



Oxford Cambridge and RSA

Monday 10 June 2024 – Morning

A Level Chemistry B (Salters)

H433/01 Fundamentals of Chemistry

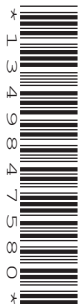
Time allowed: 2 hours 15 minutes

You must have:

- the Data Sheet for Chemistry B

You can use:

- a scientific or graphical calculator
- an HB pencil



Please write clearly in black ink. **Do not write in the barcodes.**

Centre number

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Candidate number

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First name(s)

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Last name

StemUp Model Solution

INSTRUCTIONS

- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION

- The total mark for this paper is **110**.
- The marks for each question are shown in brackets [].
- Quality of extended response will be assessed in questions marked with an asterisk (*).
- This document has **36** pages.

ADVICE

- Read each question carefully before you start your answer.

Section A

You should spend a **maximum** of **40 minutes** on this section.

Write your answer to each question in the box provided.

- 1 An isotope of an element has a mass number of 25.

What is correct for an atom of this isotope?

- A It has 12 neutrons.
- B It has 25 electrons.
- C It has 25 protons.
- D The sum of its protons and neutrons is 25.

Your answer

D

[1]

- 2 What is correct about s orbitals?

- A Only elements in Group 1 or Group 2 have them.
- B They always contain 2 electrons.
- C They are spherical in shape.
- D They can contain up to 6 electrons.

Your answer

C

[1]

- 3 Which species have an electron configuration ending in s^1 ?

- A atoms of some d-block elements
- B atoms of Group 13
- C ions of Group 2
- D ions of Group 16

Your answer

A

[1]

4 Which row has the radiations arranged in order of **increasing** wavelength?

- A infrared < ultraviolet < visible
B infrared < visible < ultraviolet
C ultraviolet < infrared < visible
D ultraviolet < visible < infrared

Your answer

D

[1]

5 What is correct about nuclear fusion reactions?

- A They are the way in which all elements are formed.
B They join together atoms to make heavier atoms.
C They only occur under conditions of high temperature and pressure.
D They turn neutrons into protons.

Your answer

C

[1]

6 Which species is present in an acidic solution of glycine, $\text{H}_2\text{NCH}_2\text{COOH}$?

- A $\text{H}_3\text{N}^+\text{CH}_2\text{COOH}$
B $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$
C $\text{H}_2\text{NCH}_2\text{COO}^-$
D $\text{H}_2\text{NCH}_2\text{COOH}_2^+$

Your answer

A

[1]

7 In the mass spectrum of ethanoic acid ($M_r = 60$), what is the cause of the very small peak at $m/z = 61$?

- A the presence of an ethanol impurity in the ethanoic acid
- B the presence of small amounts of $\text{CH}_3\text{COOH}_2^+$
- C the presence of ^{13}C in the ethanoic acid
- D the presence of ^1H in the ethanoic acid

Your answer

C

[1]

8 Which compound has optical isomers?

- A $\text{CH}_3\text{CH}_2\text{COOH}$
- B $\text{CH}_3\text{CH}_2\text{CONH}_2$
- C $\text{H}_2\text{NCH}_2\text{COOH}$
- D $\text{H}_2\text{NCH}(\text{CH}_3)\text{COOH}$

Your answer

D

[1]

9 Which compound will react with sodium carbonate?

- A CH_3COCH_3
- B $\text{CH}_3\text{COOCH}_3$
- C $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- D $\text{CH}_3\text{CH}_2\text{COOH}$

Your answer

D

[1]

10 Which option occurred first in the discovery of atomic structure?

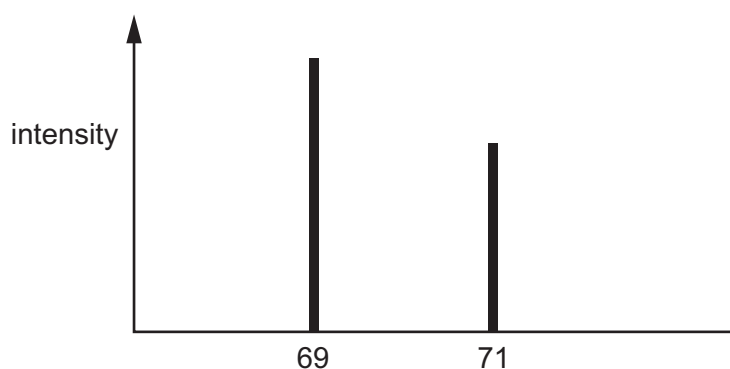
- A the Geiger-Marsden experiment
- B the idea of an atom with electrons embedded in positive charge
- C the idea that electrons are arranged in shells
- D the idea that the nucleus consists of protons and neutrons

Your answer

B

[1]

11 The mass spectrum of a sample of an element is shown:



What is the relative atomic mass of the sample?

- A 69.2
- B 69.5
- C 69.8
- D 70.0

Your answer

C

[1]

12 Which of the following is correct for a C=C bond?

- A All the electrons are between the C atoms.
- B There are two π -bonds.
- C There is one σ -bond.
- D The bond can freely rotate.

Your answer

C

[1]

13 The Table shows the concentrations of some noble gases in the atmosphere.

Gas	Concentration by volume
He	5ppm
Ne	2 parts in 10^5
Kr	0.0001%
Xe	1 part in 10^7

Which gas has the **highest** concentration?

- A He
- B Ne
- C Kr
- D Xe

Your answer

B

[1]

14 Which reaction has the **smallest** atom economy for the formation of the organic product?

- A $\text{C}_2\text{H}_4 + \text{HCl} \rightarrow \text{C}_2\text{H}_5\text{Cl}$
- B $\text{C}_2\text{H}_4 + \text{HBr} \rightarrow \text{C}_2\text{H}_5\text{Br}$
- C $\text{C}_2\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{HCl}$
- D $\text{C}_2\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{HBr}$

Your answer

D

[1]

15 Which of 1-iodobutane and 1-chlorobutane has the higher boiling point and why?

- A 1-Chlorobutane because its molecules have the stronger permanent dipole–dipole bonds.
- B 1-Chlorobutane because its molecules have the stronger instantaneous dipole–induced dipole bonds.
- C 1-Iodobutane because its molecules have the stronger permanent dipole–dipole bonds.
- D 1-Iodobutane because its molecules have the stronger instantaneous dipole–induced dipole bonds.

Your answer

D

[1]

16 Which reaction has an increase in entropy?

- A $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
- B $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
- C $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$
- D $\text{C}(\text{CH}_3)_4(\text{g}) \rightarrow \text{CH}_3(\text{CH}_2)_3\text{CH}_3(\text{l})$

Your answer

B

[1]

17 The compounds below have negative lattice enthalpies.

Which option shows the compounds in order of more negative lattice enthalpies from left to right?

