FOR OFFICIAL USE

AH

National
Qualifications
2022

Mark

X813/77/01

Chemistry
Section 1 — Answer grid and Section 2

FRIDAY, 29 APRIL

9:00 AM – 12:00 NOON

* X 8 1 3 7 7 0 1 *

Fill in these boxes and read what is printed below.

Full name of centre

Town

Forename(s)

Surname

Number of seat

Date of birth

Day Month Year

Scottish candidate number

You may refer to the Chemistry Data Booklet for Higher and Advanced Higher.

Total marks — 110

SECTION 1 — 25 marks

Attempt ALL questions.

Instructions for the completion of Section 1 are given on *page 02*.

SECTION 2 — 85 marks

Attempt ALL questions.

Write your answers clearly in the spaces provided in this booklet. Additional space for answers and rough work is provided at the end of this booklet. If you use this space you must clearly identify the question number you are attempting. Any rough work must be written in this booklet. You should score through your rough work when you have written your final copy.

Use **blue** or **black** ink.

Before leaving the examination room you must give this booklet to the Invigilator; if you do not, you may lose all the marks for this paper.

* X 8 1 3 7 7 0 1 0 1 *

The questions for Section 1 are contained in the question paper X813/77/02.

Read these and record your answers on the answer grid on *page 03* opposite.

Use **blue** or **black** ink. Do NOT use gel pens or pencil.

1. The answer to each question is **either** A, B, C or D. Decide what your answer is, then fill in the appropriate bubble (see sample question below).

2. There is **only one correct** answer to each question.

3. Any rough working should be done on the additional space for answers and rough work at the end of this booklet.

Sample question

To show that the ink in a ball-pen consists of a mixture of dyes, the method of separation would be:

A fractional distillation

B chromatography

C fractional crystallisation

D filtration.

The correct answer is **B** — chromatography. The answer **B** bubble has been clearly filled in (see below).

A	**B**	**C**	**D**
○	●	○	○

Changing an answer

If you decide to change your answer, cancel your first answer by putting a cross through it (see below) and fill in the answer you want. The answer below has been changed to **D**.

A	**B**	**C**	**D**
○	⊗	○	●

If you then decide to change back to an answer you have already scored out, put a tick (✓) to the **right** of the answer you want, as shown below:

A	**B**	**C**	**D**
○	⊗ ✓	○	⊗

or

A	**B**	**C**	**D**
○	⊗ ✓	○	○

X813770102

SECTION 1 — Answer grid

OBJ25AD1

	A	B	C	D
1	◯	◯	◯	◯
2	◯	◯	◯	◯
3	◯	◯	◯	◯
4	◯	◯	◯	◯
5	◯	◯	◯	◯
6	◯	◯	◯	◯
7	◯	◯	◯	◯
8	◯	◯	◯	◯
9	◯	◯	◯	◯
10	◯	◯	◯	◯
11	◯	◯	◯	◯
12	◯	◯	◯	◯
13	◯	◯	◯	◯
14	◯	◯	◯	◯
15	◯	◯	◯	◯
16	◯	◯	◯	◯
17	◯	◯	◯	◯
18	◯	◯	◯	◯
19	◯	◯	◯	◯
20	◯	◯	◯	◯
21	◯	◯	◯	◯
22	◯	◯	◯	◯
23	◯	◯	◯	◯
24	◯	◯	◯	◯
25	◯	◯	◯	◯

X813770103

[BLANK PAGE]

DO NOT WRITE ON THIS PAGE

X813770104

SECTION 2 — 85 marks

Attempt ALL questions

1. Oxygen is found in the p-block of the periodic table.

(a) The electronic configuration of an oxygen atom is $1s^2 2s^2 2p^4$.

(i) Draw the shape of a p orbital. **1**

(ii) For a 2p electron in oxygen, complete the table to show one possible set of values for the quantum numbers. **1**

