X273/13/02

NATIONAL QUALIFICATIONS 2015

THURSDAY, 28 MAY
1.00 PM – 3.30 PM

CHEMISTRY
ADVANCED HIGHER (REVISED)

Reference may be made to the Chemistry Higher and Advanced Higher Data Booklet.

SECTION A – 30 marks

Instructions for completion of **SECTION A** are given on page two.

For this section of the examination you must use an **HB pencil.**

SECTION B – 70 marks

All questions should be attempted.

Answers must be written clearly and legibly in ink.

SECTION A

Read carefully

1 Check that the answer sheet provided is for **Chemistry Advanced Higher (Revised) (Section A)**.

2 For this section of the examination you must use an **HB pencil** and, where necessary, an eraser.

3 Check that the answer sheet you have been given has **your name**, **date of birth**, **SCN** (Scottish Candidate Number) and **Centre Name** printed on it.

Do not change any of these details.

4 If any of this information is wrong, tell the Invigilator immediately.

5 If this information is correct, **print** your name and seat number in the boxes provided.

6 The answer to each question is **either** A, B, C or D. Decide what your answer is, then, using your pencil, put a horizontal line in the space provided (see sample question below).

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

8 Any rough working should be done on the question paper or the rough working sheet, **not** on your answer sheet.

9 At the end of the exam, put the **answer sheet for Section A inside the front cover of your answer book**.

Sample Question

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

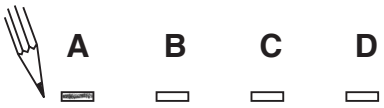
A chromatography

B fractional distillation

C fractional crystallisation

D filtration.

The correct answer is **A**—chromatography. The answer **A** has been clearly marked in **pencil** with a horizontal line (see below).



Changing an answer

If you decide to change your answer, carefully erase your first answer and using your pencil, fill in the answer you want. The answer below has been changed to **D**.

1. Infrared radiation can be used in the analysis and identification of organic compounds. Compared to visible radiation, infrared radiation has a

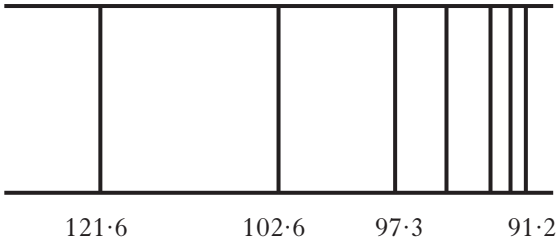
A shorter wavelength and higher frequency

B longer wavelength and lower velocity

C longer wavelength and lower frequency

D shorter wavelength and higher velocity.

2. The diagram shows one of the series of lines in the hydrogen emission spectrum.



Each line

A represents an energy level within a hydrogen atom

B results from an electron moving to a higher energy level

C lies within the visible part of the electromagnetic spectrum

D results from an excited electron dropping to a lower energy level.

3. The electronic configuration of a krypton atom is

$1s^2\ 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$.

Which of the following ions does **not** have this configuration?

A Sr^{2+}

B Se^{2-}

C As^{3-}

D Zr^{3+}

4. A Lewis base may be regarded as a substance which is capable of donating an unshared pair of electrons to form a covalent bond.

Which of the following could act as a Lewis base?

A Co^{3+}

B PH_3

C BCl_3

D NH_4^+

5. Which line in the table represents the shape and the number of bonding and non-bonding pairs of electrons in the H_3O^+ ion?

	Shape	**Bonding pairs**	**Non-bonding pairs**
A	tetrahedral	2	2
B	pyramidal	3	1
C	pyramidal	3	0
D	trigonal planar	3	0

6. The formula for the tetraamminedichlorocopper(II) complex is

A $[Cu(NH_3)_4Cl_2]^{2-}$

B $[Cu(NH_3)_4Cl_2]$

C $[Cu(NH_3)_4Cl_2]^{2+}$

D $[Cu(NH_3)_4Cl_2]^{4+}$.