- A NaF, KF, RbF
- B Na_2O , K_2O , Rb_2O
- C Na_2O , MgO, Al_2O_3
- D NaF, NaCl, NaBr

Your answer

C

[1]

18 A colorimeter is used to determine the concentration of copper(II) ions in solution.

What is correct?

- A Absorbance increases with the concentration of copper(II) ions.
- B In the colorimeter the filter is positioned between the cuvette and the detector.
- C The filter should be blue because copper(II) ions are blue.
- D The zero reading on the colorimeter is taken using an empty cuvette.

Your answer

A

[1]

19 What is correct about propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, and propanone, CH_3COCH_3 ?

- A Only propanal can be oxidised by acidified dichromate.
- B Only propanal forms a 'silver mirror' with Fehling's solution.
- C Only propanone forms a cyanohydrin with hydrogen cyanide.
- D Propanal has a higher boiling point than propanone because propanal can form hydrogen bonds.

Your answer

A

[1]

- 20 A student is measuring the relative rates of reaction of 1-chlorobutane, 1-bromobutane and 1-iodobutane with aqueous silver nitrate.

Which statement is correct?

- A 1-Chlorobutane is slowest and gives a white precipitate.
- B 1-Bromobutane is slowest and gives a yellow precipitate.
- C 1-Iodobutane is fastest and gives a white precipitate.
- D 1-Iodobutane is slowest and gives a yellow precipitate.

Your answer

A

[1]

- 21 Wood is used to make a sample of bioethanol. The bioethanol is used to fuel a car engine.

What is correct?

- A Carbon dioxide is the only pollutant produced by the car engine.
- B The amount of carbon dioxide given out when the fuel is fully burned is equal to the amount of carbon dioxide absorbed when the wood is grown.
- C The fuel is made from the wood by cracking.
- D The wood is never grown where other crops could be planted.

Your answer

B

[1]

- 22 Which of the following represents poly(propene)?

- A $-\text{CH}_2-\text{CH}(\text{CH}_3)-$
- B $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$
- C $-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-$
- D $-\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)-$

Your answer

A

[1]

- 23 10 cm³ of an alkane react exactly with 35 cm³ oxygen in complete combustion at RTP.

What is the alkane?

- A CH₄
- B C₂H₆
- C C₃H₈
- D C₄H₁₀

Your answer

B

[1]

- 24 50 cm³ of 0.30 mol dm⁻³ Fe(II) in acid solution exactly reduces 25 cm³ of 0.10 mol dm⁻³ NaClO₃ solution. Fe(III) is formed.

What is the oxidation state of chlorine in the product?

- A +3
- B +2
- C 0
- D -1

Your answer

D

[1]

- 25** Methane reacts with chlorine by a radical mechanism.

There is an initiation reaction, two propagation reactions and various termination reactions.

The overall equation for the main reaction is $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$

Which statement is correct for this reaction?

- A** CH_3Cl is formed in the first propagation reaction.
- B** HCl is formed in the second propagation reaction.
- C** One termination reaction involves the formation of ethane.
- D** Two radicals react in the first propagation step.

Your answer

C

[1]

- 26** The solubility of lead(II) chloride is $0.0388 \text{ mol dm}^{-3}$ at 293 K.

What is the correct numerical value of the solubility product at this temperature?

- A** 5.84×10^{-5}
- B** 2.34×10^{-4}
- C** 1.51×10^{-3}
- D** 3.01×10^{-3}

Your answer

B

[1]

27 Ethanal, CH_3CHO , reacts with cyanide in a two-step mechanism.

What is correct about this mechanism?

- A** In step 1 the nitrogen on the cyanide ion attacks the carbonyl carbon of ethanal.
- B** In step 2 the intermediate formed in step 1 reacts with H^+ .
- C** The intermediate formed in step 1 has the following structure: $\text{H}_3\text{C}-\overset{\text{CN}}{\underset{\text{CN}}{\text{C}}}=\text{O}$
- D** The overall reaction is electrophilic addition.

Your answer

B

[1]

28 Which of the following radiations can break covalent bonds?

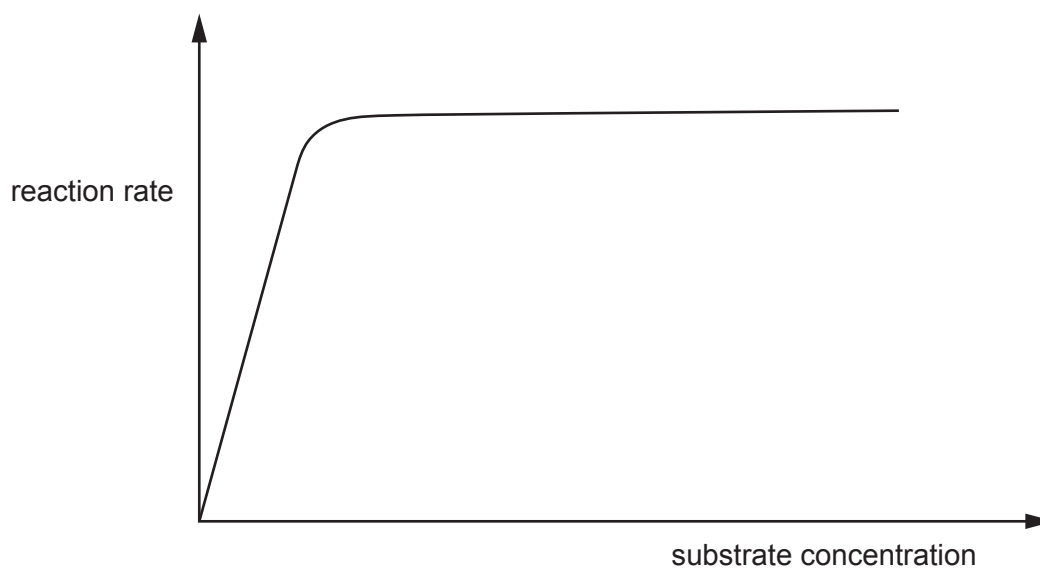
- 1** ultraviolet
 - 2** x-rays (which have higher frequency than ultraviolet rays)
 - 3** infrared
- A** 1, 2 and 3
- B** Only 1 and 2
- C** Only 2 and 3
- D** Only 1

Your answer

B

[1]

- 29 The graph shows how the rate of an enzyme catalysed reaction varies with substrate concentration.



At low substrate concentration, which of the following is/are correct?

