OCR
RECOGNISING ACHIEVEMENT

OXFORD CAMBRIDGE AND RSA EXAMINATIONS
Advanced GCE

CHEMISTRY (SALTERS) 2854

Chemistry by Design

Tuesday **24 JUNE 2003** Morning 2 hours

Candidates answer on the question paper
Additional materials:
Data Sheet for Chemistry (Salters)
Scientific Calculator

Candidate Name	Centre Number	Candidate Number

TIME 2 hours

INSTRUCTIONS TO CANDIDATES

- Write your name in the space above.
- Write your Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers in the spaces provided on the question paper.
- Read each question carefully and make sure you know what you have to do before starting your answer.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [ ] at the end of each question or part question.
- 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 a *Data Sheet for Chemistry (Salters)*.
- You are advised to show all the steps in calculations.

FOR EXAMINER'S USE		
Qu.	Max.	Mark
1	20	
2	16	
3	23	
4	17	
5	15	
6	29	
TOTAL	120	

This question paper consists of 20 printed pages.

For Examiner's Use

Answer **all** the questions.

1 Methanol is an important chemical used to make many different polymers. The 'synthesis gas' for methanol production is a mixture of carbon monoxide, carbon dioxide and hydrogen. The plants used in 1923 operated at temperatures of around 670 K and pressures of about 200 atmospheres using a catalyst based on zinc and chromium.

More recently, the production of cleaner synthesis gas allowed the use of catalysts based on copper. This modern process operates at 525-575 K and 100 atmospheres. Modern methanol plants produce as much as 1500 tonnes per day.

(a) In 1923, coal was the feedstock for the production of synthesis gas. Today, naphtha is the main feedstock.

(i) Name a raw material from which naphtha is obtained.

..... [1]

(ii) Synthesis gas from coal has a high impurity content. The impurities poison the catalyst. Explain how an impurity might act as a catalyst poison.

.....

.....

..... [2]

(b) One problem with the modern copper-based catalyst is that the copper 'sinters'. This means that the copper crystals on the surface of the catalyst become larger. Explain why this sintering process reduces the efficiency of the catalyst.

.....

.....

..... [2]

(c) Synthesis gas is converted to methanol by two main reactions.

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

$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$ $\Delta H = -49\ kJ\ mol^{-1}$ **equation 1.2**

The modern process for methanol synthesis operates at a lower temperature and a lower pressure than the older process.

For Examiner's Use

(i) Use your understanding of Le Chatelier's Principle to explain why it is an advantage to use a **lower temperature** for methanol synthesis.

.....

.....

.....

.....

.....

..... [3]

(ii) Write an expression, **in terms of partial pressures**, for the equilibrium constant, K_p, for **equation 1.2**.

[2]

(iii) Suggest **two** advantages of the old high pressure (200 atmospheres) process for methanol synthesis over the modern low pressure process (100 atmospheres).

.....

.....

..... [2]

(iv) Suggest **one** reason why a low pressure plant costs less to operate than a high pressure plant.

.....

.....

..... [1]

[Turn over

For Examiner's Use

(d) Ammonia and methanol are often manufactured on the same site. Surplus hydrogen from methanol manufacture can be used to make ammonia.

(i) Write an equation for the production of ammonia by the Haber process. Include state symbols.

..... [2]

(ii) State the essential conditions of temperature, pressure and catalyst used in the manufacture of ammonia by the Haber process.

.....

.....

..... [3]

(e) In the Haber process, carbon dioxide is often removed from the feedstock gases by reaction with an inorganic base, usually a solution of potassium carbonate.

$$K_2CO_3(aq) + H_2O(l) + CO_2(g) \longrightarrow 2KHCO_3(aq)$$ **equation 1.3**

The potassium hydrogencarbonate solution, $KHCO_3(aq)$, is then heated to regenerate potassium carbonate. The carbon dioxide escapes into the atmosphere or is sold for use in other processes.

Write the equation for the thermal decomposition of potassium hydrogencarbonate described above.

..... [2]

[Total: 20]

For Examiner's Use

2 The exciting discovery that a simple polymer could be made to conduct electricity was made in 1970. Shirakawa and his colleagues in Japan polymerised ethyne, C_2H_2, to produce a film. When they performed the reaction at −78 °C a red polymer was formed. At 100 °C the polymer was blue.

(a) Ethyne is the simplest alkyne. It has the structure H–C≡C–H. It is a linear molecule.

(i) Draw a dot-cross diagram for ethyne. [2]

(ii) Suggest why ethyne is a linear molecule.

