



30513402



RECOGNISING ACHIEVEMENT

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE



2854

CHEMISTRY (SALTERS)

Chemistry by Design

Tuesday 29 JUNE 2004

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, Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers in the spaces provided on the question paper.
- DO NOT ANSWER IN PENCIL. DO NOT WRITE IN THE BARCODE. DO NOT WRITE IN THE GREY AREAS BETWEEN THE PAGES.**
- 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	32	
2	26	
3	18	
4	31	
5	13	
TOTAL	120	

This question paper consists of 15 printed pages and 1 blank page.

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2

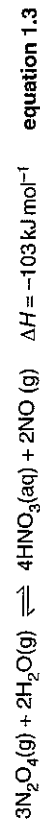
Answer **all** the questions.

1 Nitric acid is made from ammonia by the Ostwald process.

The ammonia is converted to nitrogen monoxide, NO, which is then reacted with air.



The N₂O₄ is then dissolved in water. The overall reaction is shown below.



(a) (i) Give the name of the substance NO₂.
.....[1]

(ii) Suggest **one** use for the nitric acid that is made in this process.
.....[1]

(b) Give the oxidation states of nitrogen in the compounds shown below.

NH₃ N₂O₄ HNO₃ [3]

(c) Look at equation 1.1. Explain the effect of increasing the temperature on the rate of the reaction and the yield of NO₂.

(i) Explain the effect of increasing the temperature on the rate of reaction.
.....
.....
.....
.....[3]

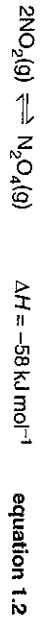
(ii) Explain the effect of increasing the temperature on the yield of NO₂.
.....
.....
.....
.....
.....
.....
.....[3]



(d) In view of your answers to (c)(i) and (ii), suggest why a temperature of 25 °C is used for the reaction in equation 1.1.

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

(e) (i) Write an expression for the equilibrium constant, K_p , for the reaction in equation 1.2.



$K_p =$

[2]

(ii) Give the units of K_p when partial pressures are measured in atmospheres.

units of K_p

[1]

(iii) At 25 °C, K_p has a numerical value of 8.7. Calculate the partial pressure of $\text{N}_2\text{O}_4(\text{g})$ in an equilibrium mixture where the partial pressure of $\text{NO}_2(\text{g})$ is 0.60 atm. Give your answer to a suitable number of significant figures.

partial pressure of $\text{N}_2\text{O}_4 =$ atm [2]

(f) N_2O_4 is an acidic oxide of an element in Period 2. Suggest two other elements in this period that form acidic oxides.

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

(g) (i) The $\text{NO}(\text{g})$ formed in equation 1.3 must not be allowed to escape into the atmosphere, as it is a pollutant. Give two harmful effects of this gas.

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

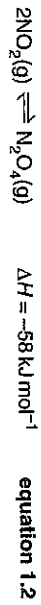
(ii) Suggest what happens to the $\text{NO}(\text{g})$ formed in the industrial process.

..... [1]

[Turn over



(h) For the forward reaction in equation 1.2, deduce the signs of the following entropy changes, giving your reasons.



(i) ΔS_{sys}

[1]

(ii) ΔS_{sur}

[1]

(iii) ΔS_{total}

[2]

(i) Nitric acid, HNO_3 , is a strong acid in aqueous solution.

(i) Explain what is meant by the term *strong acid*.

..... [1]

(ii) Write a chemical equation for the reaction that occurs when HNO_3 dissolves in water.

[2]

(iii) Calculate the pH of a 0.050 mol dm⁻³ solution of nitric acid.

pH = [2]

[Total: 32]

2 Some female moths can attract male moths from great distances by emitting minute quantities of a substance called a pheromone. The formula of one such pheromone is shown below.



(a) Name two different functional groups in the pheromone structure.

[2]

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

Initial analysis of the structure of the pheromone was done using spectroscopy. Describe how **Infrared spectroscopy** and **mass spectrometry** could be used to help to identify the pheromone structure.