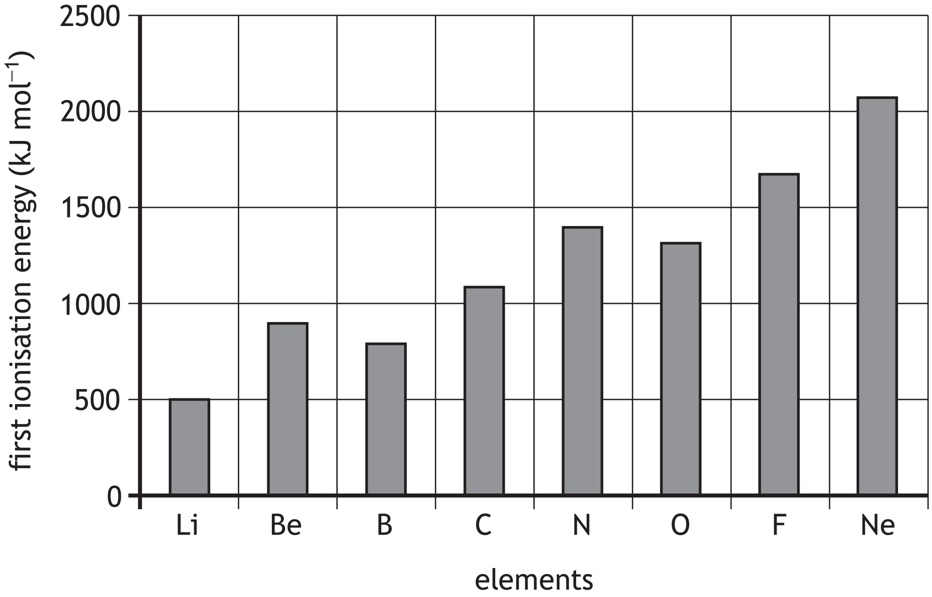
Quantum number	Value
n	2
l	
m_l	
m_s	

[Turn over

MARKS DO NOT WRITE IN THIS MARGIN

1. (continued)

(b) The graph shows the trend in first ionisation energy from lithium to neon.



Explain, in terms of electronic structure, why the first ionisation energy of oxygen is less than the first ionisation energy of nitrogen. **1**

X813770106

1. (continued)

(c) The remains of a star were found to be rich in oxygen. Some of the oxygen atoms had been ionised to single electron ions, O^{7+}. The emission spectrum of O^{7+} has a characteristic spectral line.

The energy, E, of this spectral line is given by the equation

$$E = R\,Z^2\left(1-\frac{1}{n^2}\right)$$

where: E is the energy, in J

Z is the atomic number

n is the principal quantum number of the second energy level

R is the Rydberg energy, with a value of 2.18×10^{-18} J.

Calculate the energy, in J, of this O^{7+} spectral line. **1**

[Turn over

2. Nitrogen monoxide, NO, is an important oxide of nitrogen.

(a) Photochemical smog is a type of air pollution. It is formed through a sequence of atmospheric reactions involving nitrogen monoxide. One of the reactions is

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \rightarrow NO(g)$$

Substance	ΔH_f° ($kJ\,mol^{-1}$)	S° ($J\,K^{-1}\,mol^{-1}$)
$N_2(g)$	0	192
$O_2(g)$	0	205
$NO(g)$	90.3	211

Use the data in the table to determine if the reaction is feasible at 298 K. **3**

(*Clearly show your working for the calculation.*)

2. (continued)

(b) The UK workplace exposure limit for nitrogen monoxide is 2 ppm.

A worker inhales 5 litres of air per minute containing 2 ppm of nitrogen monoxide.

Calculate the mass of nitrogen monoxide inhaled in one hour by the worker. **2**

(c) Nitrogen monoxide can react with nitrogen dioxide to form dinitrogen trioxide.

$$NO(g) + NO_2(\ell) \rightarrow N_2O_3(s)$$

Complete the table to show the oxidation number of nitrogen in each oxide. **1**

Oxide	Oxidation number of nitrogen
NO	+2
NO_2	
N_2O_3	

[Turn over

2. (continued)

(d) At high temperatures, nitrogen monoxide can also react with hydrogen.

A proposed reaction mechanism is

Step 1 $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ (slow)

Step 2 $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ (fast)

(i) (A) Write a rate equation for this reaction. **1**

(B) The experimental rate constant is $2.7 \times 10^3\ l^2\ mol^{-2}\ s^{-1}$.

The table shows experimental rate data for the reaction.

[NO] ($mol\ l^{-1}$)	[H_2] ($mol\ l^{-1}$)	Initial reaction rate ($mol\ l^{-1}\ s^{-1}$)
	0.015	0.0040

Complete the table to show the concentration of nitrogen monoxide. **1**

(ii) Write a balanced equation for the overall reaction. **1**

X813770110

MARKS DO NOT WRITE IN THIS MARGIN

3. Hydrofluoric acid, HF, is a weak acid.

$$HF(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

(a) State what is meant by a weak acid. **1**

(b) $3.75\ mol\,l^{-1}$ hydrofluoric acid solution can be used to engrave glass.

(i) Calculate the pH of this hydrofluoric acid solution. **2**

(ii) The concentration of commercially available hydrofluoric acid solution is expressed in terms of percentage by mass.

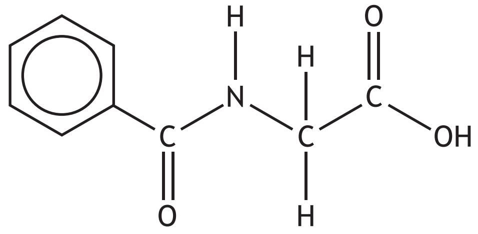
Calculate the percentage by mass of a $3.75\ mol\,l^{-1}$ hydrofluoric acid solution. **2**

(iii) Hydrofluoric acid solution reacts with the silicon dioxide in glass to produce silicon fluoride, SiF_4.

