes are made by coupling two components. One of these is often an aromatic amine, the simplest of which is phenylamine (aniline) made from benzene.




**benzene** **compound C** **phenylamine**

**(a) (i)** Name **compound C**.

..... [1]

**(ii)** Give the reagents and conditions for **step 1**.

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..... [3]

**(iii)** Use your *Data Sheet* to give the reagents and conditions for **step 2**.

.....

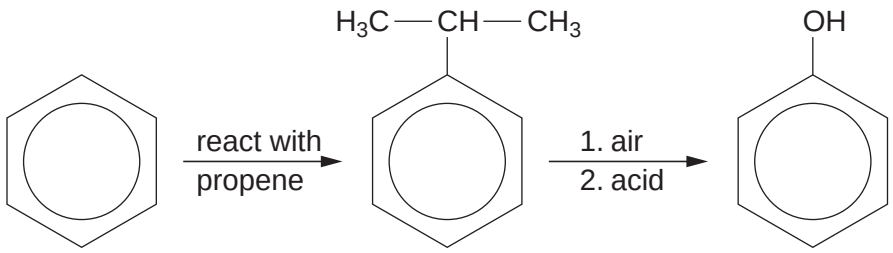
..... [1]

**(iv)** Benzene is made from crude oil fractions by processes such as reforming.

Give the equation for the reforming reaction in which benzene is made from hexane.

[2]

**(b)** The other component for making azo dyes is often a phenol. Phenol itself is made by the following route.




**benzene** **'cumene'** **phenol**

**(i)** The reaction with propene is a Friedel-Crafts reaction. Give the catalyst and conditions for this reaction.

.....

..... [2]

**(ii)** There is a simple test for the phenol group. Describe this test and its result.

.....

.....

..... [2]

**(iii)** In a manufacturing process, 1000 g of benzene gives 1050 g of phenol. Calculate the percentage yield of the process.

$A_r$: C, 12; H, 1.0; O, 16

yield = ..... % [2]

**(c)** Phenylamine is made into a diazonium salt by reaction with cold nitrous acid. The diazonium salt then reacts with phenol in a coupling reaction.

**(i)** Give the conditions for the coupling reaction.

.....

..... [2]

**(ii)** Draw the structure of the azo dye that is formed.

[2]

**(d)** Benzene and phenylamine can be distinguished by their ultraviolet spectra. Benzene absorbs at 204 nm wavelength and phenylamine absorbs at 230 nm wavelength.

Suggest a feature of the phenylamine molecule that enables it to absorb at a higher wavelength (lower frequency).

.....

..... [1]

**(e)** In this question, two marks are available for the quality of the use and organisation of scientific terms.

The azo dye in **c(ii)** is red–orange. Explain, in terms of electron energy levels, why the dye is coloured while benzene is colourless.

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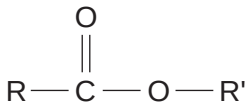
..... [5]

Quality of Written Communication [2]

[Total: 25]

**5** Permethrin pesticides consist of large non-polar groups joined by an ester link. These molecules are much more soluble in fats than they are in water.

In the diagram below, the large non-polar groups are represented by R and R'.




**(a)** Fats in insect bodies consist mainly of triglycerides. (These are esters of propane-1,2,3-triol.)

Draw the full structural formula of a triglyceride, representing long carbon chains by R.

[2]

**(b)** The intermolecular forces between adjacent fat molecules are of similar strength to those between fat molecules and pesticide molecules.

**(i)** Name the **main** type of intermolecular force involved.

..... [1]

**(ii)** Pesticides are soluble in fats. The reason for the solubility is that the entropy of the system increases.

Explain the entropy increase.

.....

..... [1]

**(c)** $K_{ow}$ is used to measure the relative solubilities of a pesticide in octan-1-ol and water. Octan-1-ol resembles a fat in its solvent properties.

**(i)** Suggest why octan-1-ol behaves like a fat in its ability to act as a solvent for pesticides.

.....

..... [1]

**(ii)** Explain why the most efficient pesticides have high $K_{ow}$ values.

.....

.....

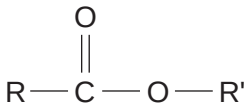
.....

.....

..... [3]

**(d)** When permethrin pesticides reach the soil, they are rapidly hydrolysed. The products of hydrolysis are more soluble in water.

**(i)** Draw the structures of an organic ion and an organic molecule resulting from the **alkaline** hydrolysis of the pesticide represented by the molecule below.




| organic ion | organic molecule |
| --- | --- |
| | |

[2]

**(ii)** The organic molecule dissolves because it forms hydrogen bonds with water.

Draw a diagram below to show the formation of **one** such hydrogen bond between the organic molecule and a molecule of water.

Show lone pairs and partial charges.

[4]

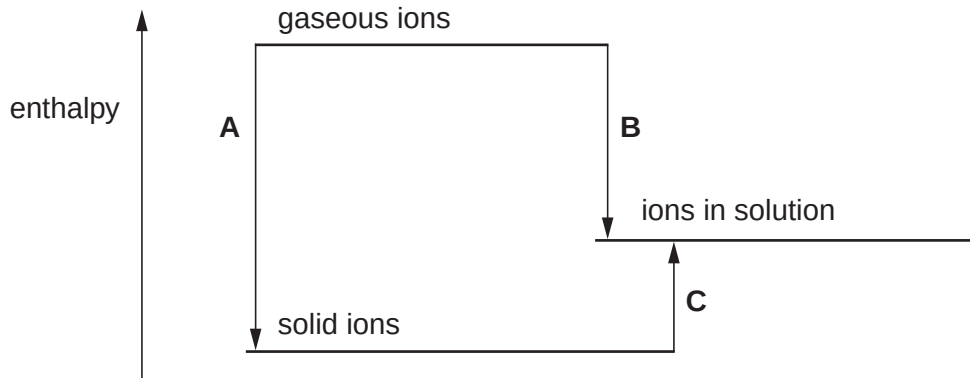
**(iii)** The organic ion dissolves because it is hydrated by water molecules.

Draw a diagram to illustrate this.

Represent the ion by **X**.

[2]

**(e)** The dissolving of some ionic solids can be represented by the enthalpy level diagram below.




**(i)** Write appropriate labels for the enthalpy changes **A**, **B** and **C** in the table below. [4]

| letter | label | value / kJ mol$^{-1}$ |
|---|---|---|
| **A** | | –3728 |
| **B** | | –3725 |
| **C** | | |

**(ii)** Calculate the value of enthalpy change **C** and write it in the table with the appropriate sign. [1]

[Total: 21]

**END OF QUESTION PAPER**

**PLEASE DO NOT WRITE ON THIS PAGE**