7. Which of the following would **not** act as a ligand in the formation of a complex with a transition metal ion?

A O^{2-}

B $NH_2C_2H_4NH_2$

C $C_2H_5NH_3^+$

D
$$\begin{array}{l} COO^- \\ | \\ COO^- \end{array}$$

8. What is the co-ordination number of the transition metal in $[Co(NH_3)_4(H_2O)_2]Cl_3$?

A 3

B 4

C 6

D 9

9. Which of the following solids would form a colourless aqueous solution?

A $ZnSO_4.7H_2O$

B $NiSO_4.6H_2O$

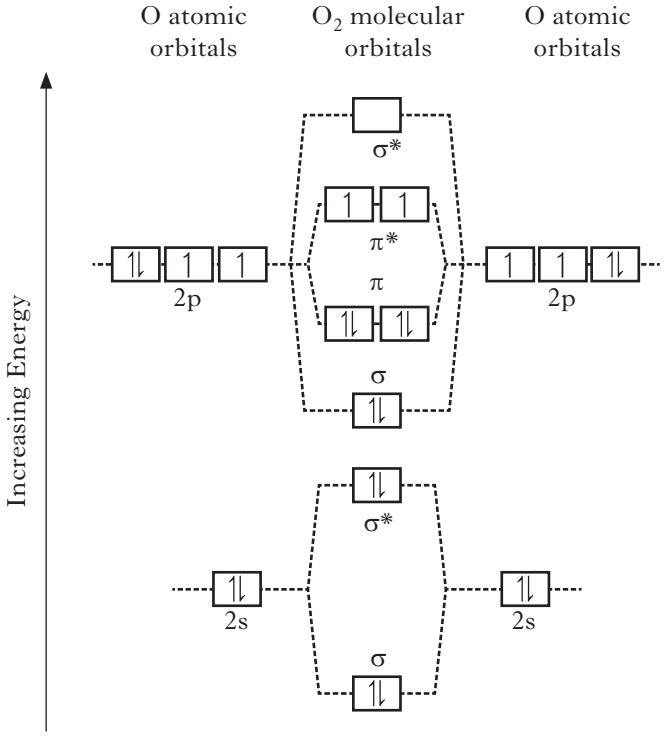
C K_2CrO_4

D $CoCl_2$

10. The stability of a covalent bond is related to its bond order, which can be defined as follows:

bond order = $\frac{1}{2}$ (number of bonding electrons – number of anti-bonding electrons)

The molecular orbital diagram for oxygen is shown. The anti-bonding orbitals are denoted by *.



The bond order for a molecule of oxygen is

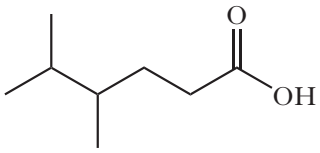
A 0

B 1

C 2

D 3.

11.



The name of the compound shown above is

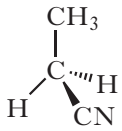
A 2,3-dimethylpentanoic acid

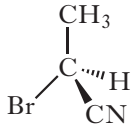
B 2,3-dimethylhexanoic acid

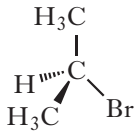
C 4,5-dimethylhexanoic acid

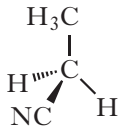
D 4,5,5-trimethylpentanoic acid.

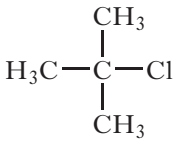
12. Which of the following compounds will have an enantiomer?

A 

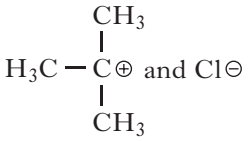
B 

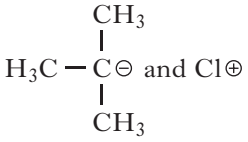
C 

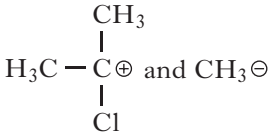
D 

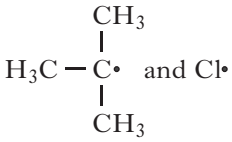
13. 

Which of the following would be the most likely products of heterolytic bond fission of the above compound?

A 

B 

C 

D 

14. Which of the following equations does **not** involve a nucleophilic substitution?

A $C_2H_5Br + NaOH \xrightarrow{\text{water}} C_2H_5OH + NaBr$

B $C_3H_7Br + KCN \xrightarrow{\text{ethanol}} C_3H_7CN + KBr$

C $C_2H_5Cl + C_2H_5ONa \xrightarrow{\text{ethanol}} C_2H_5OC_2H_5 + NaCl$

D $C_3H_7Br + KOH \xrightarrow{\text{ethanol}} C_3H_6 + KBr + H_2O$

[Turn over

15. Which of the following reacts with ethanol to form the ethoxide ion?

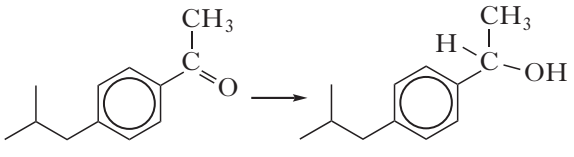
A Na(s)

B $Na_2O(s)$

C NaCl(aq)

D NaOH(aq)

16. One of the stages in the preparation of Ibuprofen is shown.



Which of the following reagents could bring about this change?

A HCl

B $LiAlH_4$

C HCN

D H_2O

17. Which of the following compounds will react with both dilute hydrochloric acid and sodium hydroxide solution?

A C_6H_5OH

B $C_6H_5NH_2$

C HOC_6H_4COOH

D $H_2NC_6H_4COOH$

18. Lycopene and ß-carotene are coloured organic compounds found in ripened tomatoes. Both absorb light in the visible region. Lycopene is red and ß-carotene is orange.

Which of the following statements is true about the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in lycopene and ß-carotene?