[5]

Quality of Written Communication [2]

(c) After spectroscopy, chemical reactions were used to continue the analysis. When the pheromone is distilled with acidified potassium dichromate(VI), partial oxidation occurs to give an aldehyde group.

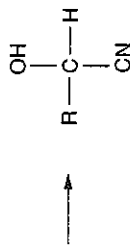
(i) Draw the **full structural** formula of the aldehyde group -CHO.

[1]



(ii) When an aldehyde RCHO reacts with HCN, a compound Q is formed.

Draw diagrams to illustrate the **mechanism** of the attack of CN⁻ on the aldehyde RCHO, followed by the attack of an H⁺ ion on the intermediate to give compound Q.



compound Q

[3]

(d) A technique called ozonolysis breaks the pheromone molecule at its double bonds. The carbon atoms on either side of the break are oxidised to carboxylic acid groups. The smallest molecule produced is HOOC-CH₂-COOH, propanedioic acid.

(i) Propanedioic acid can be detected by its n.m.r. spectrum. Give the number of peaks you would expect in this n.m.r. spectrum and their relative areas.

[2]

(ii) Give the formula of another molecule that would be produced as a result of ozonolysis of the pheromone.

[2]



The shape of the pheromone molecule is affected by its two double bonds that have different arrangements of the groups around them. Name the **type** of geometric isomerism shown at double bonds A and B in the structure above.

A

B

[2]



(f) Suggest how the male moth detects the pheromone on a molecular level. Say why the shape of the pheromone molecule is important in this process.

.....

.....

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.....

.....

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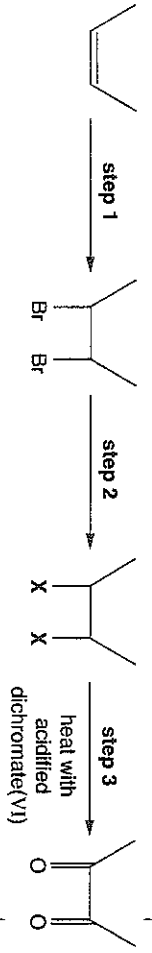
.....

.....

[3]

(g) A chemist set out to synthesise a new compound from the pheromone.

This involved the following synthetic route.



(i) Suggest a reagent for step 1 [1]

(ii) Suggest the identity of the functional group X [1]

(iii) Give the reagent and conditions for step 2 [2]

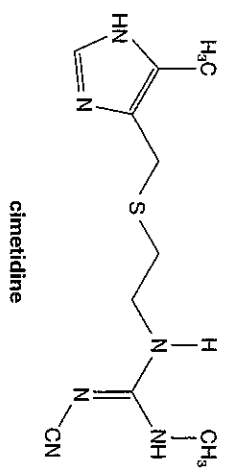
[Total: 26]

For Examiner's Use

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3 The compound cimetidine is an effective anti-ulcer medicine that works by decreasing acid secretion in the stomach. It was one of the first medicines to be designed logically from first principles, based on an understanding of the chemical processes that take place in the body.



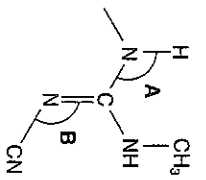
cimetidine

(a) (i) Work out from the formula the number of carbon and hydrogen atoms in a molecule of cimetidine.

carbon atoms

hydrogen atoms

(ii) Suggest values for the bond angles A and B in the part of the cimetidine molecule shown below.



