OCR
RECOGNISING ACHIEVEMENT

ADVANCED GCE **2854/01**

CHEMISTRY (SALTERS)

Chemistry by Design

MONDAY 25 JUNE 2007 Morning

Time: 2 hours

Additional materials: Scientific calculator
Data Sheet for Chemistry (Salters) (Inserted)

Candidate Name

Centre Number

Candidate Number

INSTRUCTIONS TO CANDIDATES

- Write your name, Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Use blue or black ink. Pencil may be used for graphs and diagrams only.
- Read each question carefully and make sure you know what you have to do before starting your answer.
- Do **not** write in the bar code.
- Do **not** write outside the box bordering each page.
- WRITE YOUR ANSWER TO EACH QUESTION IN THE SPACE PROVIDED. ANSWERS WRITTEN ELSEWHERE WILL NOT BE MARKED.

INFORMATION FOR CANDIDATES

- The number of marks for each question 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.
- A copy of the *Data Sheet for Chemistry (Salters)* is provided as an insert with this question paper.
- You are advised to show all the steps in any calculations.

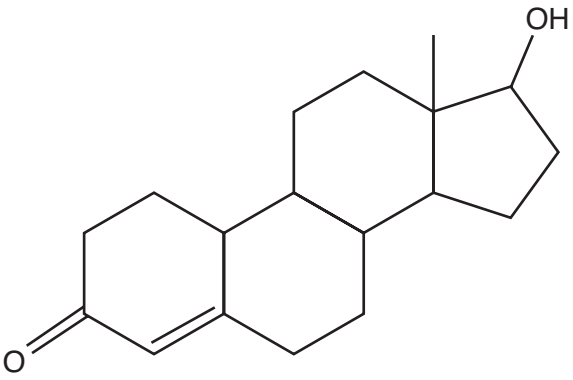
FOR EXAMINER'S USE		
Qu.	**Max.**	**Mark**
1	**26**	
2	**17**	
3	**27**	
4	**26**	
5	**24**	
TOTAL	**120**	

This document consists of **19** printed pages, **1** blank page and a *Data Sheet for Chemistry (Salters)*.

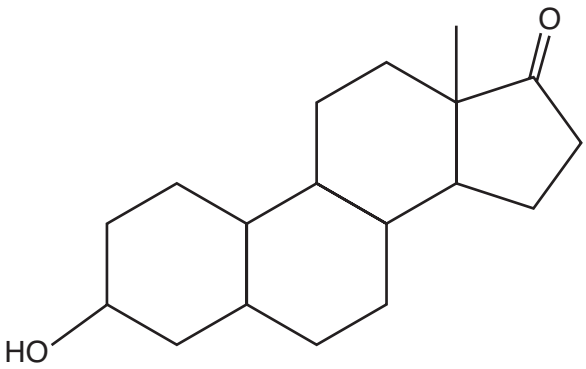
[Turn over

Answer **all** the questions.

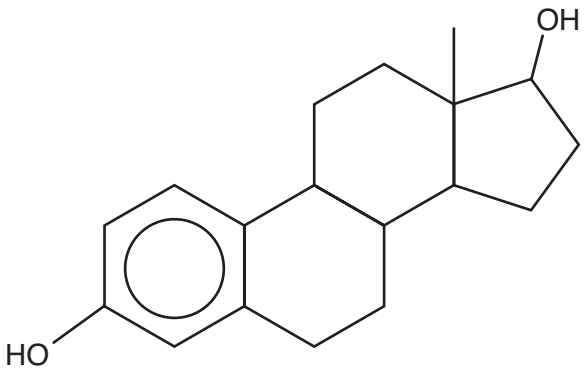
1 Nandrolone, an anabolic steroid, is a drug that is illegally used by some athletes to build up their body mass. Some anabolic steroids act like *female* sex hormones, such as oestradiol. Nandrolone, however, is very similar to a *male* sex hormone. Nandrolone is converted to norandrosterone in the body.



nandrolone



norandrosterone



oestradiol

(a) How many hydrogen atoms are there in a molecule of **nandrolone**?