State the shape of SiF_4 molecules. **1**

* X 8 1 3 7 7 0 1 1 1 *

4. Hippuric acid is found in urine.

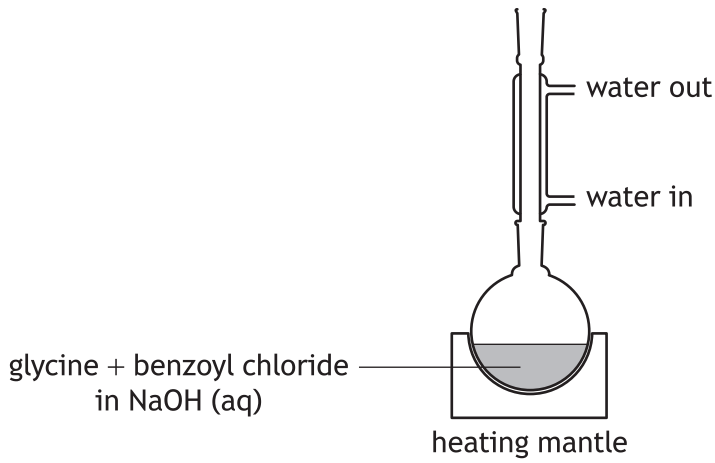


hippuric acid

(a) Hippuric acid can be made in the laboratory.

(i) The first step of the procedure involves heating a mixture of glycine and benzoyl chloride with excess dilute sodium hydroxide solution.

The diagram shows the apparatus used to heat the mixture.



(A) Name the technique shown in the diagram. **1**

(B) State what else should be added to the round-bottomed flask before heating the mixture. **1**

4. (a) (continued)

(ii) The sodium salt of hippuric acid formed in the reaction mixture during the first step is then treated with dilute hydrochloric acid. A white precipitate of hippuric acid is formed.

Explain why adding hydrogen ions to the salt of a weak acid results in the formation of undissociated weak acid molecules. **1**

(iii) The reaction mixture was filtered and the hippuric acid was recrystallised from hot water.

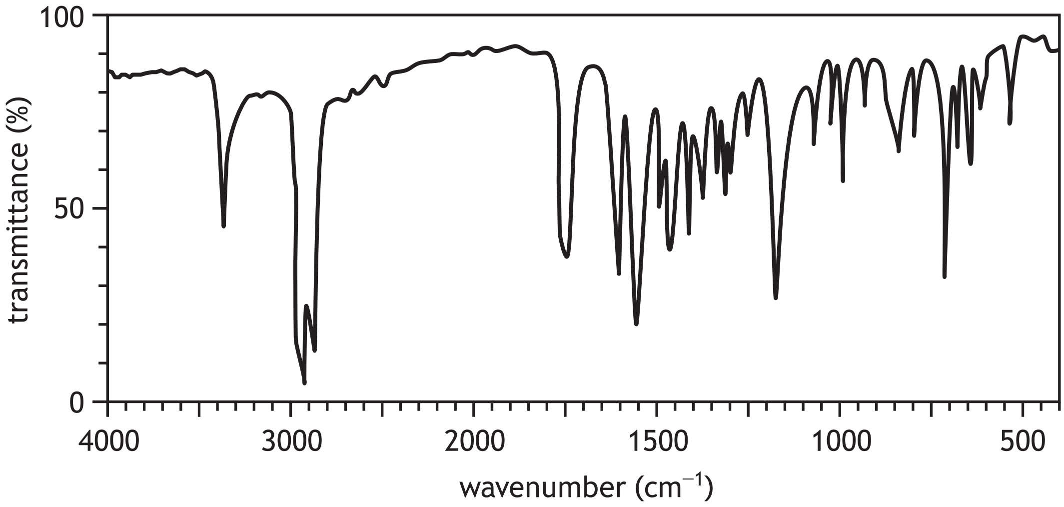
(A) Describe how the filtration should have been carried out to ensure that the hippuric acid was separated quickly from the reaction mixture. **1**

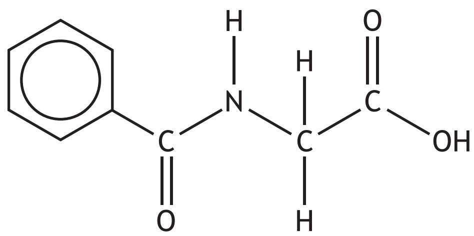
(B) State why the hippuric acid was recrystallised. **1**

[Turn over

4. (continued)

(b) An infrared spectrum for hippuric acid is shown below.