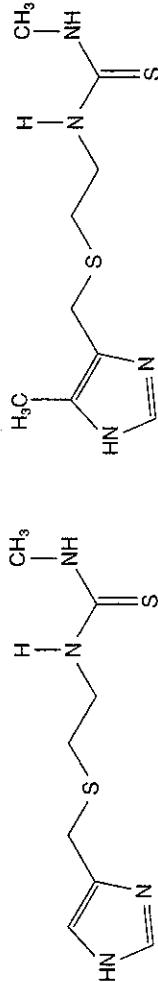
A B [2]

For Examiner's Use

001	002	003	004	005	006	007	008	009	010	011	012	013	014	015	016	017	018	019	020	021	022	023	024	025	026	027	028	029	030	031	032	033	034	035	036	037	038	039	040	041	042	043	044	045	046	047	048	049	050	051	052	053	054	055	056	057	058	059	060	061	062	063	064	065	066	067	068	069	070	071	072	073	074	075	076	077	078	079	080	081	082	083	084	085	086	087	088	089	090	091	092	093	094	095	096	097	098	099	100
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Turn over

(b) As part of the development, **compound A** was synthesised and this showed anti-ulcer activity. **Compound A** was not entirely satisfactory, however, so further development produced metiamide.



compound A

metiamide

Suggest why early versions of pharmaceutical products are not always entirely satisfactory.

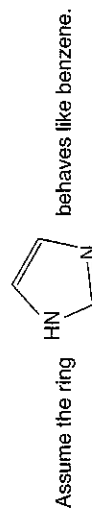
.....[1]

(c) The ring structure in the two compounds above shows aromatic character, similar to that in benzene.

(i) Benzene has delocalised electrons. Explain how delocalisation occurs in the benzene ring, giving one important consequence.

.....[4]

(ii) Suggest reagents and conditions for making metiamide from **compound A**.



.....[3]



(iii) Circle a word in the list below that describes the substitution reactions of benzene.

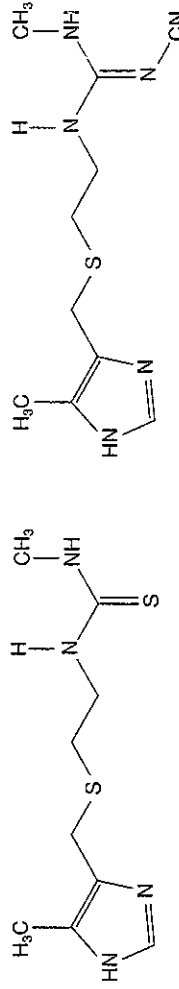
nucleophilic **electrophilic** **radical**

(iv) Some compounds with delocalised electrons (like **compound A**, metiamide and benzene) are colourless.

Other substances with delocalised electrons (like dyes) are coloured.

Explain, in terms of transitions between electronic energy levels, why some compounds with delocalised electrons are coloured while others are colourless.

(d) Metiamide still caused a few problems in trials, so its structure was modified to cimetidine which has the same pharmacophore as metiamide but works better.



metiamide

cimetidine

Draw a ring round the pharmacophore on the cimetidine structure.

[1]

[Total: 18]