..... [1]

(b) Name the two different hydroxyl groups in **oestradiol**.

..... [2]

(c) Oestradiol contains a benzene ring and also saturated rings.

Describe the difference in the way that electrons are arranged in a benzene ring, compared with a saturated ring.

.....

.....

.....

..... [2]

(d) Drug testing centres look for the presence of nandrolone and norandrosterone in the bloodstream.

(i) Name **one** functional group present in nandrolone that is not present in norandrosterone.

..... [1]

(ii) Describe a test for this group.

..... [2]

(e) Describe and explain **two** ways in which the infrared spectra of nandrolone and norandrosterone would be the same and **one** way in which they would differ.

Give the bonds and absorption ranges of the peaks you consider.

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..... [6]

(f) Describe how secondary alcohols can be converted to ketones in the laboratory.

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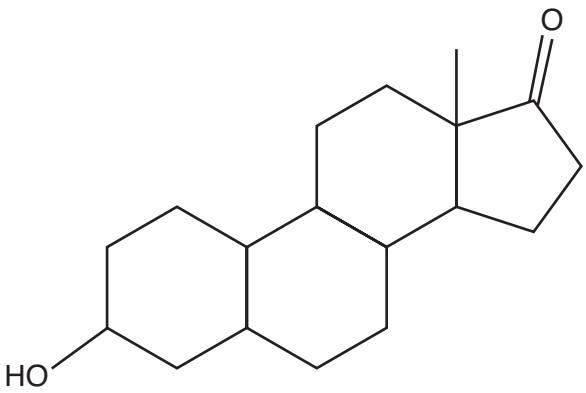
..... [2]



norandrosterone
$C_{18}H_{28}O_2$

(g) Norandrosterone has several chiral carbon atoms in its structure.

(i) Circle **two** chiral carbon atoms on the norandrosterone structure above. [1]

(ii) Say how you recognise that these carbon atoms are chiral.

.....

..... [1]

(iii) For a molecule with one chiral carbon atom, state how the shapes of the two optical isomers are related.

..... [1]

(h) The International Olympic Committee has set a limit of 2×10^{-9} **g cm^{-3}** of norandrosterone in urine. Above that they will take action.

The urine of an athlete was analysed and shown to have a concentration of 2.2×10^{-9} **mol dm^{-3}** of norandrosterone.

(i) Calculate how many grams per cm^3 this represents.

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

concentration of norandrosterone = ... g cm^{-3} [3]

The method of analysis involves gas-liquid chromatography, followed by mass spectrometry.

(ii) Chromatography involves a stationary phase and a mobile phase. Describe the nature of the substances that make up these phases for gas-liquid chromatography.

stationary phase .....

..... [2]

mobile phase .....

..... [1]

(iii) Give **one** piece of information about a compound that can be obtained from its mass spectrum.

.....

..... [1]

[Total: 26]

2 Verdigris is a blue-green pigment that was used in paintings in antiquity and through to the Middle Ages. It consists of a mixture of copper hydroxide and copper ethanoate.

It can be made in the laboratory by the following reactions.

$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$ **equation 2.1**
light blue — pale blue precipitate

$Cu(OH)_2(s) + 2CH_3COOH(aq) \rightarrow Cu(CH_3COO)_2(s) + 2H_2O(l)$ **equation 2.2**
pale blue — green

(a) Draw the **full** structural formula of the ethanoate ion, showing the charge.

[1]

(b) Suggest suitable solutions that could be used as the source of the ions shown below.

$Cu^{2+}(aq)$ .....