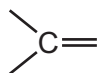
- 1 Not all enzyme active sites have a substrate molecule attached.
 - 2 The reaction is first order with respect to substrate.
 - 3 The rate determining step involves both enzyme and substrate.
- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

A

[1]

30 A carbon atom has the bonding shown.



Which of the following is/are correct for this carbon atom?

- 1 The shape is trigonal around the carbon atom.
 - 2 The atoms attached to the bonds are all in the same plane.
 - 3 The angle between the single bonds is 109° .
- A 1, 2 and 3
- B Only 1 and 2
- C Only 2 and 3
- D Only 1

Your answer

B

[1]

15
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Turn over for Section B

Section B

31 Fireworks contain metal compounds that produce intense colours when they are burned.

(a) Give the colour from a firework containing barium carbonate.

(apple) green [1]

(b) The atomic **emission** spectrum of barium appears as a series of coloured lines at specific frequencies on a black background.

Describe the appearance of the atomic **absorption** spectrum of barium.

How is the absorption spectrum related to the emission spectrum?

A continuous spectrum (all the colours) crossed by a series of black lines, i.e.
black lines on a coloured background.
The black lines are at exactly the same frequencies (wavelengths) as the
coloured lines in the emission spectrum. [2]

(c) One line in the barium spectrum has a wavelength of 5.54×10^{-5} cm.

Calculate the frequency of this line (in Hz).

$$\lambda = 5.54 \times 10^{-5} \text{ cm} = 5.54 \times 10^{-7} \text{ m}$$

$$f = c / \lambda = 3.00 \times 10^8 / 5.54 \times 10^{-7}$$

$$f = 5.42 \times 10^{14} \text{ Hz}$$

frequency = ... 5.42×10^{14} Hz [2]

- (d) Strontium carbonate is another compound used in fireworks.
- (i) Write the equation for the thermal decomposition of SrCO_3 .



[1]

- (ii) There is a trend in the stability of the Group 2 carbonates.

A student says:

- Barium carbonate decomposes at a higher temperature than strontium carbonate.
- This is because the carbonate ion has a stronger bond to the more reactive barium ion.

Comment on the student's statements giving the correct chemistry where necessary.

The first statement is correct: BaCO_3 does decompose at a higher temperature than SrCO_3 . (stability increases down the group).

The reason is wrong. Ba^{2+} has the same charge as Sr^{2+} but is larger, so Ba^{2+} has a lower charge density. Ba^{2+} polarises (distorts) the carbonate ion's electron cloud less, so the C-O bonds are weakened less and more energy is needed to decompose BaCO_3 . The attraction to Ba^{2+} is weaker (it is larger), and reactivity is not the reason.

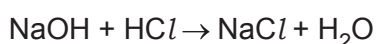
[4]

- (e) A group of students identify an insoluble Group 2 carbonate, MCO_3 , by calculating its M_r .

The students' procedure and results are:

- They weigh out 3.02 g of MCO_3 .
- They add the MCO_3 to 50.0 cm³ of 2.00 mol dm⁻³ HCl (an excess).
- When the reaction has finished they make the solution up to 250 cm³ in a volumetric flask.
- They titrate 25.0 cm³ of the diluted solution with 0.108 mol dm⁻³ NaOH.
- Their mean titre is 26.15 cm³.

The reaction between HCl and NaOH is:



The reaction between MCO_3 and HCl is:



- (i) Describe the procedure they should use for weighing out the 3.02 g of MCO_3 .

*Put the MCO_3 into a weighing bottle on a balance (2 d.p.) until about 3.02 g
and record the mass of bottle + solid.
Tip the solid into the beaker of acid, reweigh the empty bottle and take the
difference as the mass of MCO_3 .* [2]

- (ii) Calculate the M_r of MCO_3 .

$$n(\text{NaOH}) = 26.15/1000 \times 0.108 = 2.8242 \times 10^{-3} \text{ mol}$$

$$n(\text{HCl}) \text{ left in } 25.0 \text{ cm}^3 = 2.8242 \times 10^{-3} \text{ mol (1 : 1)}$$

$$n(\text{HCl}) \text{ left in } 250 \text{ cm}^3 = 10 \times 2.8242 \times 10^{-3} = 2.8242 \times 10^{-2} \text{ mol}$$

$$n(\text{HCl}) \text{ added} = 50.0/1000 \times 2.00 = 0.100 \text{ mol}$$

$$n(\text{HCl}) \text{ reacted} = 0.100 - 0.028242 = 7.1758 \times 10^{-2} \text{ mol}$$

$$n(\text{MCO}_3) = \frac{1}{2} \times 7.1758 \times 10^{-2} = 3.5879 \times 10^{-2} \text{ mol}$$

$$M_r = \text{mass} / \text{moles} = 3.02 / 3.5879 \times 10^{-2} = 84.2$$

$$M_r = \dots\dots\dots 84.2 \dots\dots\dots [5]$$

(iii) The 25.0cm^3 of the solution used for the titration is measured using a volumetric pipette.

The uncertainty in reading the volumetric pipette is 0.06cm^3 .

Calculate the percentage uncertainty in using this pipette.

Give your answer to an **appropriate** number of significant figures.

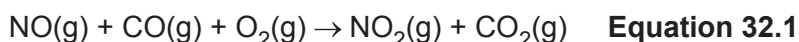
$$\% \text{ uncertainty} = 0.06 / 25.0 \times 100$$

$$= 0.24 \% = 0.2 \% (1 \text{ s.f.})$$

percentage uncertainty = ...0.2..... % [1]

32 Chemists study the rates of reactions that occur in car engines.

(a) **Equation 32.1** shows a reaction that occurs in catalytic converters.



A chemist measures the initial rate of reaction for different initial concentrations of reactants at constant temperature.

The results are given in the table.