[Turn over

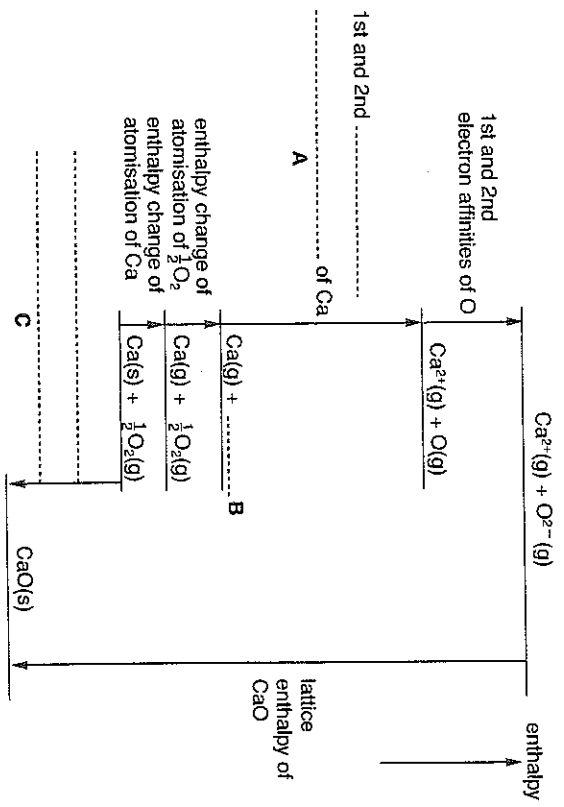


4 Farmers add slaked lime, calcium hydroxide, to their fields to neutralise the acidity of clay soils. Slaked lime is produced from limestone, CaCO_3 . The limestone is first heated to form calcium oxide, CaO . A controlled amount of water is then added to the calcium oxide to produce solid slaked lime.

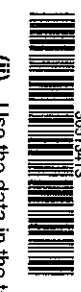
- (a) (i) Write a balanced chemical equation for the action of heat on calcium carbonate. [1]
- (ii) Calculate the mass of calcium oxide made by complete decomposition of 1.0 kg of calcium carbonate.
 A: Ca, 40; C, 12; O, 16 [2]

(b) Draw a dot-cross diagram to show the ions present in calcium oxide, CaO . mass =g [2]

(c) (i) A Born-Haber cycle for calcium oxide is shown. Complete the cycle by writing suitable labels on the dotted lines at points A, B and C. [2]



[3]



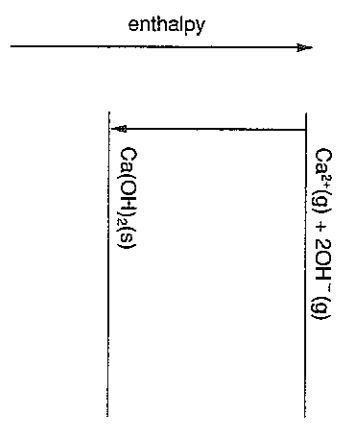
(ii) Use the data in the table and the cycle in (i) to calculate a value for the sum of the first and second electron affinities of $\text{O}(\text{g})$. Give a sign with your answer.

enthalpy change	value/ kJ mol^{-1}
A	+1748
C	-635
lattice enthalpy of $\text{CaO}(\text{s})$	-3419
atomisation of $\text{Ca}(\text{s})$	+178
atomisation of $\frac{1}{2}\text{O}_2(\text{g})$	+249

sum of first and second electron affinities of $\text{O}(\text{g}) = \dots\dots\dots \text{kJ mol}^{-1}$ [3]

(d) Calcium hydroxide, $\text{Ca}(\text{OH})_2$, is formed by the reaction of calcium oxide with water. Calcium hydroxide is only slightly soluble in water. One reason for this is its positive enthalpy change of solution in water.

- (i) Part of an enthalpy level diagram to show the dissolving of calcium hydroxide in water is given. Complete the diagram by following the instructions below.
- Draw an appropriate enthalpy level for aqueous calcium hydroxide and label it.
 - Label the enthalpy change that is shown by the arrow on the diagram.
 - Draw in and label the remaining enthalpy changes involved in the cycle.



(ii) Describe the trend of solubilities in the Group 2 hydroxides.

..... [1]

[4]

(e) The solubility of calcium hydroxide in water is $0.016 \text{ mol dm}^{-3}$ at 298 K.
 (i) Calculate the concentration of hydroxide ions in a saturated solution of calcium hydroxide, $\text{Ca}(\text{OH})_2$, at 298 K, assuming that it is a strong base.

$[\text{OH}^-] = \dots\dots\dots \text{mol dm}^{-3}$ [2]

(ii) $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K.
 Calculate the pH of a saturated solution of calcium hydroxide at this temperature.

pH = [3]

(iii) Write a balanced equation for the reaction of calcium hydroxide with hydrochloric acid. [2]

(iv) Calculate the volume of $0.0200 \text{ mol dm}^{-3}$ hydrochloric acid which would react exactly with 10.0 cm^3 of $0.0150 \text{ mol dm}^{-3}$ calcium hydroxide. [2]

volume = cm^3 [2]

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

As the H^+ ions in the soil solution are neutralised by the OH^- ions in the slaked lime, they are replaced by the H^+ ions adsorbed on the surface of the clay. The calcium ions take the place of the H^+ ions in the clay.