$OH^-(aq)$ ..... [2]

(c) Colour changes are often associated with the following types of process.

acid-base **polymorphism** **precipitation** **redox**

Use a term from the list to describe each of the reactions above.

equation 2.1 .....

equation 2.2 ..... [2]

(d) As time goes by, the colour of verdigris does not fade or change much.

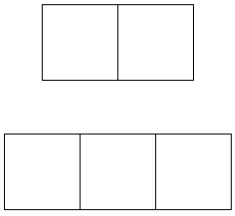
Suggest a possible reason for this.

.....

..... [1]

(e) Use the diagram below to help to explain the following:

- the origin of colour in transition metal complexes;
- why the colour varies with the nature of the ligand.



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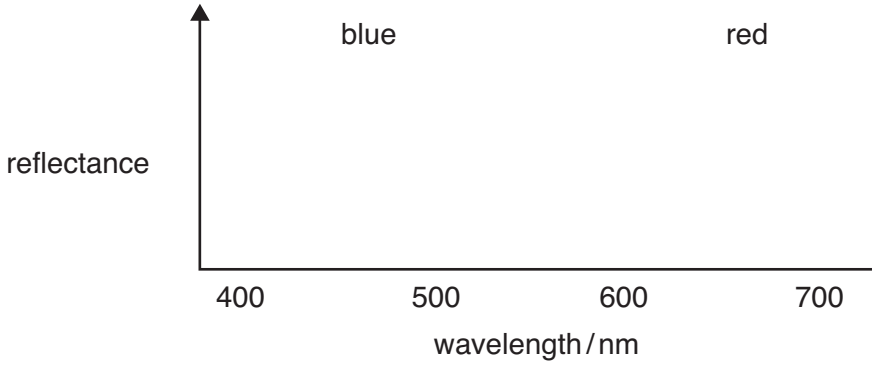
..... [5]

(f) Reflectance spectroscopy can be used to identify coloured pigments. On the axes below, sketch a possible shape for the reflectance spectrum of the blue-green verdigris.



[2]

(g) (i) In ancient paintings, verdigris was often glazed over with tin-lead yellow to make it less transparent.

How could the atomic **emission** spectrum of a green area of a painting be used to show the presence of copper, tin and lead?

.....

.....

..... [2]

(ii) What is occurring in the atoms of the elements concerned to produce an atomic **emission** spectrum and why are the spectra of the elements different?

.....

.....

.....

..... [2]

[Total: 17]

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3 A mixture of thallium bromide (T*l*Br) and thallium iodide (T*l*I) is used to form lenses and other optical parts of infrared spectrometers. Thallium (T*l*) has atomic number 81.

(a) Suggest why glass cannot be used for these components.

.....

..... [1]

(b) **(i)** Give the **outer shell** electron configuration for thallium, T*l* (e.g. that for oxygen would be $2s^2\ 2p^4$).

..... [2]

(ii) Explain why patterns in the Periodic Table might lead you to expect that the formula of thallium bromide would be $Tl Br_3$, rather than T*l*Br.

.....