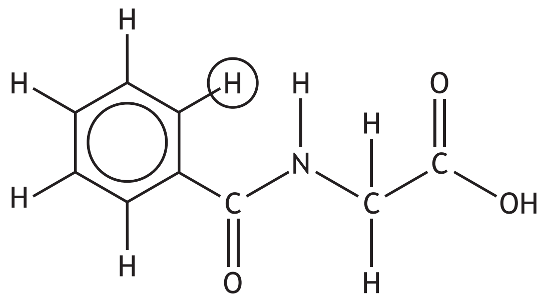
hippuric acid

(i) State a reason why different bonds absorb different wavenumbers of infrared radiation. **1**

(ii) State the wavenumber, in cm^{-1}, of the peak in this infrared spectrum caused by the N–H bond. **1**

4. (continued)

(c) The structure of hippuric acid can be investigated using ^1H NMR spectroscopy.



hippuric acid

(i) State the number of ^1H environments in hippuric acid. **1**

(ii) Predict the splitting pattern in a high resolution ^1H NMR spectrum that would be observed for the hydrogen atom circled in the structure above. **1**

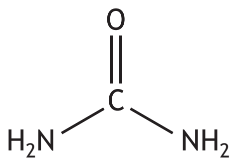
(iii) The absorption of radiation in the radiofrequency region causes ^1H nuclei to adopt a high energy state aligned against a strong magnetic field.

Explain how this leads to peaks in an NMR spectrum corresponding to different ^1H environments. **2**

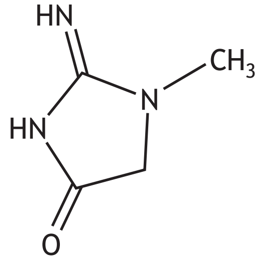
MARKS DO NOT WRITE IN THIS MARGIN

4. **(continued)**

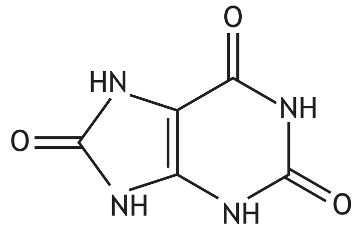
(d) Human urine is mostly water (91% to 96%) with organic solutes including urea, creatinine and uric acid, with trace amounts of other substances such as carboxylic acids, enzymes, carbohydrates, pigments and salts. The pH of human urine can vary throughout the day.



urea



creatinine



uric acid

Using your knowledge of chemistry, comment on the likely pH range of human urine. **3**

DO NOT WRITE IN THIS MARGIN

4. (d) (continued)

[Turn over

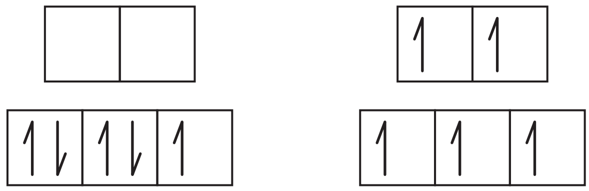
X813770117

MARKS | DO NOT WRITE IN THIS MARGIN

5. Cobalt can bind to different ligands to form octahedral complexes where the d orbitals are split into higher and lower energies.

(a) State what causes the d orbital splitting in octahedral complexes. **1**

(b) In some complex ions, the electrons in the d orbitals exist in a 'low spin state' and in other complex ions, the electrons exist in a 'high spin state'. The low spin state and high spin state electron arrangements of a complex ion with five d electrons are shown below.



low spin state high spin state

(i) The filling of orbitals obeys the aufbau principle.

State the aufbau principle. **1**

X813770118

5. (b) (continued)

(ii) Information about some complex ions of cobalt is shown in the table.

Complex ion	P ($kJ\ mol^{-1}$)	Δ ($kJ\ mol^{-1}$)	Spin state
$[Co(OH_2)_6]^{2+}$	250	111	high
$[CoF_6]^{3-}$	283	156	high
$[Co(OH_2)_6]^{3+}$	283	323	low
$[Co(CN)_6]^{3-}$	283	416	low

where: P is the energy required to pair two electrons with opposite spin

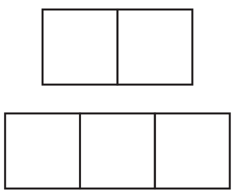
Δ is the difference in energy between subsets of d orbitals.

(A) From the information in the table, give two conclusions. **2**

(B) Write the name of the complex ion $[CoF_6]^{3-}$. **1**

(C) Complete the diagram to show the arrangement of the d electrons in $[CoF_6]^{3-}$. **1**

(An additional diagram, if required, can be found on *page 34*.)