Experiment number	[NO] / mol dm ⁻³	[CO] / mol dm ⁻³	[O ₂] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	2.0 × 10 ⁻²	1.0 × 10 ⁻²	1.0 × 10 ⁻²	0.17
2	6.0 × 10 ⁻²	1.0 × 10 ⁻²	1.0 × 10 ⁻²	1.53
3	2.0 × 10 ⁻²	2.0 × 10 ⁻²	1.0 × 10 ⁻²	0.17
4	4.0 × 10 ⁻²	1.0 × 10 ⁻²	2.0 × 10 ⁻²	0.68

(i) Use the results to show that the rate equation is:

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

Exp 1 to 2: [NO] × 3, [CO] and [O₂] constant, rate × 9 (0.17 to 1.53) = 3², so second order in NO.
 Exp 1 to 3: [CO] × 2, others constant, rate unchanged (0.17), so zero order in CO.
 Exp 1 to 4: [NO] × 2 and [O₂] × 2, rate × 4 = 2², all due to NO, so zero order in O₂. Rate = k[NO]² [3]

(ii) Calculate the rate constant, *k*, for the reaction in **Equation 32.1** and give its units.

$$k = \text{rate} / [\text{NO}]^2 \quad (\text{Exp 1})$$

$$k = 0.17 / (2.0 \times 10^{-2})^2 = 0.17 / 4.0 \times 10^{-4} = 425$$

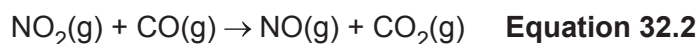
$$\text{units} = \text{mol dm}^{-3} \text{ s}^{-1} / (\text{mol dm}^{-3})^2 = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k = 425 \text{ units } \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad [2]$$

21
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Question 32(b) begins on page 22

- (b) Another reaction that occurs in a catalytic converter is shown in **Equation 32.2**.



- (i) The rate equation for this reaction is:

$$\text{Rate} = k[\text{NO}_2]^2$$

A student says that this reaction takes place in a single step.

Explain why this cannot be correct and give a possible mechanism for the reaction, indicating the rate-determining step.

CO is zero order so it is not in the rate-determining step; the rate equation

shows two NO₂ react in the slow step, so it cannot be one step.

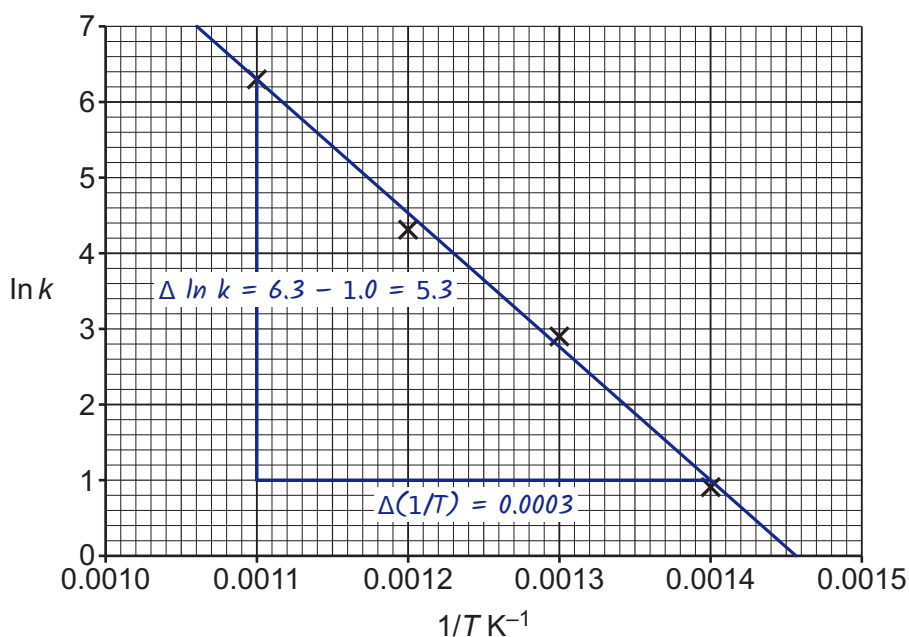
Step 1: 2NO₂ → NO + NO₃ (slow, rate-determining step)

Step 2: NO₃ + CO → NO₂ + CO₂ (fast)

[3]

- (ii) A chemist studies the reaction in **Equation 32.2** and measures the rate constant, k , at different temperatures.

The chemist plots $\ln k$ against $1/T$ on a graph as shown.



Calculate the activation enthalpy (in kJ mol^{-1}) for the reaction in **Equation 32.2**.

line of best fit through (0.0011, 6.3) and (0.0014, 1.0)

$$\text{gradient} = (1.0 - 6.3) / (0.0014 - 0.0011) = -5.3 / 0.0003$$

$$\text{gradient} = -1.77 \times 10^4 \text{ K}$$

$$\ln k = \ln A - E_a/RT, \text{ so gradient} = -E_a/R$$

$$E_a = -\text{gradient} \times R = 1.77 \times 10^4 \times 8.314$$

$$E_a = 1.47 \times 10^5 \text{ J mol}^{-1} = +147 \text{ kJ mol}^{-1}$$

activation enthalpy = ...**+147**..... kJ mol^{-1} [4]

33 Ammonium nitrate, NH_4NO_3 , is a fertiliser.

One of the steps in the manufacture of NH_4NO_3 is the oxidation of NO by the reaction in **Equation 33.1**.



(a) Give the appearance of $\text{NO}_2(\text{g})$.

brown (gas) [1]

(b) Give the test and its result that shows that a solid contains nitrate ions.

Warm the solid with Devarda's alloy (Al) and sodium hydroxide solution.

Ammonia gas is given off, which turns damp red litmus paper blue.

..... [2]

(c) The reaction in **Equation 33.1** is an example of a chemical equilibrium.

(i) A student says that once the position of equilibrium has been reached, the reaction has stopped so the concentration of $\text{NO}_2(\text{g})$ remains constant.

Evaluate what the student says and give correct chemistry where necessary.

The concentration of $\text{NO}_2(\text{g})$ does remain constant at equilibrium, so that part is correct.

But the reaction has not stopped; it is a dynamic equilibrium in which the rate of the forward reaction = the rate of the reverse reaction. [2]

(ii) For the reaction in **Equation 33.1** at a certain temperature,

$$K_c = 6.9 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$$

In an industrial plant, operating at that temperature:

$$\text{Equilibrium concentration, } [\text{NO(g)}] = 0.250 \text{ mol dm}^{-3}$$

$$\text{Equilibrium concentration, } [\text{O}_2(\text{g})] = 0.180 \text{ mol dm}^{-3}$$

Write the expression for K_c and calculate the equilibrium concentration of $\text{NO}_2(\text{g})$.

$$K_c = [\text{NO}_2(\text{g})]^2 / ([\text{NO}(\text{g})]^2 [\text{O}_2(\text{g})])$$

$$6.9 \times 10^2 = [\text{NO}_2]^2 / (0.250^2 \times 0.180)$$

$$[\text{NO}_2]^2 = 6.9 \times 10^2 \times 0.01125 = 7.7625$$

$$[\text{NO}_2] = \sqrt{7.7625} = 2.8 \text{ mol dm}^{-3}$$

$$\text{equilibrium concentration, } [\text{NO}_2(\text{g})] = \dots\dots\dots 2.8 \dots\dots\dots \text{ mol dm}^{-3} \quad [3]$$

(iii) Explain how increasing temperature affects the value of K_c for the reaction in **Equation 33.1**.