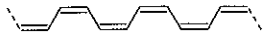
.....

.....

..... [2]

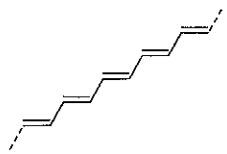
For Examiner's Use

(b) Poly(ethyne) has alternating single and double bonds. There are two forms of poly(ethyne).



***cis*-poly(ethyne)**

red



***trans*-poly(ethyne)**

blue

(i) Molecules with alternate single and double bonds are said to have conjugated systems. Electrons in the double bonds are delocalised.

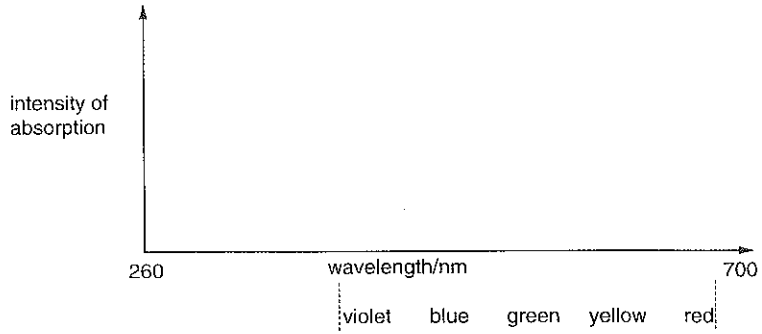
Use this example to explain what is meant by the term *delocalised*.

.....

.....

..... [2]

(ii) Sketch the **absorption spectrum** you would expect to see for the *trans*-isomer.



[2]

For Examiner's Use

(iii) Use your understanding of energy levels to explain why the *cis* and *trans* isomers have different colours. Explain how the energy levels in *cis*- and *trans*-poly(ethyne) differ to cause one to be red and the other blue. You may find it helpful to include a diagram in your answer.

.....

.....

.....

.....

.....

.....

.....

.....

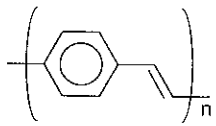
.....

.....

.....

..... [6]

(c) In 1989, conjugated polymers that emit light were discovered. The first polymer to be studied was PPV. PPV emits green light when a voltage is applied.



PPV

Suggest how the structure of the polymer could be adapted so that it emits a different colour when a voltage is applied.

.....

.....

..... [2]

[Total: 16]

[Turn over

For Examiner's Use

3 Plant scientists study the structure of soil so they can find out how plants remove nutrients from the soil. Soil contains clay minerals and organic matter (humus). Clay minerals have negatively charged surfaces which attract positive ions from solution.

The positive ions held by the clay or humus are in equilibrium with free, hydrated ions in the soil solution. Plant roots withdraw nutrients from this pool of exchangeable ions.

(a) Positive ions, such as calcium, Ca^{2+}, and ammonium, NH_4^+, exist in the soil solution as hydrated ions. Draw a diagram to show a hydrated calcium ion.

[4]

(b) An isolated calcium ion, Ca^{2+}, has a radius of 0.100 nm whereas an isolated ammonium ion, NH_4^+, has a radius of 0.150 nm.

Calcium ions are more strongly hydrated in water than ammonium ions.

Aqueous calcium ions are less strongly adsorbed onto clay minerals in the soil than are aqueous ammonium ions.

(i) Explain why calcium ions are more strongly hydrated.

.....

..... [2]

(ii) Explain why aqueous calcium ions are less strongly adsorbed by the clay.

.....

..... [2]

For Examiner's Use

(c) A common fertiliser is ammonium nitrate, NH_4NO_3. The ammonium ions are oxidised by bacteria in the soil. The overall equation for this process is given below.

$$4NH_4^+ + 8O_2 \longrightarrow 4NO_3^- + 8H^+ + 4H_2O \qquad \textbf{equation 3.3}$$

This process increases the acidity of the soil.

(i) Explain why ammonium ions are retained in the soil longer than nitrate ions.

.....

..... [2]

(ii) Give the oxidation state of the nitrogen in

NH_4^+ ..... and NO_3^- ..... [2]

(iii) Why does the oxidation of ammonium ions **in equation 3.3** increase the acidity of the soil?

.....

..... [2]

(iv) Suggest why increasing the acidity of the soil reduces its capacity to hold nutrient ions like Ca^{2+}.

.....

.....

..... [2]

(d) In order to increase the pH of soil, powdered limestone ($CaCO_3$) can be spread on the soil surface. Using H_3O^+ to represent the acid, write a balanced equation for the reaction between acid and limestone. Include state symbols.