X813770119

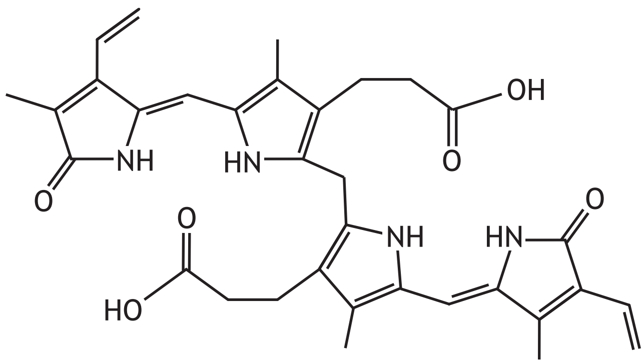
MARKS | DO NOT WRITE IN THIS MARGIN

6. Jaundice is a condition caused by a yellow compound in the body called bilirubin.

The structure of bilirubin has two chromophores.

(a) (i) Circle one of the chromophores in the structure of bilirubin below. **1**

(An additional diagram, if required, can be found on *page 34*.)



(ii) Bilirubin is coloured due to the presence of bonding molecular orbitals and antibonding molecular orbitals.

State one difference between a bonding molecular orbital and an antibonding molecular orbital. **1**

(b) Bilirubin can have cis or trans isomerism.

(i) Explain fully why cis and trans isomerism can exist in some compounds with carbon–carbon double bonds. **2**

X813770120

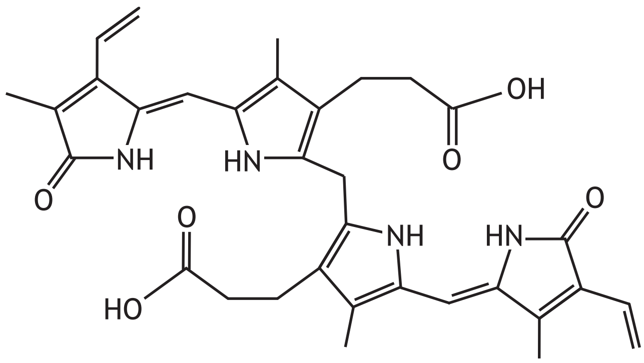
MARKS DO NOT WRITE IN THIS MARGIN

6. (b) (continued)

(ii) One isomer of bilirubin is insoluble in water due to the presence of internal hydrogen bonding.

On the diagram below draw a dotted line to show one internal hydrogen bond. **1**

(An additional diagram, if required, can be found on *page 34*.)



(c) One treatment for jaundice in new-born babies is to expose them to blue light. This causes the yellow bilirubin to change into compounds that can be excreted by the body.

(i) Suggest why blue light is used in this treatment. **1**

(ii) Calculate the energy, in kJ mol^{-1}, associated with blue light with a wavelength of 465 nm. **2**

7. Fertilisers and other garden chemicals may contain small quantities of different metals.

(a) The concentration of manganese(II) ions, Mn^{2+}, in a fertiliser can be determined by colorimetry.

5.66 g of fertiliser was weighed by difference, dissolved in deionised water and heated with a strong oxidising agent. The Mn^{2+} ions were oxidised to purple permanganate ions, MnO_4^-.

$$Mn^{2+}(aq) + 8H^+(aq) + 5e^- \rightarrow MnO_4^-(aq) + 4H_2O(\ell)$$

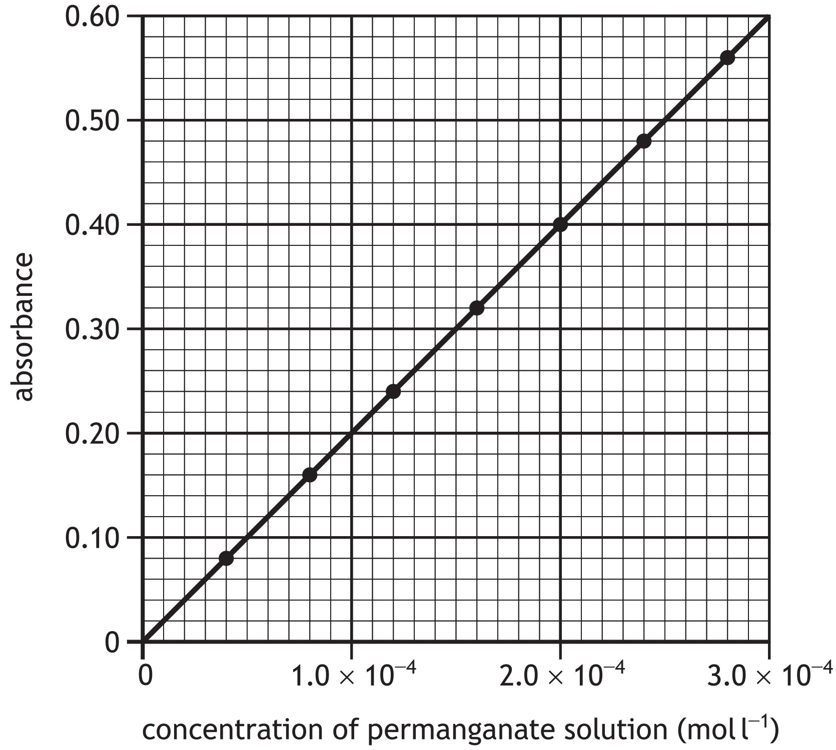
The resulting permanganate solution was transferred to a 100 cm^3 standard flask and made up to the mark with deionised water.