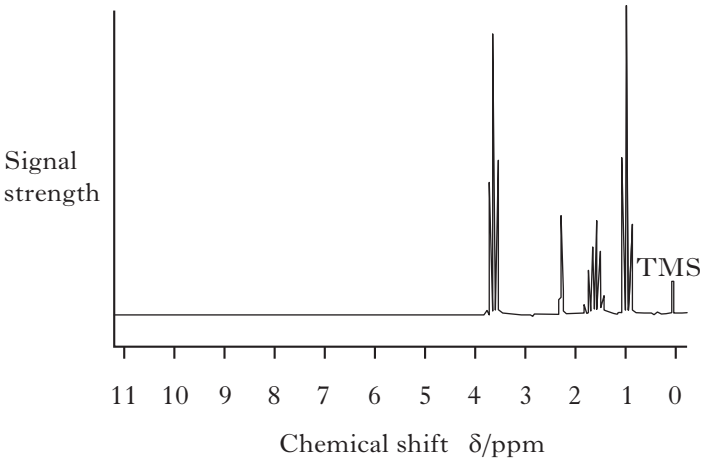
A ß-Carotene has a higher energy gap between HOMO and LUMO than lycopene.

B Lycopene has a higher energy gap between HOMO and LUMO than ß-carotene.

C ß-Carotene has the same energy gap between HOMO and LUMO as lycopene.

D The colour of ß-carotene and lycopene is not affected by the energy gap between HOMO and LUMO.

19. The high resolution proton NMR spectrum of compound **X** is shown below.



X could be

A propanal

B propanone

C propan-l-ol

D propanoic acid.

20. Which of the following salts will form a solution with the lowest pH?

A Potassium chloride

B Potassium ethanoate

C Ammonium chloride

D Ammonium ethanoate

21. Which of the following would **not** be suitable as a buffer solution?

A Boric acid and sodium borate

B Nitric acid and sodium nitrate

C Benzoic acid and sodium benzoate

D Propanoic acid and sodium propanoate

22. The standard entropy of a perfect crystal is zero at

A 0 K

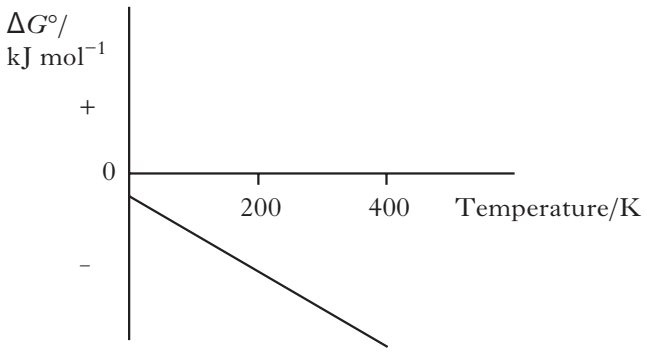
B 25 K

C 273 K

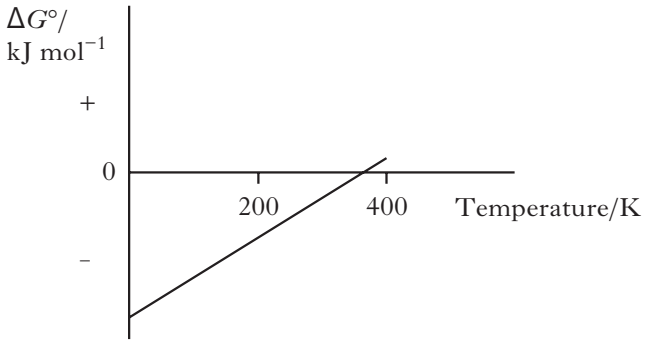
D 298 K.

23. Which of the following graphs shows the variation in ΔG° with temperature for a reaction which is always feasible?

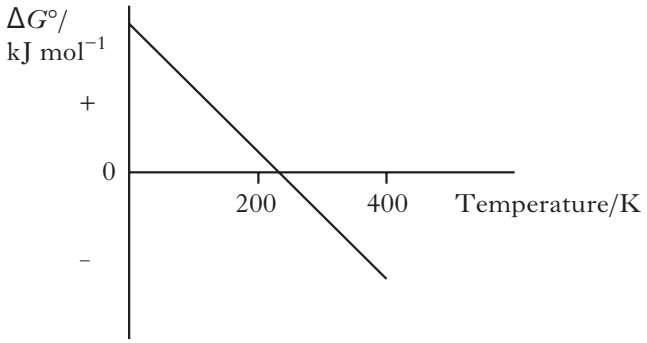
A



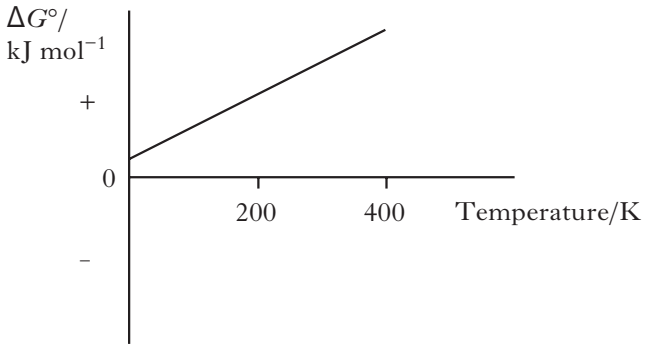
B



C



D



24. The reaction

$2SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons 2SO_3(g)$

is reversible. After equilibrium has been established the reaction mixture was found to contain 0·2 moles of SO_2, 0·2 moles of O_2 and 16 moles of SO_3.