The forward reaction is exothermic (ΔH is negative).
Increasing the temperature shifts the position of equilibrium to the left
(endothermic direction), so $[\text{NO}_2]$ falls and the value of K_c decreases.
 [2]

Equation 33.1 is repeated: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \quad \Delta H = -114 \text{ kJ mol}^{-1}$ **Equation 33.1**

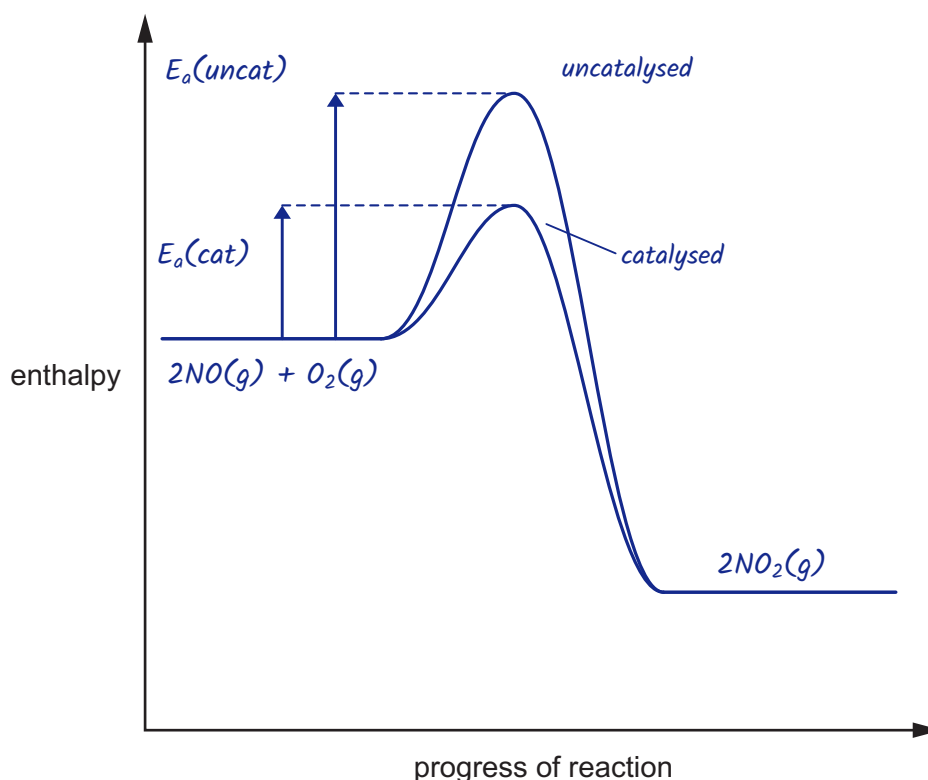
(d) The reaction in **Equation 33.1** uses a heterogeneous catalyst.

(i) Explain the meaning of the term **heterogeneous** here.

The catalyst is in a different phase (state) from the reactants: a solid catalyst with gaseous reactants. [1]

(ii) Draw an enthalpy profile diagram for the reaction in **Equation 33.1** and label the catalysed and uncatalysed reactions.

Show the reactants and products and the activation enthalpies. [2]



(iii) The catalyst used in the reaction in **Equation 33.1** is a solid mixture of platinum and rhodium.

Explain why this solid is able to behave as a catalyst.

Pt. and Rh. have d electrons (partly filled d orbitals) on their surface. These form weak bonds to the reactant molecules (adsorption), weakening the bonds in the reactants and holding them close together; the products then desorb. [2]

- (e) The standard entropies of the substances involved in **Equation 33.1** are shown in the table.

Substance	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
$\text{O}_2(\text{g})$	205.0
$\text{NO}(\text{g})$	210.7
$\text{NO}_2(\text{g})$	240.0

Calculate the total entropy change, $\Delta_{\text{tot}}S$, (in $\text{J mol}^{-1} \text{K}^{-1}$) for the reaction in **Equation 33.1** at 50°C .

$$\Delta S_{\text{sys}} = 2(240.0) - (2(210.7) + 205.0)$$

$$= 480.0 - 626.4 = -146.4 \text{ J mol}^{-1} \text{K}^{-1}$$

$$\Delta S_{\text{surr}} = -\Delta H / T = -(-114 \times 1000) / (50 + 273)$$

$$= 114000 / 323 = +352.9 \text{ J mol}^{-1} \text{K}^{-1}$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -146.4 + 352.9$$

$$\Delta S_{\text{tot}} = +206.5 = +207 \text{ J mol}^{-1} \text{K}^{-1}$$

$$\Delta_{\text{tot}}S = \dots\dots\dots +207 \dots\dots\dots \text{J mol}^{-1} \text{K}^{-1} \text{ [4]}$$

34 The plastic welding agent butanone, $\text{CH}_3\text{CH}_2\text{COCH}_3$, is sold as “model cement” and used for joining the plastic parts of scale model kits.

(a) Butanone can be formed by the oxidation of the alcohol $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$.

Classify this alcohol as primary, secondary or tertiary.

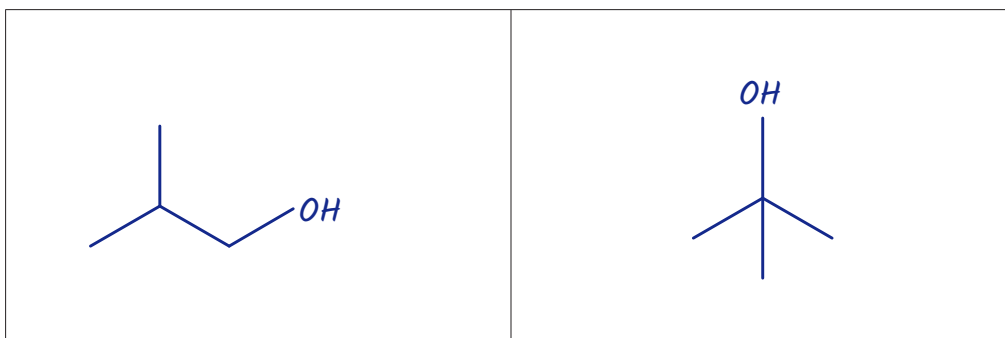
Give the structural reason for the classification you have chosen.

Classification: *secondary (2°)*

Reason: *The carbon atom bonded to the OH group is attached to two other carbon atoms (R groups) and one hydrogen atom.* [2]

(b) There are other alcohols that are structural isomers of $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$.

Draw the **skeletal** formulae for the **two branched-chain** isomers.



[2]

(c) The alcohol $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ can be made by reacting $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$ with aqueous sodium hydroxide.