The absorbance of this solution was measured using a colorimeter. The concentration of the solution was then determined from a calibration graph.

(i) Describe fully the procedure of weighing by difference. **2**

7. (a) (continued)

(ii) The calibration graph obtained is shown below.



The absorbance of the permanganate solution was 0.42.

Use this information and the calibration graph to calculate the percentage by mass of manganese(II) ions in the fertiliser. **2**

7. (continued)

(b) Lawn sand, which is used to kill moss in lawns, contains iron(II) ions, Fe^{2+}.

The percentage of iron(II) ions in lawn sand can be determined by redox titration with standard acidified potassium dichromate solution, $K_2Cr_2O_7(aq)$.

(i) State one characteristic of potassium dichromate that makes it suitable for use as a primary standard. **1**

(ii) A sample of lawn sand was mixed with dilute sulfuric acid. The solution was filtered into a 250 cm^3 standard flask with rinsing and made up to the mark with deionised water.

25.0 cm^3 samples of the iron(II) solution were titrated with 0.0050 mol l^{-1} acidified potassium dichromate solution and the average titre was found to be 21.4 cm^3.

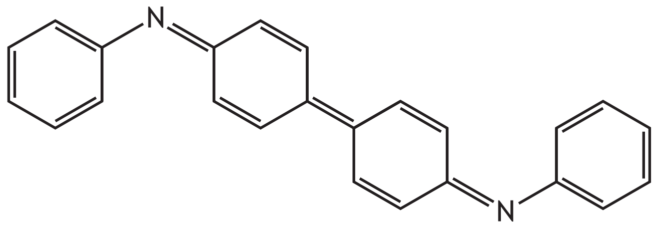
$$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(\ell)$$

Calculate the mass, in g, of iron(II) ions in the lawn sand sample. **3**

7. (b) (continued)

(iii) The titration can be carried out using diphenylbenzidine indicator. Diphenylbenzidine is oxidised to a violet compound at the end-point.

The oxidised form of this indicator contains a conjugated system.



oxidised form of diphenylbenzidine

Explain fully how the violet colour arises in the oxidised form of diphenylbenzidine. **2**

[Turn over

MARKS | DO NOT WRITE IN THIS MARGIN

8. Acid chlorides are useful reagents in organic synthesis.

(a) Ethanoyl chloride is an acid chloride that can be prepared by the reaction between ethanoic acid and phosphorus trichloride.

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + \mathbf{X}$$

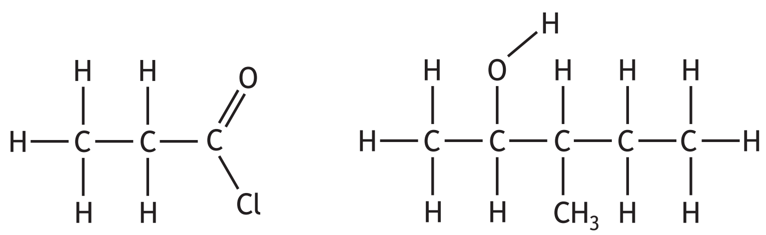
Write a formula for **X**. **1**

(b) Propanoyl chloride reacts with 3-methylpentan-2-ol to form an ester. The first step in this reaction involves nucleophilic attack.

(i) State what is meant by the term nucleophile. **1**

(ii) Add a curly arrow between the structures below to show the nucleophilic attack step. **1**

(An additional diagram, if required, can be found on *page 35*.)