..... [3]

[Turn over

For Examiner's Use

(e) Soils also become more acidic due to rainwater. Rainwater is naturally slightly acidic because it reacts with carbon dioxide in the atmosphere. 'Natural' rainwater has a hydrogen ion concentration of about 2.5×10^{-6} mol dm^{-3}.

(i) Calculate the pH of 'natural' rainwater.

answer ..... [2]

(ii) The pH of rainwater in central Europe is 4.1. Suggest a reason why the rain in central Europe is more acidic than 'natural' rainwater.

.....

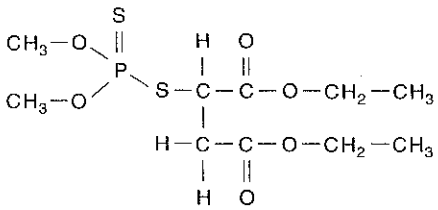
..... [2]

[Total: 23]

For Examiner's Use

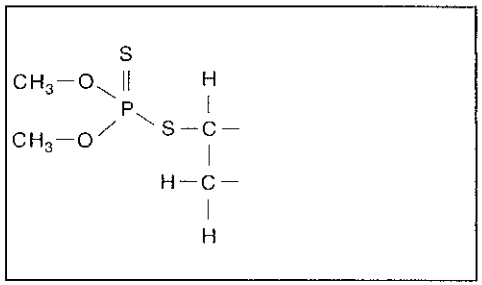
4 Diseases and pests can reduce crop yields worldwide by 30 – 40%. The development of new insecticides is an important area of research.

Many of the insecticides used today are organophosphates. *Malathion* is a widely used insecticide, because it is effective at killing insects but is non-toxic to mammals. Mammals have enzymes which can hydrolyse the ester groups in *Malathion.*



Malathion

(a) (i) The ester groups in *Malathion* are hydrolysed to give **two** products, **compound A** and **compound B**. Complete the structure of **compound A** below and write the formula of **compound B**.



compound A

compound B

[3]

(ii) Give the systematic name for **compound B**.

..... [1]

(iii) Suggest the reagents and conditions which could be used to hydrolyse the ester groups in *Malathion* in the laboratory.

.....

..... [2]

[Turn over

For Examiner's Use

(b) In this question, one mark is available for the quality of written communication.

Scientists test insecticides in several ways. One test is to compare the solubility of an insecticide in water and in octan-1-ol.

Explain, in terms of intermolecular forces, why the two liquids octan-1-ol and water do not mix.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

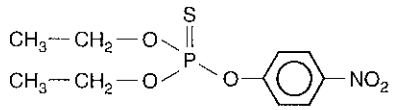
.....

.....

..... [7]

Quality of Written Communication [1]

(c) *Parathion* is an organophosphate insecticide that is rarely used because it is toxic. Its toxicity arises because it is more soluble in fats than in water.



Parathion

The difference in solubility in two solvents can be measured as a **partition coefficient**. This difference in solubility is shown by the partition coefficient, K_{ow}, between octan-1-ol and water.

$$\text{partition coefficient, } K_{ow} = \frac{\textit{Parathion} \text{ concentration in octan-1-ol}}{\textit{Parathion} \text{ concentration in water}}$$

For Examiner's Use

Explain why you would expect K_{ow} to be large for *Parathion*.

.....

.....

.....

..... [3]

[Total: 17]

5 Seawater contains varying amounts of dissolved salts. The most abundant cation is Na^+ and the most abundant anion is Cl^-. The concentration of chloride ions can be determined by titration with silver nitrate solution of known concentration using a potassium chromate(VI) indicator.

$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$ **equation 5.1**

(a) 10.0 cm^3 of seawater required 24.7 cm^3 of 0.0500 mol dm^{-3} silver nitrate solution to achieve the endpoint.

(i) Calculate the amount in moles of silver nitrate, $AgNO_3$, used in the titration.

answer ..... mol [1]

(ii) Write down the amount in moles of $NaCl$ present in 10.0 cm^3 of the seawater.

answer ..... mol [1]

(iii) Calculate the concentration of chloride ions in seawater in g dm^{-3}.
A_r: Cl, 35.5

answer ..... g dm^{-3} [3]

[Turn over

For Examiner's Use

(b) The method of measuring the end point depends on the fact that silver chloride is a sparingly soluble solid. A sparingly soluble ionic solid in contact with a solution of its ions reaches chemical equilibrium. This equilibrium is shown below for silver chloride.

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ **equation 5.2**

(i) Use **equation 5.2** to write the expression for K_{sp} for $AgCl(s)$.