Which of the following is correct?

A $K > 1$ and $\Delta G^\circ > 0$

B $K > 1$ and $\Delta G^\circ < 0$

C $K < 1$ and $\Delta G^\circ > 0$

D $K < 1$ and $\Delta G^\circ < 0$

25. In a chemical reaction the rate is doubled for every 10 °C rise in temperature. When the temperature is increased from 20 °C to 60 °C, the rate of the reaction will become faster by a factor of

A 3

B 4

C 8

D 16.

26. Two mechanisms have been proposed for the hydrolysis of 2-bromo-2-methylpropane.

One of these has only one step

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

The other has two steps

$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ (Slow)

$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ (Fast)

The reaction is observed to follow first order kinetics. The rate equation for the overall reaction is

A rate = $k[(CH_3)_3CBr]$

B rate = $k[(CH_3)_3CBr][OH^-]$

C rate = $k[(CH_3)_3C^+]$

D rate = $k[(CH_3)_3C^+][OH^-]$.

27. Which one of the following is **not** suitable for the preparation of a primary standard in volumetric analysis?

A Anhydrous sodium carbonate

B Sodium hydroxide

C Oxalic acid

D Potassium iodate

28. The most appropriate pieces of equipment to use when diluting a solution by a factor of 10 would be

A a 10·0 cm^3 pipette and a 100 cm^3 measuring cylinder

B a 10·0 cm^3 pipette and a 50 cm^3 standard flask

C a 25·0 cm^3 measuring cylinder and a 250 cm^3 standard flask

D a 25·0 cm^3 pipette and a 250 cm^3 standard flask.

29. Using thin-layer chromatography the components of a mixture can be identified by their R_f values.

Which of the following statements is **true** about the R_f value of an individual component of a mixture?

A The type of stationary phase has no effect on the R_f value.

B The polarity of the component has no effect on the R_f value.

C The composition of the mobile phase has no effect on the R_f value.

D The distance the solvent front moves has no effect on the R_f value.

30. An excess of sodium sulfate was added to a solution of a barium compound to precipitate all the barium ions as barium sulfate, $BaSO_4$. (GFM of $BaSO_4$ = 233·4 g).

How many grams of barium are in 0·458 g of the barium compound if a solution of this sample gave 0·513 g of $BaSO_4$ precipitate?

A 0·032 g

B 0·055 g

C 0·269 g

D 0·302 g

[*END OF SECTION A*]

Candidates are reminded that the answer sheet for Section A MUST be placed INSIDE the front cover of your answer book.

[Turn over for SECTION B on *Page ten*

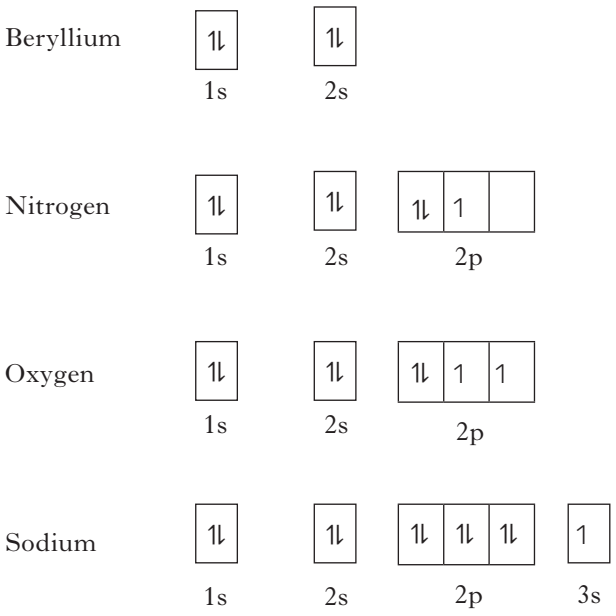
SECTION B

Marks

70 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

1. (*a*) A student wrote the following ground state electronic configurations for atoms of beryllium, nitrogen, oxygen and sodium, where ↿ denotes an electron.



(i) The three atomic orbitals in the 2p subshell are said to be degenerate.

What is meant by the term degenerate? **1**

(ii) Explain why the electronic configuration for nitrogen shown above is incorrect. **1**

(iii) Each electron in an atom is described by four quantum numbers.

The table shows the values of the quantum numbers for the 1s electrons in beryllium.

	Quantum number			
Electron	**Principal (n)**	**Angular momentum(l)**	**Magnetic (m)**	**Spin (s)**
1s ↿	1	0	0	$+\frac{1}{2}$
1s ↾	1	0	0	$-\frac{1}{2}$

State the values of the 4 quantum numbers for the 3s electron in sodium. **1**

(*b*) The first ionisation energy of sodium is 502 kJ mol^{-1}.