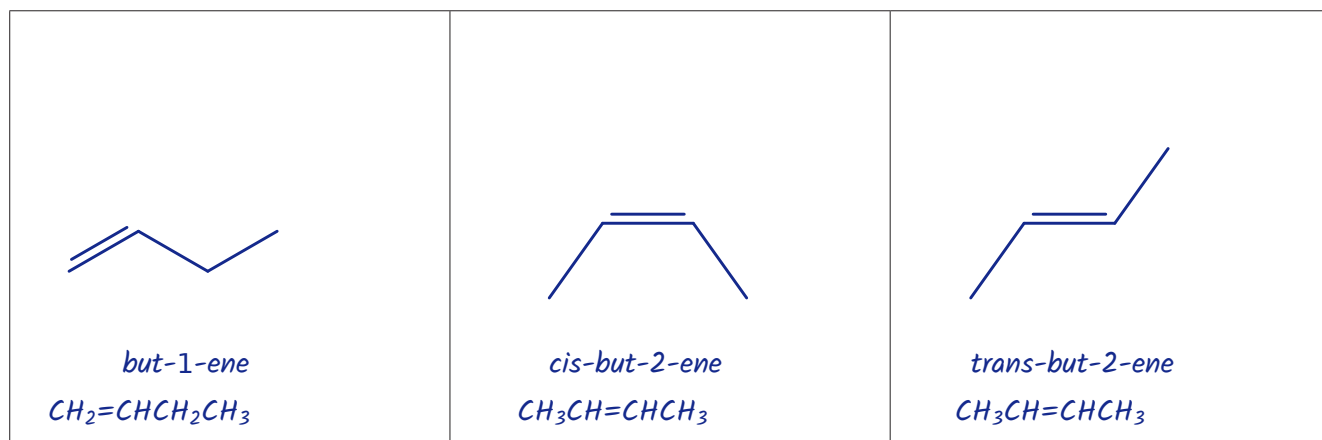
Name the mechanism of this reaction.

nucleophilic substitution [1]

(d) Alcohols can be dehydrated by heating with concentrated sulfuric acid.

When dehydrated, $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ produces a mixture of three isomeric products.

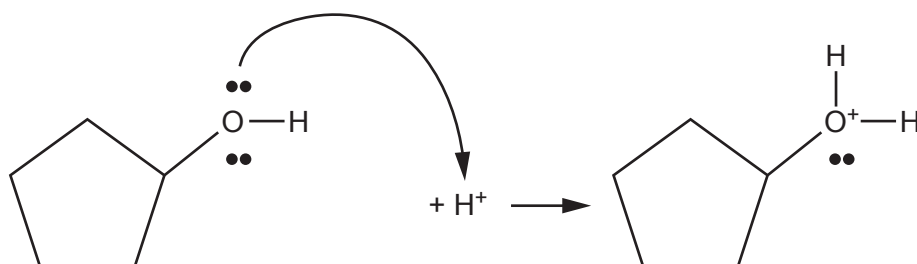
Draw the structures of these **three** isomeric products.



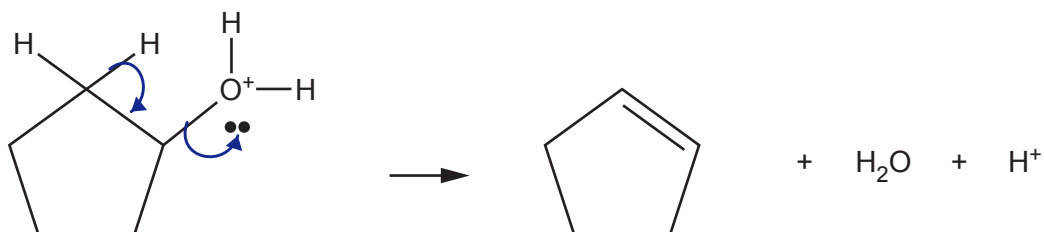
[3]

(e) The mechanism for the dehydration of a cyclic alcohol using concentrated sulfuric acid takes place in two steps.

Step 1:



Step 2:

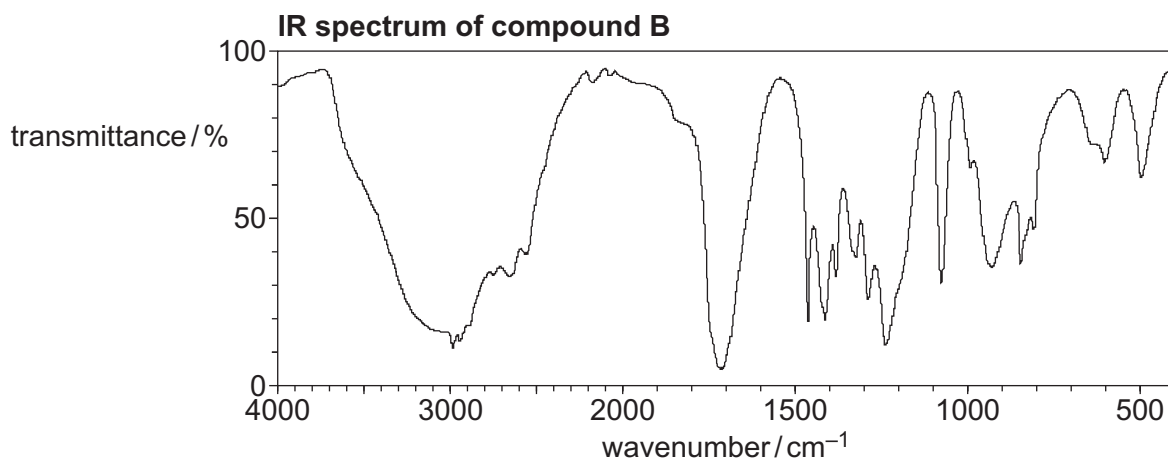
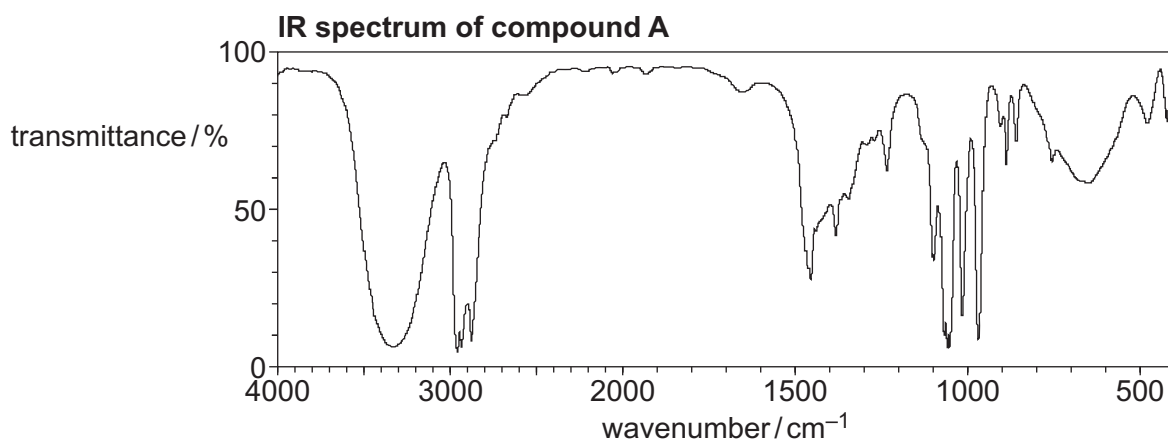
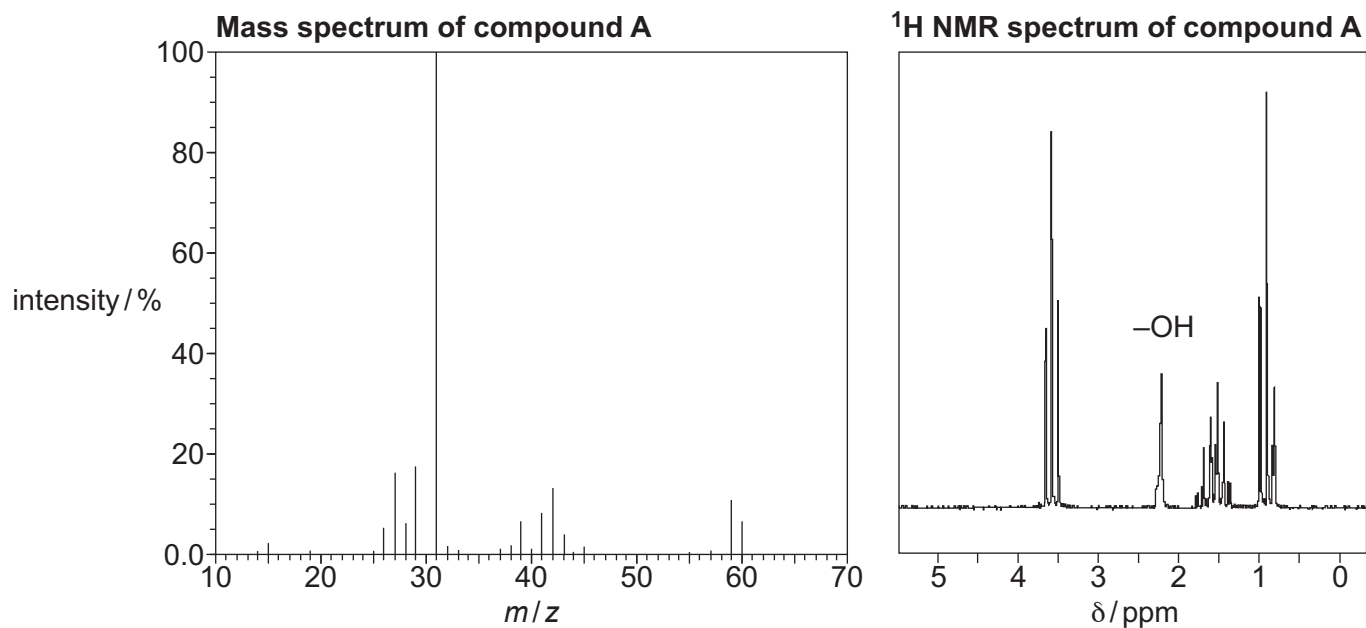


Add curly errors to **Step 2** to show the electron movements in the mechanism.

[2]

(f)* A chemist sets out to identify **compound A** and its oxidation product, **compound B**.

The chemist has the mass spectrum, the IR spectrum and the ^1H NMR spectrum of **compound A**, and the IR spectrum of **compound B**.



You may do working on this page but it will not be marked.

Use evidence from **all** the spectra to identify the formulae for **compound A** and **compound B**.

Mass spectrum of A: molecular ion peak at $m/z = 60$, so $M_r = 60$. Peak at $m/z = 31$ is CH_2OH^+ ; the difference $60 - 31 = 29$ is C_2H_5 , so A contains CH_3CH_2- joined to $-\text{CH}_2\text{OH}$.

IR of A: broad peak at 3200 to 3600 cm^{-1} is O-H of an alcohol and there is no C=O peak near 1700 cm^{-1} .

NMR of A: 4 peaks, so 4 proton environments (3 CH environments plus the OH peak). Triplet at $\delta = 0.9$ is CH_3 next to a CH_2 (CH_3-CH_2-). Multiplet (sextet) at $\delta = 1.5$ is the CH_2 in $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{O}$, with 5 neighbouring H. Triplet at $\delta = 3.5$ is CH_2 in the $\text{H}_2\text{C}-\text{O}$ region, split by one CH_2 , so the OH is on a CH_2 ; A is a primary alcohol.

IR of B: very broad peak at 2500 to 3300 cm^{-1} is O-H of a carboxylic acid and a strong peak at about 1700 cm^{-1} is C=O.

So A is propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, and B is propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$. This fits because B is a carboxylic acid, and only a primary alcohol is oxidised to a carboxylic acid (a secondary alcohol gives a ketone).

[6]

Extra answer space if required.

.....

.....