MARKS DO NOT WRITE IN THIS MARGIN

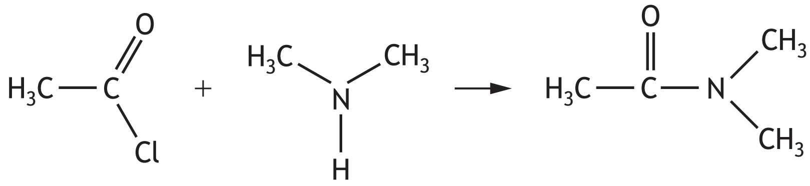
8. (b) (continued)

(iii) Draw a structural formula for the ester formed in this reaction. **1**

(iv) Name the other product of this reaction. **1**

(v) State why acid chlorides are preferred to carboxylic acids for the preparation of esters. **1**

(c) Acid chlorides react with some amines.



compound **Y**

(i) State the type of amine used in this reaction. **1**

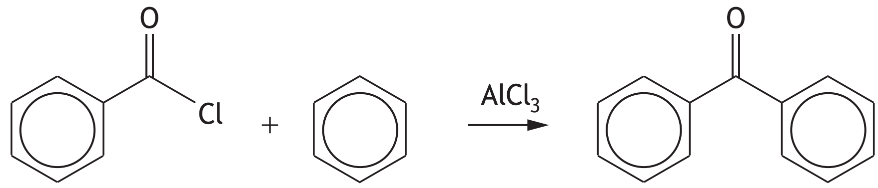
(ii) State the class of compound to which compound **Y** belongs. **1**

* X 8 1 3 7 7 0 1 2 7 *

MARKS | DO NOT WRITE IN THIS MARGIN

8. (continued)

(d) Benzophenone is used as a fragrance enhancer in some cosmetic products. It can be produced by reacting benzoyl chloride with benzene in the presence of aluminium chloride.



benzoyl chloride | benzophenone

(i) Suggest a name for the type of reaction taking place. **1**

(ii) 21.8 g of benzoyl chloride (GFM = 140.5 g) was reacted with excess benzene, producing 18.4 g of benzophenone (GFM = 182 g).

Calculate the percentage yield. **2**

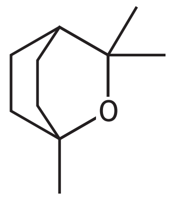
X813770128

9. Haloalkanes can react with sodium hydroxide in elimination reactions and nucleophilic substitution reactions.

A student reacted 2-bromopentane with sodium hydroxide in ethanol. Analysis of the reaction mixture showed a complex mixture of products.

Using your knowledge of chemistry, suggest how these products might form and how they could be identified. **3**

10. Eucalyptol is a natural antagonist that is used as an anti-inflammatory drug. **MARKS** DO NOT WRITE IN THIS MARGIN



eucalyptol

(a) State what is meant by the term antagonist. **1**

(b) Homeopathy is an alternative therapy based on the use of highly diluted substances.

500 cm^3 of a stock solution was prepared by diluting eucalyptol with water by a factor of one in one hundred.

(i) State the volume, in cm^3, of eucalyptol required to prepare this stock solution. **1**

(ii) Eucalyptol ($GFM = 154$ g) has a density of 0.921 $g\,cm^{-3}$.

Calculate the concentration, in $mol\,l^{-1}$, of the stock solution. **2**

(iii) A homeopathic solution of eucalyptol was prepared by further dilution giving a concentration of 9.97×10^{-24} $mol\,l^{-1}$.

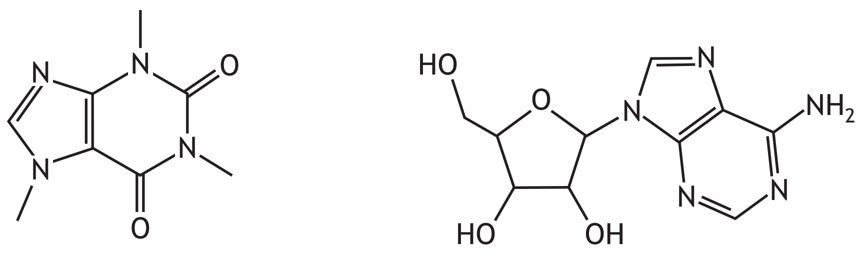
The number of molecules in 1 mole of eucalyptol is 6.02×10^{23}.

Calculate the number of molecules in 1 litre of the homeopathic solution. **1**

* X 8 1 3 7 7 0 1 3 0 *

11. Caffeine is found in many soft drinks. It acts as an adenosine receptor antagonist. Adenosine is a chemical that binds to receptors in the brain and promotes sleep.

The structures of caffeine and adenosine are shown.



caffeine adenosine

(a) (i) Write the molecular formula for caffeine. **1**

(ii) Suggest why caffeine and adenosine can bind to the same receptors. **1**

[Turn over

11. (continued)

(b) 100 cm^3 of a soft drink contained 32 mg of caffeine. The caffeine was separated by solvent extraction using dichloromethane.

The following equilibrium was established.

$$\text{caffeine (aq)} \rightleftharpoons \text{caffeine (dichloromethane)}$$

(i) To determine the equilibrium constant, a single extraction of caffeine was carried out using 100 cm^3 of the soft drink and 60 cm^3 of dichloromethane. The mass of caffeine in the dichloromethane was found to be 23.5 mg.