(i) Calculate the wavelength of light corresponding to this ionisation energy. **3**

(ii) Explain whether visible light would provide sufficient energy to ionise gaseous sodium atoms. **1**

(7)

Marks

2. Zinc oxide can be reduced to zinc in a blast furnace.

One of the reactions taking place in the furnace is shown.

$$ZnO(s) + CO(g) \rightarrow Zn(g) + CO_2(g)$$

Substance	**Standard enthalpy of formation, ΔH_f°/ kJ mol^{-1}**	**Standard entropy, S°/ J K^{-1} mol^{-1}**
ZnO(s)	−348	44
CO(g)	−110	198
Zn(g)	+130	161
CO_2(g)	−394	214

For the reduction of zinc oxide with carbon monoxide, use the data in the table to calculate:

(*a*) the standard enthalpy change, ΔH°, in kJ mol^{-1}; **1**

(*b*) the standard entropy change, ΔS°, in J K^{-1} mol^{-1}; **1**

(*c*) the theoretical temperature above which the reaction becomes feasible. **2**

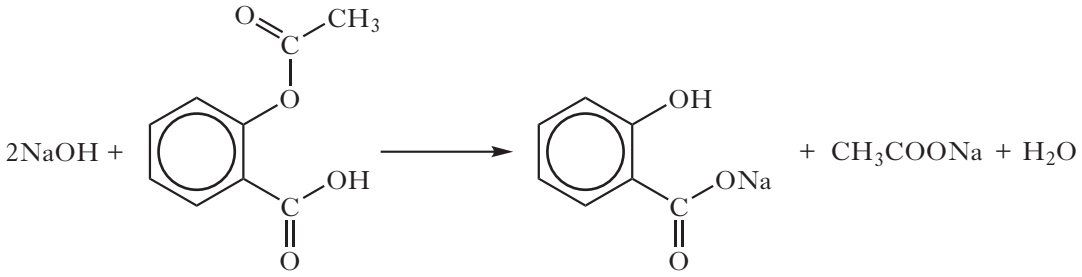
(4)

[Turn over

Marks

3. The active ingredient in aspirin tablets is acetylsalicylic acid, $C_9H_8O_4$. The acetylsalicylic acid content of an aspirin tablet can be determined using a back titration.

Five aspirin tablets were crushed and added to 25·0 cm^3 of 1·00 mol l^{-1} sodium hydroxide solution. The mixture was heated and allowed to simmer for 30 minutes.



The resulting mixture was allowed to cool before being transferred to a 250 cm^3 standard flask and made up to the mark with deionised water.

25·0 cm^3 samples of this solution were titrated with 0·050 mol l^{-1} sulfuric acid.

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

The results of the titration are shown in the table.

	Rough titration	**1st titration**	**2nd titration**
Initial burette reading/cm^3	0·0	9·0	17·7
Final burette reading/cm^3	9·0	17·7	26·3
Volume used/cm^3	9·0	8·7	8·6

(*a*) What is a back titration? **1**

(*b*) (i) Calculate the number of moles of sulfuric acid in the average titre. **1**

(ii) Calculate the number of moles of excess sodium hydroxide in the **standard flask**. **1**

(iii) Calculate the number of moles of sodium hydroxide which reacted with the acetylsalicylic acid. **1**

(iv) The mass of one mole of acetylsalicylic acid is 180 g.

Use this and your answer to part (*b*)(iii) to calculate the mass of acetylsalicylic acid in one aspirin tablet. **2**

(*c*) It is good practice to carry out a control experiment.

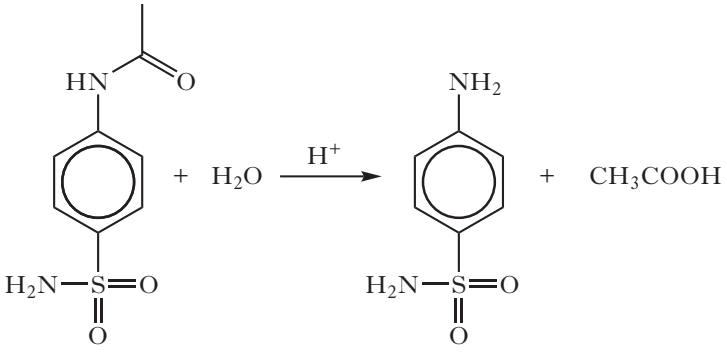
Suggest a control experiment that could be carried out for this back titration. **1**

(7)

Marks

4. Sulfa drugs are compounds with antibiotic properties. Sulfa drugs can be prepared from a solid compound called sulfanilamide.

Sulfanilamide is prepared in a six stage synthesis. The equation for the final step in the synthesis is shown.