[1]

(ii) The value of K_{sp} for silver chloride is 1.8×10^{-10} mol^2 dm^{-6} at 298 K. A student added 100 cm^3 of 0.010 mol dm^{-3} silver nitrate solution to 100 cm^3 of 0.0010 mol dm^{-3} sodium chloride.

Work out the concentrations of the $Ag^+(aq)$ and $Cl^-(aq)$ ions **in the mixture** and then use a calculation to predict whether or not a precipitate of silver chloride will form, giving the reason for your answer.

Concentration of $Ag^+(aq)$:

Concentration of $Cl^-(aq)$:

Prediction of whether a precipitate will form:

.....

..... [4]

(c) When silver nitrate solution reacts with sodium chloride solution there is an entropy change.

$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$ **equation 5.1**

(i) The sign of the value for ΔS_{sys} for **equation 5.1** is negative. Explain why.

.....

..... [2]

(ii) Explain why you would predict that ΔS_{surr} for the reaction in **equation 5.1** should be a positive value.

.....

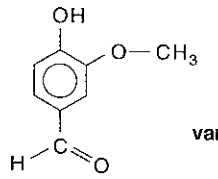
.....

..... [3]

[Total: 15]

For Examiner's Use

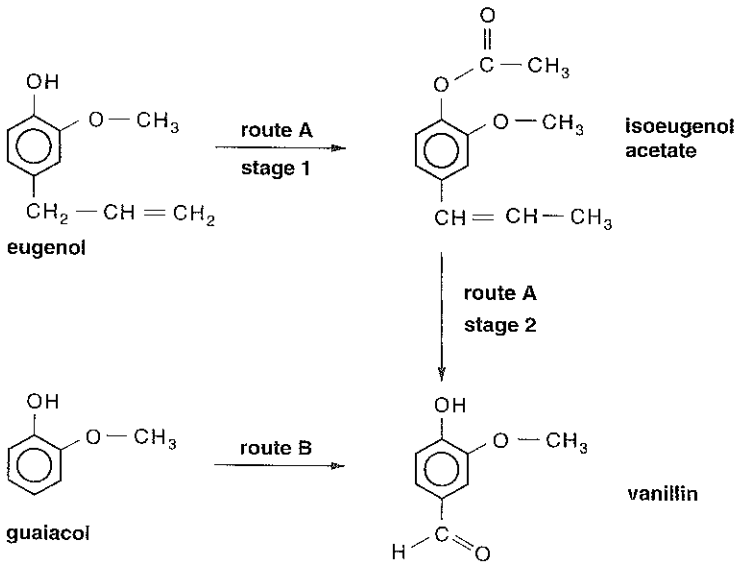
6 Vanillin is the fragrant constituent of the extract of vanilla bean. It is one of the most common flavouring ingredients found in foods.



vanillin

In the 1950s, chemists discovered methods for synthesising vanillin from the waste products of the wood pulp industry. This synthetic vanillin is chemically identical to natural vanillin but is much cheaper to produce.

Two synthetic routes are shown below.



(a) (i) Name **three** functional groups found in **isoeugenol acetate**.

.....

..... [3]

(ii) Describe and explain how a simple chemical test could be used to show if eugenol is still present in the reaction mixture produced by **stage 1**.

.....

.....

.....

..... [3]

[Turn over

For Examiner's Use

(iii) Suggest the reagents and conditions needed to achieve the following conversion.

.....

..... [2]

(iv) Classify the type of reaction described in **(iii)**.

..... [1]

(b) In this question, one mark is available for the quality of written communication.

Vanillin is a white solid at room temperature. It is slightly soluble in water (1 g per 100 g of water at 25 °C) and solubility increases with increasing temperature. Vanillin is very soluble in ethanol at 25 °C.

Explain why water, rather than ethanol, is a better solvent to use when recrystallising vanillin.

.....

.....

.....

.....

.....

.....

.....

.....

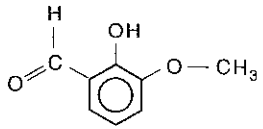
.....

..... [5]

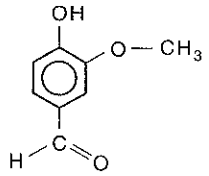
Quality of Written Communication [1]

For Examiner's Use

(c) **Route B** for the synthesis of vanillin also produces **compound Y** as a by-product.



compound Y



vanillin

(i) **Compound Y** and vanillin are isomers. Name the type of isomerism.