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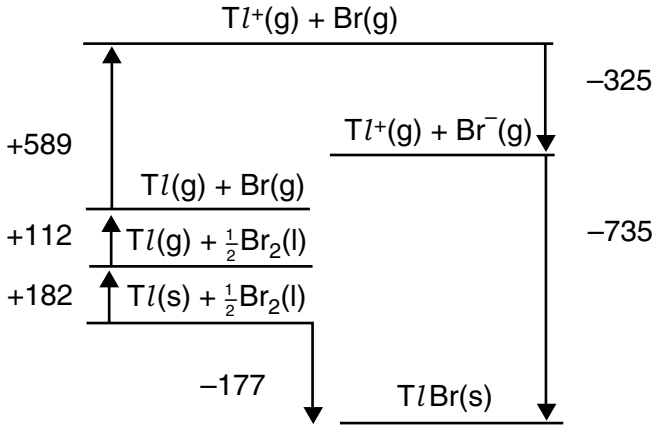
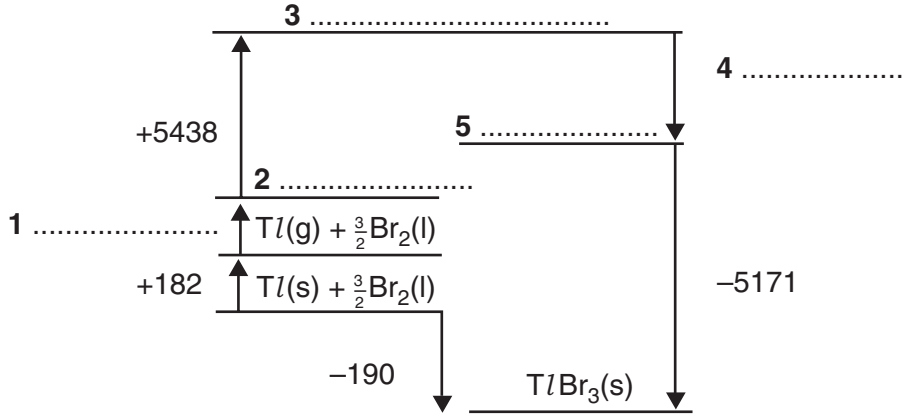
..... [2]

(c) A Born-Haber cycle for T*l*Br is given below. The enthalpy change values are in kJ mol^{-1}.



(i) Use data from this cycle to complete the Born-Haber cycle for $Tl Br_3$. Places where you have to write are labelled **1** to **5**.



[5]

(ii) In the $Tl Br_3$ cycle, name the enthalpy change represented by the value +5438 kJ mol^{-1}.

.....

..... [2]

(iii) Which enthalpy change in a Born-Haber cycle is the best measure of the stability of the compound concerned?

.....

..... [1]

(d) The mixture of $TlBr$ and TlI used in infrared spectrometers is described as having '42 mole% $TlBr$', that is, 42 moles out of every hundred are $TlBr$.

Calculate the **mass** of iodine that would be present for each 1.0 g of bromine.

A_r: Br, 80; I, 127.

mass of iodine = ... g [2]

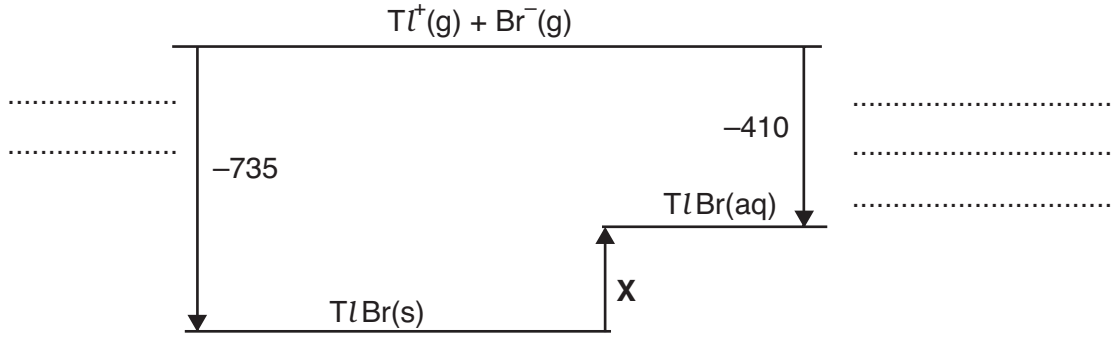
(e) **(i)** Thallium(I) bromide is insoluble in water. The main reason for this is the small size of the negative hydration enthalpy of the Tl^+ ion. Give **two** reasons why this value is small.

.....

.....

..... [2]

(ii) An enthalpy level diagram for the dissolving of $TlBr$ is shown below. Write labels on the dotted lines to name the enthalpy changes concerned.