$C_8H_{10}N_2SO_3$ $C_6H_8N_2SO_2$

4-acetamidobenzenesulfonamide sulfanilamide

(*a*) What type of reaction is this? **1**

(*b*) The sulfanilamide is separated from the reaction mixture and recrystallised from boiling water.

Why is the recrystallisation necessary? **1**

(*c*) Calculate the percentage yield of sulfanilamide if 4·282 g of 4-acetamidobenzenesulfonamide produced 2·237 g of sulfanilamide. **3**

(*d*) Describe how a mixed melting point experiment would be carried out and the result used to confirm that the product was pure. **2**

(*e*) Suggest another analytical technique which could be used to indicate whether the final sample is pure. **1**

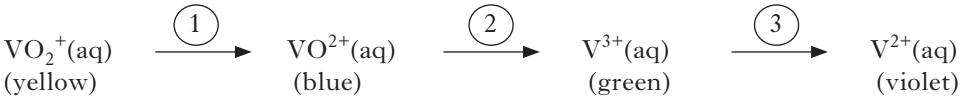
(8)

[Turn over

Marks

5. A classic chemistry demonstration involves vanadium changing oxidation states.

Some zinc metal is added to a flask containing an acidified solution of the dioxovanadium(V) ion, $VO_2^+(aq)$. The flask is stoppered with some cotton wool and gently swirled. The colour of the solution turns from yellow to blue. Further swirling turns the solution from blue to green. Finally, the flask is shaken vigorously and a violet colour is produced. The observed colours are due to the changing oxidation state of vanadium.



(*a*) Determine the oxidation number of vanadium in the blue $VO^{2+}(aq)$ ion. **1**

(*b*) It was observed during the demonstration that the yellow solution turned green before turning blue in reaction (1).

Suggest a reason for this. **1**

(c) In reaction (3) $V^{2+}(aq)$ ions are produced.

How many d electrons does a $V^{2+}(aq)$ ion have? **1**

(*d*) When the cotton wool stopper is removed the violet solution slowly changes back to blue.

Suggest why this happens. **1**

(4)

Marks

6. Nitrogen forms a variety of oxides.

(*a*) Dinitrogen tetroxide, $N_2O_4(g)$, dissociates to form nitrogen dioxide, $NO_2(g)$, according to the equation.

$$N_2O_4(g) \quad \rightleftharpoons \quad 2NO_2(g)$$

0·28 mol of N_2O_4 gas is placed in an empty 1·00 litre flask and heated to 127 °C. When the system reaches equilibrium, 0·24 mol of NO_2 gas is present in the flask.

(i) Calculate the equilibrium constant, K, for the reaction at 127 °C. **3**

(ii) At 25 °C, the numerical value of the equilibrium constant for this reaction is 0·12.

Explain whether the forward reaction is endothermic or exothermic. **1**

(*b*) Nitrogen monoxide reacts with hydrogen as shown.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

In a series of experiments, at a fixed temperature, the initial rates of this reaction were measured.

Experiment	**Initial [NO]/ mol l^{-1}**	**Initial [H_2]/ mol l^{-1}**	**Initial rate/ mol $l^{-1}s^{-1}$**
1	$2{\cdot}00 \times 10^{-3}$	$1{\cdot}20 \times 10^{-3}$	$7{\cdot}40 \times 10^{-4}$
2	$2{\cdot}00 \times 10^{-3}$	$2{\cdot}40 \times 10^{-3}$	**x**
3	$4{\cdot}00 \times 10^{-3}$	$2{\cdot}40 \times 10^{-3}$	**y**

The following rate equation was deduced.

$$\text{Rate} = k[NO]^2$$

(i) Using the information above, determine the numerical values for **x** and **y**. **2**

(ii) For experiment 1, calculate the value of the rate constant, k, including the appropriate units. **2**

(8)

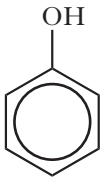
7. During a lesson students asked their teacher, "What is chemistry all about?" The teacher replied, "Electrons."

Using your knowledge of chemistry, comment on the teacher's response. **(3)**

[Turn over

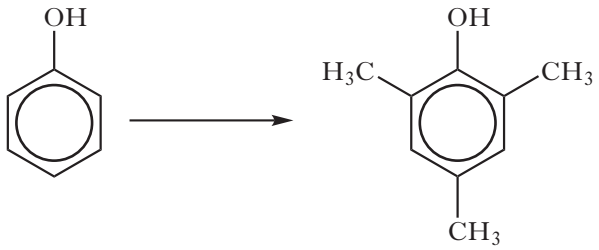
Marks

8. Phenol is an aromatic compound with the following structure.



(*a*) What type of hybridisation do the carbon atoms exhibit in phenol? **1**

(*b*) Phenol takes part in the following reaction.



phenol 2,4,6-trimethylphenol

(i) Suggest a suitable reagent and catalyst for this reaction. **1**

(ii) What type of reaction is taking place? **1**

(*c*) Phenol can be converted into 2,4,6-trinitrophenol using a mixture of concentrated nitric acid and concentrated sulfuric acid.