..... [1]

(ii) **Compound Y** does not have the same smell as vanillin. Suggest why **compound Y** and vanillin are detected by different receptors in the nose.

.....

..... [2]

(iii) Suggest a technique for separating a mixture of vanillin and **compound Y**.

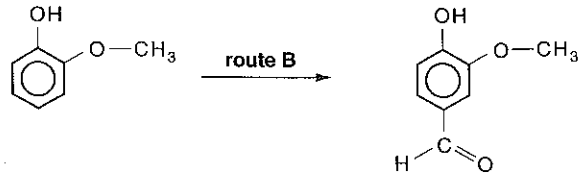
.....

..... [1]

[Turn over

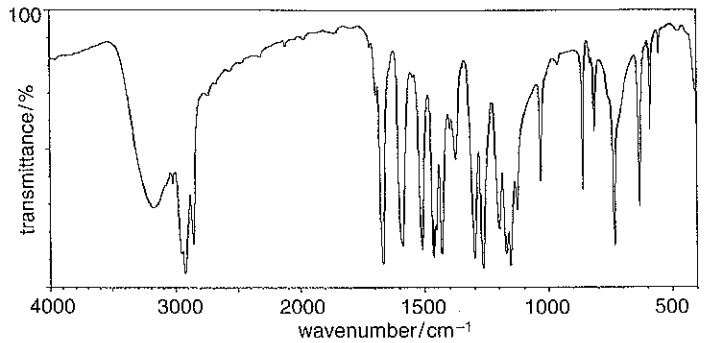
For Examiner's Use

(d) A student attempted to prepare a sample of vanillin by **route B**.

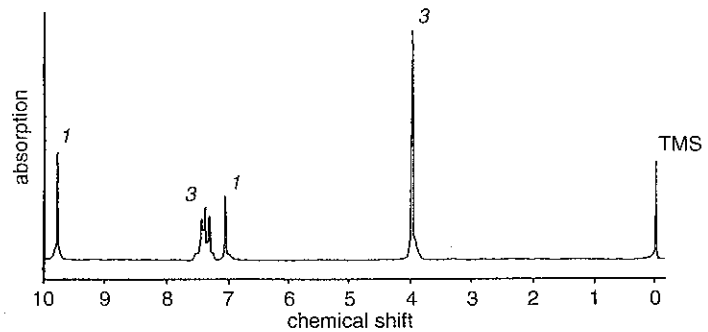


guaiacol **vanillin**

In order to see if the reaction had gone to completion, the student analysed the product by infra-red and n.m.r spectroscopy. The spectra are shown below.



infrared spectrum of product



proton n.m.r. spectrum of product

(Figures in italics represent the relative numbers of protons contributing to each signal)

For Examiner's Use

(i) In this question, one mark is available for the quality of written communication.

Explain how the spectra can be used to show that the guaiacol has been converted into vanillin. Use the Data Sheet provided. (Remember that the values on the Data Sheet give an average range for each absorption. Atoms or groups attached to a benzene ring often absorb slightly outside these ranges.)

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

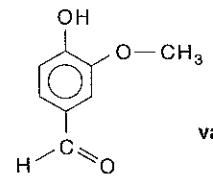
..... [7]

Quality of Written Communication [1]

[Turn over

For Examiner's Use

(ii) Give the molecular formula of vanillin.

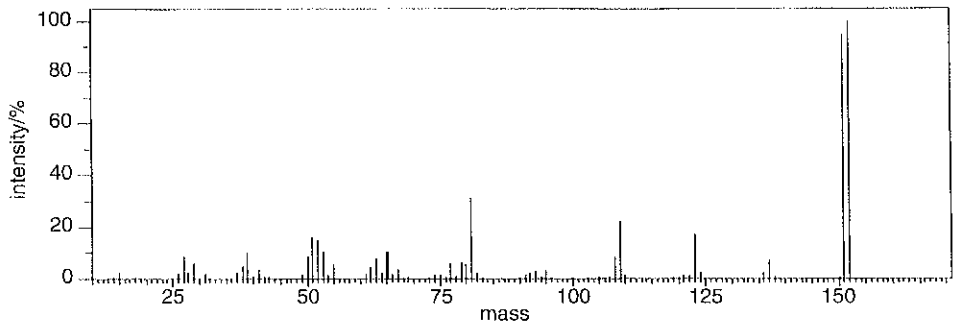


vanillin

.....

..... [1]

(iii) The mass spectrum of vanillin is shown below.



mass spectrum of vanillin

How does the mass spectrum support your answer to **(ii)**?

.....

..... [1]

[Total: 29]