[3]

(iii) Name the enthalpy change labelled **X** in the diagram and calculate its value, given that the data is in $kJ\,mol^{-1}$ units.

name of enthalpy change .....

value (with sign) ..... $kJ\,mol^{-1}$ [2]

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

Suggest **two** other properties (apart from solubility) of $TlBr$.

Explain how these properties can be deduced from its ionic structure.

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..... [4]

Quality of Written Communication [1]

[Total: 27]

4 When nitrate fertilisers are used, they often run off into water-courses. Unless they are removed they can finish up in water supplies where some are changed to nitrites.

Nitrite ions, NO_2^-, are particularly poisonous to babies as these ions can combine with the babies' haemoglobin to prevent oxygen take-up.

(a) Write down the oxidation states of nitrogen in:

nitrate, NO_3^- .....

nitrite, NO_2^- ..... [2]

(b) Nitrites are salts of nitrous acid, which is a weak acid.

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq) \qquad \textbf{equation 4.1}$$

(i) Explain the term *weak* in the description *weak acid*.

.....

..... [1]

(ii) Write the expression for the acidity constant, K_a, for nitrous acid.

[1]

(iii) K_a for nitrous acid has the value 4.7×10^{-4} mol dm^{-3}. Calculate the pH of a 0.10 mol dm^{-3} solution of nitrous acid.

pH = ... [2]

(iv) State **one** assumption you made in your method for part **(iii)**.

.....

..... [1]

(c) Nitrous acid also decomposes to give nitrogen monoxide and nitric acid.

$$3HNO_2(aq) \rightarrow 2NO(g) + HNO_3(aq) + \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{equation 4.2}$$

(i) Complete **equation 4.2**. [1]

(ii) When this reaction occurs in a test-tube, the colourless NO turns brown near the top of the tube. Suggest why this occurs.

.....

..... [2]

(d) Nitrates are made from nitric acid, which is made from ammonia.

Ammonia is made by the Haber process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \textbf{equation 4.3}$$

(i) Give the source of the nitrogen in this reaction.

..... [1]

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

A pressure of 70–200 atmospheres is used in the Haber process. Give and explain **two** reasons for using a high pressure.

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..... [6]

Quality of Written Communication [2]

(iii) Explain why an even higher pressure than 200 atmospheres is not used.

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..... [1]

(e) (i) Write the equilibrium constant expression for **equation 4.3** in terms of the partial pressures of the gases involved.

Give the units of K_p when the pressures are measured in atmospheres.

K_p =

units ..... [3]

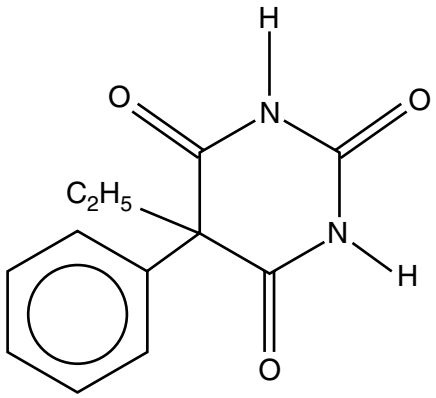
(ii) At 700 K, K_p has the value 7.76×10^{-5}. Calculate the partial pressure of ammonia in an equilibrium mixture where the partial pressure of nitrogen is 25.1 atm and the partial pressure of hydrogen is 75.3 atm.

Give your answer to a **suitable** number of significant figures.

pNH_3 = ... atm [3]

[Total: 26]

5 Phenobarbitol is a medicine which is used for the treatment of epilepsy. It is able to cross the blood/brain barrier better than many other substances.



phenobarbitol

(a) (i) Name the CONH group.

..... [1]

(ii) The proton n.m.r. spectrum of phenobarbitol has shifts at 1.0 and 1.4 from protons attached to carbon atoms. Explain the origin of these shifts, relating them to part of the molecule and give the relative areas of the peaks.