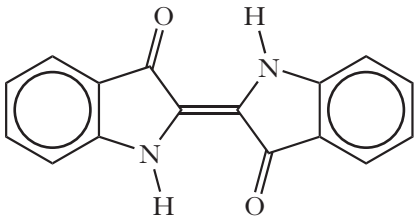
(i) Draw a structural formula for 2,4,6-trinitrophenol. **1**

(ii) Write the formula of the reactive species acting on phenol in this reaction. **1**

(5)

Marks

9. The blue colour of denim jeans comes from a dye known as indigo.



indigo

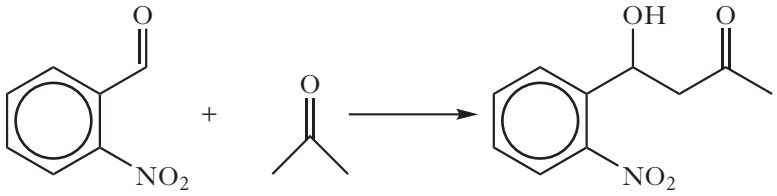
The synthesis of this dye involves a series of complex chemical reactions.

(*a*) What structural feature of indigo dye allows it to absorb light within the visible region of the electromagnetic spectrum? **1**

(*b*) Why does a dye, such as indigo, appear blue when viewed in daylight? **1**

(*c*) Draw a structural formula for the geometric isomer of indigo. **1**

(*d*) The first step in the synthesis of indigo is the reaction of 2-nitrobenzaldehyde with propanone.



2-nitrobenzaldehyde propanone 4-hydroxy-4-(2-nitrophenyl)butan-2-one

(i) Write the molecular formula for 4-hydroxy-4-(2-nitrophenyl)butan-2-one. **1**

(ii) Suggest the type of chemical reaction taking place during this step of the synthesis. **1**

(*e*) In the final step of the synthesis, the indigo dye appears as a purple precipitate.

Simple filtration to isolate the precipitate is very slow.

How could the filtration be speeded up? **1**

(6)

[Turn over

Marks

10. There are four isomers with the molecular formula C_4H_9Cl. Structural formulae for three of these isomers are

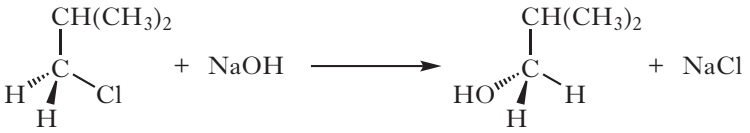
$CH_3CHClCH_2CH_3$ **A** $(CH_3)_2CHCH_2Cl$ **B** $(CH_3)_3CCl$ **C**

(*a*) What is the systematic name of isomer **C**? **1**

(*b*) When refluxed with a solution of potassium hydroxide in ethanol, compound **A** undergoes an elimination reaction. Two structural isomers are produced.

Draw a structural formula for each of these two isomers. **2**

(*c*) Isomer **B** reacts with aqueous sodium hydroxide in an S_N2 reaction.



Isomer **B** Compound **X**

(i) Name compound **X**. **1**

(ii) Draw a structure for the transition state in this reaction. **1**

(*d*) Draw a structural formula for the fourth isomer of C_4H_9Cl. **1**

(*e*) Low resolution proton NMR spectroscopy can be used to distinguish between isomers **A, B** and **C** simply by counting the different numbers of peaks in each spectrum.

How many peaks would be seen in the spectrum of isomer **B**? **1**

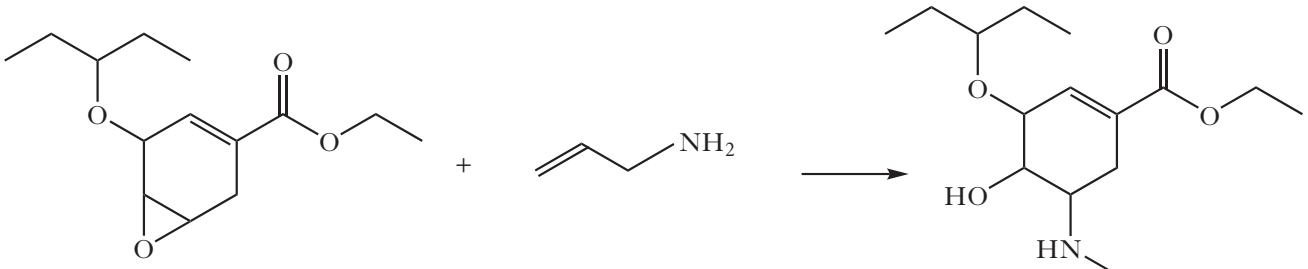
(*f*) Separate solutions of isomers **A** and **B** were analysed using plane polarised light. Neither solution showed optical rotation.

For **each isomer** explain why no optical rotation occurred. **2**

(9)

Marks

11. (*a*) One of the main drugs used in the treatment of bird flu is Tamiflu. One step in the synthesis is shown below.



reactant **A** reactant **B**

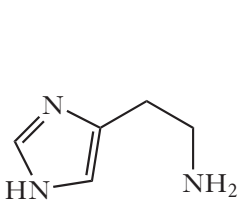
In this reaction, reactant **A** has an electrophilic centre and reactant **B** has a nucleophilic centre.