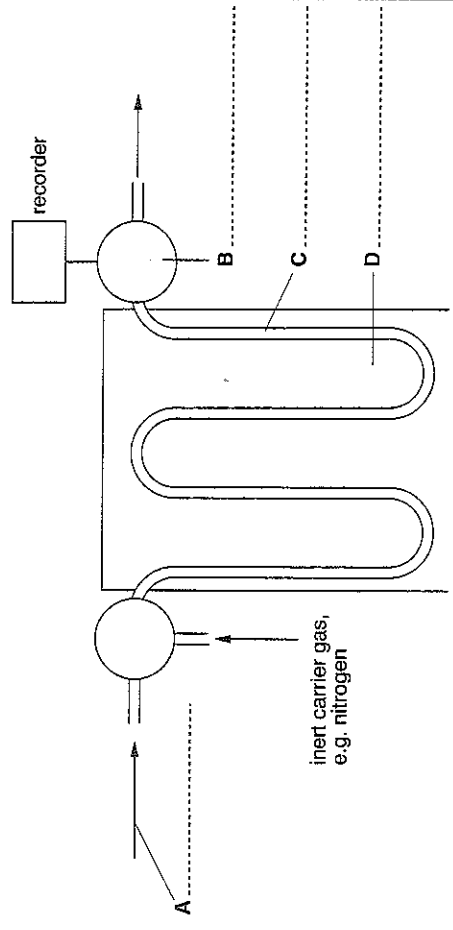
Explain how H^+ ions are held in clay soils and how they are displaced by calcium ions.

.....

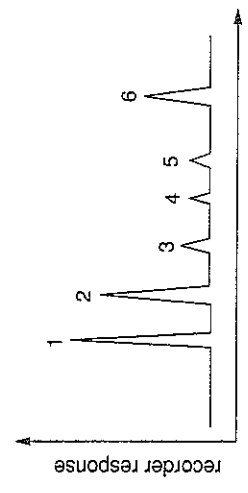
Quality of Written Communication [1] [Total: 31]

5 In 1982, King Henry VIII's flagship, the *Mary Rose*, was raised from the sea-bed where she had lain for 400 years. In the wreck was a medicine chest containing jars of ointment. Archaeologists called in chemists to identify the ointment.

(a) The main technique used was gas-liquid chromatography. A diagram of a gas-liquid chromatograph is shown below. Complete the labels A–D by writing on the dotted lines.



(b) The recorder trace obtained from the ointment is shown below. [4]



What is plotted on the horizontal axis?

..... [1]



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(c) (i) Peak 1 was caused by hexadecanoic acid, a carboxylic acid with an unbranched chain containing sixteen carbon atoms. Draw the skeletal formula for this acid.

[2]

(ii) Another smaller peak is from an *unsaturated* acid. Name the functional group present in this compound which is *not* present in hexadecanoic acid.

[1]

(iii) Another peak was identified as 'tricontanol'. Explain how this name tells you that the compound contains an alcohol group.

[1]

(iv) The substances in (i), (ii) and (iii) came from the gradual breakdown of esters in beeswax. Circle in the list below the name of the process by which beeswax changed into these substances.

condensation elimination esterification hydrolysis reduction [1]

(d) Fats and oils are triesters of glycerol. Draw the structure of the molecule formed when glycerol (propane-1,2,3-triol) reacts with three molecules of a long-chain carboxylic acid to form three ester links.

Use **full structural formulae** for the glycerol and ester parts of the molecule and **skeletal formulae** for the long chains of the carboxylic acids (the number of carbon atoms in the chain is not important).

[3]

[Total: 13]

For
Examiners
Use