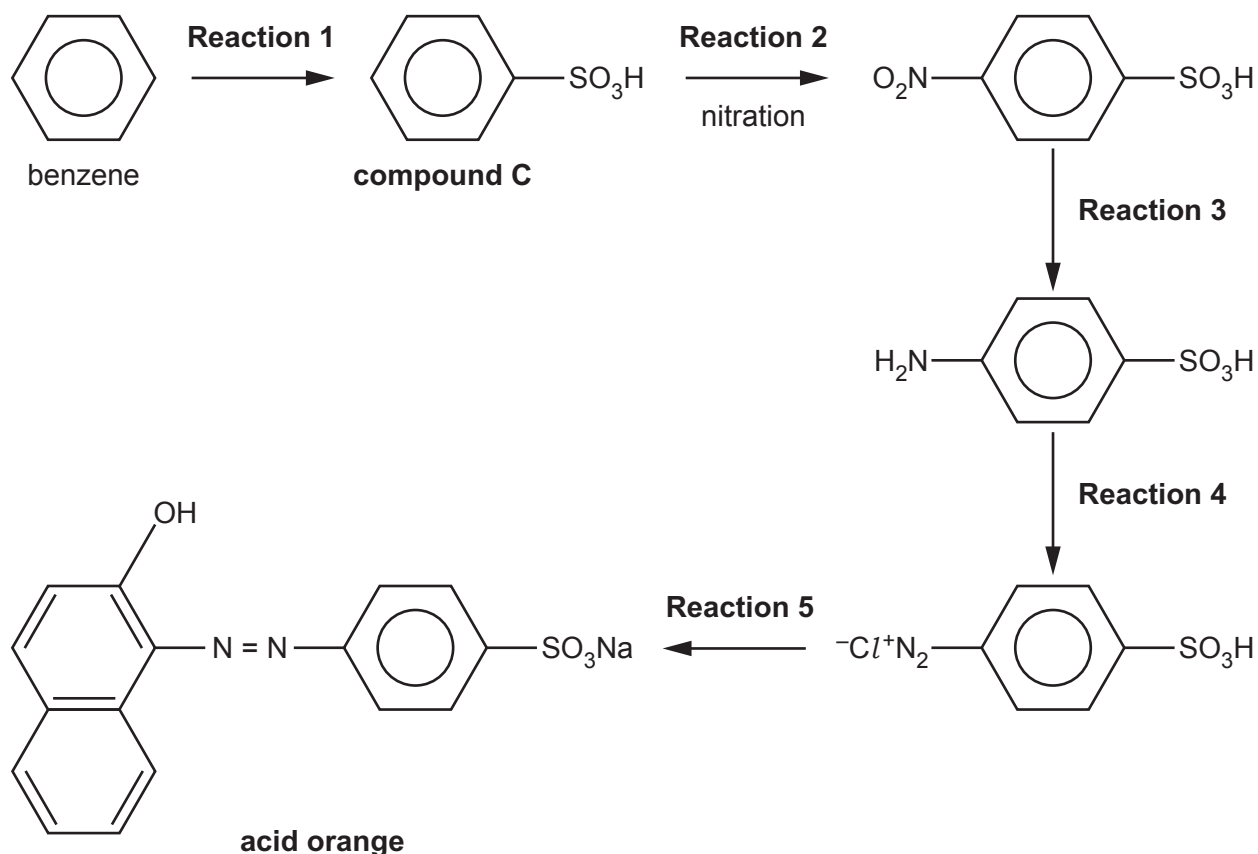
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35 Acid orange is a soluble azo dye that can be made from benzene by the following route:



(a)

(i) Name **compound C**.

benzenesulfonic acid [1]

(ii) **Reaction 1** is an electrophilic substitution using concentrated sulfuric acid.

Give the formula of the electrophile.

SO_3 [1]

(b) Use the Data Sheet to give reagents and conditions for **reaction 3**.

Tin (Sn) and concentrated hydrochloric acid, heat under reflux

..... [1]

(c) **Reaction 4** forms a diazonium salt.

Give the reagents and conditions for this reaction.

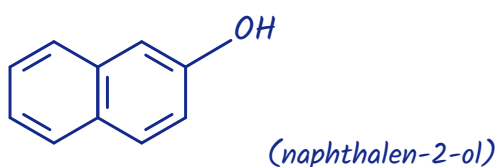
Reagents: *Sodium nitrite (sodium nitrate(III)), NaNO_2 , and hydrochloric acid, HCl*

Conditions: *Below 5°C (in an ice bath)*

[3]

(d) **Reaction 5** is a coupling reaction, using a phenol and sodium hydroxide.

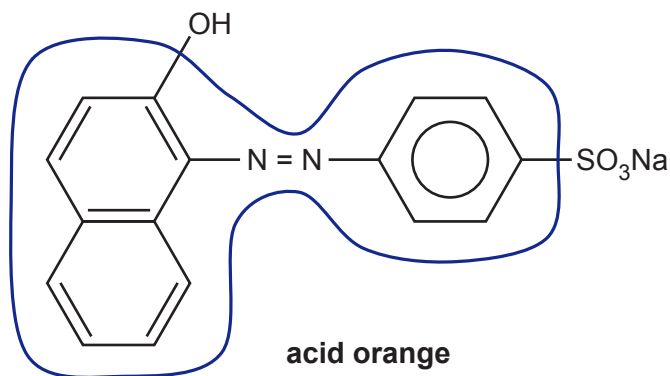
Give the formula of the phenol.



[1]

(e)

(i) Draw a ring around the **chromophore** of acid orange.



[1]

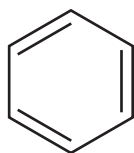
(ii) One part of its structure makes acid orange more soluble than many other azo dyes.

Give the formula of this part.

$-\text{SO}_3\text{Na}$ (the ionic $-\text{SO}_3^- \text{Na}^+$ group)

[1]

(f)* A scientist called Kekulé proposed a structure for benzene as shown:



The enthalpy change data below shows that this is not entirely correct:



- Explain why the data does not match the Kekulé structure.
- Describe a different model for the benzene structure.
- Explain how this different model accounts for the reaction of benzene with bromine better than the Kekulé structure.

Cyclohexene has one $\text{C}=\text{C}$ and $\Delta H_{\text{hydrogenation}} = -120 \text{ kJ mol}^{-1}$. The Kekulé structure has three $\text{C}=\text{C}$ bonds, so it would have $\Delta H = 3 \times (-120) = -360 \text{ kJ mol}^{-1}$.

Benzene's actual value is only -208 kJ mol^{-1} , so 152 kJ mol^{-1} less energy is released: benzene is more stable than the Kekulé structure by 152 kJ mol^{-1} , so it cannot have three separate $\text{C}=\text{C}$ bonds.

Delocalised model: benzene is a planar hexagonal ring; each C forms σ -bonds to two C atoms and one H (120°). One electron from each carbon is in a p orbital; the six p orbitals overlap sideways to form a π -bonding system above and below the ring, so six electrons are delocalised and shared by all six carbon atoms. All the C-C bonds are the same length.

Kekulé would predict electrophilic addition like an alkene, decolourising bromine at room temperature, e.g. $\text{C}_6\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_6\text{H}_6\text{Br}_2$, with a $\text{C}=\text{C}$ becoming saturated (more Br_2 could add).

In fact benzene needs a halogen carrier, FeBr_3 (or $\text{Fe} + \text{Br}_2$), to form the Br^+ electrophile, and it undergoes electrophilic substitution: $\text{C}_6\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{HBr}$ [6]

Extra answer space if required.

HBr.

The delocalised electrons spread the charge, so benzene attracts electrophiles

less than a C=C does; substitution happens instead of addition because the

delocalised ring is retained in the product, keeping its extra stability.

END OF QUESTION PAPER

[illegible]

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