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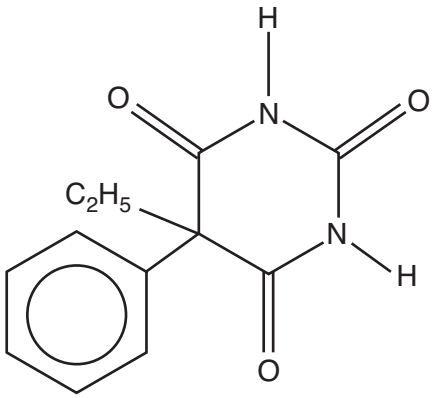
..... [3]

(b) Phenobarbitol has a low solubility of 4.3×10^{-3} mol dm^{-3} in water.

(i) The C═O and N–H groups encourage solubility in water by hydrogen bonding.

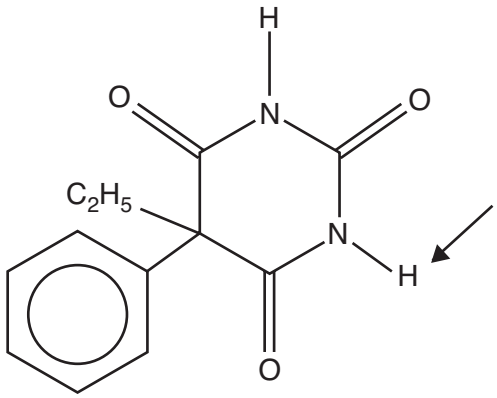
On the diagram below, show how water molecules form hydrogen bonds with each of C═O and N–H. Show lone pairs and partial charges.



[4]

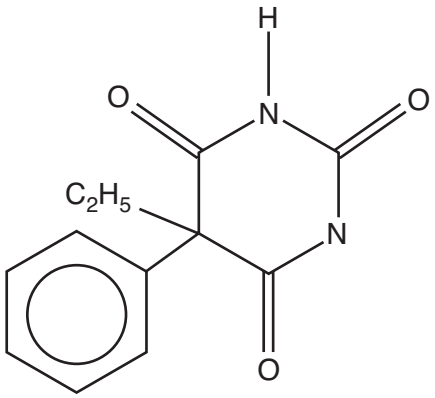
(ii) Name the part of the molecule that **inhibits** the solubility of phenobarbitol in water.

..... [1]



(c) Phenobarbitol is acidic. The acidic proton is shown by the arrow in the structure above.

Complete the structure below to show **both** the **ions** present in the salt that phenobarbitol forms with sodium hydroxide.



[2]

(d) Phenobarbitol is a weak acid. In the bloodstream, the amount of its ionisation is determined by the pH of blood, which is buffered at pH 7.4.

(i) What does a *buffer solution* do and what are its constituents?

what it does .....

.....

..... [3]

constituents .....

..... [1]

(ii) Write down the expression that relates pH to the hydrogen ion concentration.

Use this to calculate the value of $[H^+(aq)]$ in blood where the pH is 7.4.

$[H^+(aq)]$ = ... $mol\,dm^{-3}$ [2]

(iii) For phenobarbitol, $K_a = 3.9 \times 10^{-8}\,mol\,dm^{-3}$.

Use the expression $K_a = [H^+(aq)] \times [salt]/[acid]$ to calculate the ratio [salt]/[acid] for phenobarbitol in the blood.

[salt]/[acid] = ... [1]

(e) The un-ionised form of the medicine will cross the fatty blood/brain barrier from the bloodstream to the site of action of the medicine, whereas the ionised form will not.

Suggest why this is so, in terms of intermolecular forces.

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..... [4]

(f) Aspirin is an acidic medicine with a K_a of 3.3×10^{-4} mol dm^{-3}.

Show by calculation that this medicine is **less** likely than phenobarbitol to cross the blood / brain barrier.

[2]

[Total: 24]

END OF QUESTION PAPER

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