(i) Describe how reactant **B** is acting as a nucleophile in this reaction. **1**

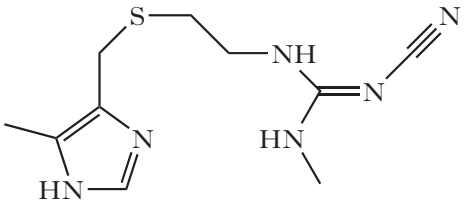
(ii) Infra-red spectroscopy can be used to identify the product. The infra-red spectrum of the product has a major absorbance peak which is not present in the spectrum of either of the reactants.

In which wave number **range**, in cm^{-1}, will this absorbance peak be found? **1**

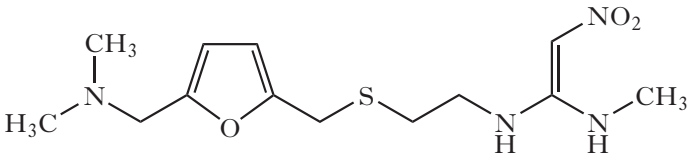
(*b*) Cimetidine, ranitidine and burimamide are drugs used to counteract the effect of histamine which is known to be involved in the production of acid in the stomach.



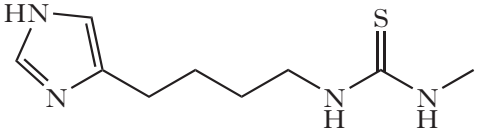
histamine



cimetidine



ranitidine



burimamide

Using your knowledge of chemistry suggest how cimetidine, ranitidine and burimamide can counteract the effect of histamine. **3**

(5)

[Turn over for Question 12 on *Page twenty*

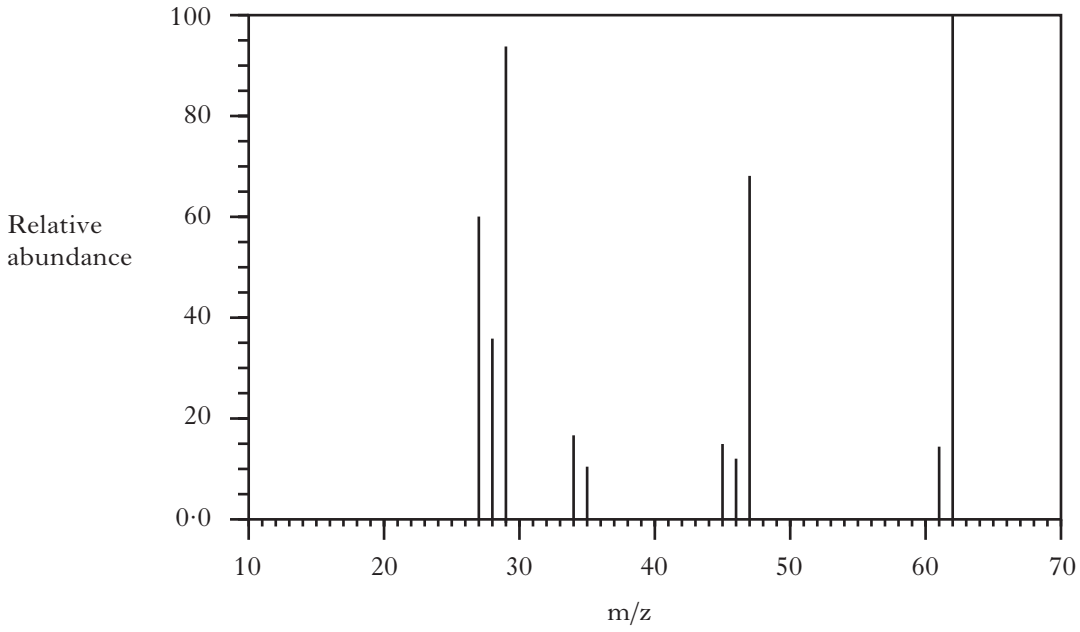
Marks

12. Compound **X** contains only carbon, hydrogen and sulfur.

(*a*) Complete combustion of **X** gave 3·52 g of carbon dioxide, 2·16 g of water and 2·56 g of sulfur dioxide.

Show, by calculation, that the empirical formula of compound **X** is C_2H_6S **2**

(*b*) The mass spectrum for compound **X** is shown below.



Suggest a possible ion fragment which may be responsible for the peak at m/z 47 in the mass spectrum. **1**

(*c*) The results of the analysis of the proton NMR spectrum of **X** are shown in the table below.

Peak	Chemical shift/ppm	Relative area under the peak
1	1·2	97
2	1·5	32
3	2·4	65

Considering all the evidence above, draw a structural formula for compound **X**. **1**

(4)

[*END OF QUESTION PAPER*]