(A) Outline the steps that would have been carried out to extract the caffeine. **2**

(B) Calculate the equilibrium constant, *K*, for this extraction. **3**

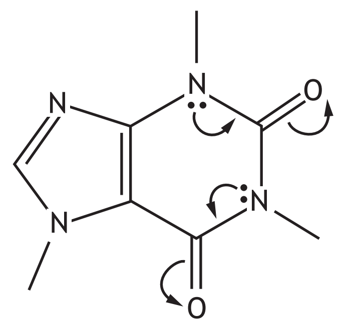
(ii) Suggest an improvement to the procedure that would maximise the mass of caffeine extracted from 100 cm^3 of the soft drink using 60 cm^3 of dichloromethane. **1**

* X 8 1 3 7 7 0 1 3 2 *

11. (continued)

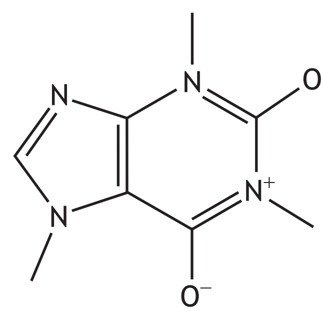
(c) A zwitterion is a molecule with positive and negative charges on different atoms. Overall, the zwitterion molecule is electrically neutral.

Caffeine can form a zwitterion due to the movement of electrons within the molecule as shown.



Complete the diagram below to show all the charges on the caffeine zwitterion resulting from the movement of electrons. **1**

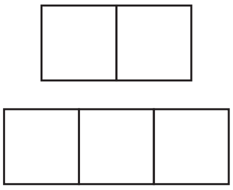
(An additional diagram, if required, can be found on *page 35*.)



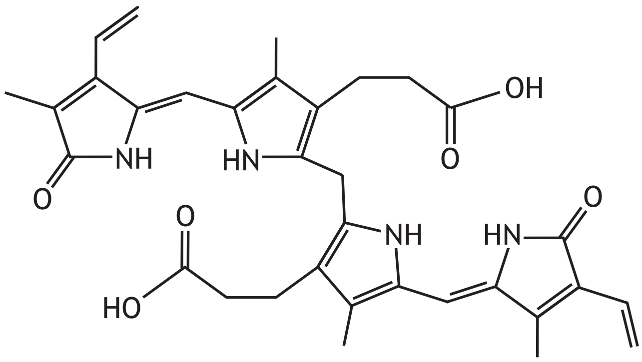
[END OF QUESTION PAPER]

ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK

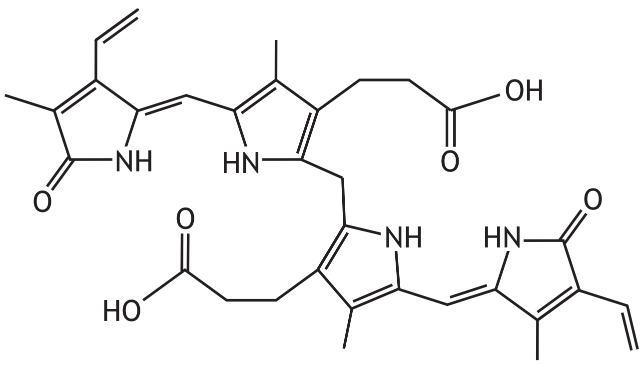
Additional diagram for use with question 5 (b) (ii) (C)



Additional diagram for use with question 6 (a) (i)

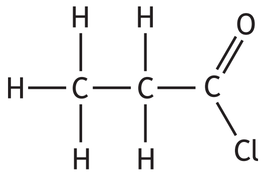


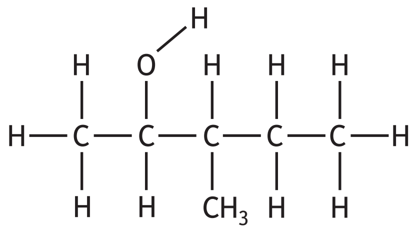
Additional diagram for use with question 6 (b) (ii)



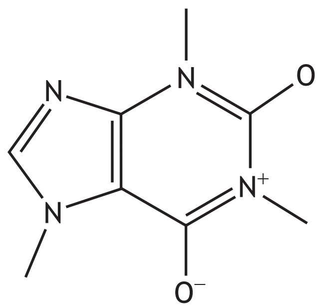
ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK

Additional diagram for use with question 8 (b) (ii)





Additional diagram for use with question 11 (c)



ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK

MARKS DO NOT WRITE IN THIS MARGIN

ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK

X813770137

MARKS DO NOT WRITE IN THIS MARGIN

ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK

X813770138

ADDITIONAL SPACE FOR ANSWERS AND ROUGH WORK

[BLANK PAGE]

DO NOT WRITE ON THIS PAGE

X813770140