



Oxford Cambridge and RSA

Friday 23 June 2023 – Morning

A Level Chemistry A

H432/03 Unified chemistry

Time allowed: 1 hour 30 minutes



You must have:

- the Data Sheet for Chemistry A

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)

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 **70**.
- 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 **24** pages.

ADVICE

- Read each question carefully before you start your answer.

1 This question is about the first 36 elements in the periodic table:

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

From these 36 elements **only**, write the symbol for the element(s) that fit each description.

- (a) The **three** elements that, when in a molecule, can form hydrogen bonds with other suitable molecules.

.....*N, O, F*..... [1]

- (b) The element in Period 2 with the successive ionisation energies shown below.

Ionisation number	1st	2nd	3rd	4th	5th	6th	7th	8th
Ionisation energy /kJ mol ⁻¹	1000	2251	3361	4564	7012	8496	27 107	31 671

.....*O*..... [1]

- (c) An element that is a solid at RTP with a simple molecular lattice structure.

.....*S*..... [1]

(d) The **two** elements with atoms containing five unpaired electrons.

..... *Cr and Mn* [2]

(e) The element in Period 3 that exists in the solid state as a network of atoms bonded by strong covalent bonds.

..... *Si* [1]

(f) The p-block element in Period 3 that forms a compound with fluorine with octahedral molecules.

..... *S* [1]

(g) The element that forms 1– ions most readily.

..... *F* [1]

(h) The element with an average atomic mass of 1.244×10^{-22} g.

..... *As* [1]

2 These questions are from different areas of chemistry.

(a) This question is about two salts of rubidium (atomic number 37): RbClO_3 and RbClO_4 .

- (i) The oxidation number of chlorine is different in the two rubidium salts, RbClO_3 and RbClO_4 .

What is the name of RbClO_4 ?

rubidium chlorate(VII) [1]

- (ii) A student carries out an experiment to determine the enthalpy change of solution of RbClO_3 using the method below.

- A 2.00 g sample of solid RbClO_3 is added to water in a well-insulated container. The initial temperature is 23.0°C .
- The mixture is stirred until all the RbClO_3 has dissolved. The final temperature is 21.5°C . The final solution has a mass of 102 g.

Determine the enthalpy change of solution, $\Delta_{\text{sol}}H$, of RbClO_3 in kJ mol^{-1} .

Assume that the specific heat capacity of the solution is the same as that of pure water.

$$\text{energy change, } q = mc\Delta T = 102 \times 4.18 \times 1.5 = 639.54 \text{ J}$$

$$q = 0.63954 \text{ kJ}$$

$$M_r(\text{RbClO}_3) = 85.5 + 35.5 + (3 \times 16.0) = 169.0$$

$$n(\text{RbClO}_3) = 2.00 \div 169.0 = 0.01183 \text{ mol}$$

The temperature falls, so dissolving is endothermic (ΔH is positive).

$$\Delta_{\text{sol}}H = +0.63954 \div 0.01183 = +54.0 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{sol}}H(\text{RbClO}_3) = \dots\dots\dots +54.0 \dots\dots\dots \text{ kJ mol}^{-1} \text{ [3]}$$

(b) A student investigates the rate of a reaction that is 1st order with respect to hydrochloric acid, HCl(aq) .

- The student carries out a reaction using $0.680 \text{ mol dm}^{-3} \text{ HCl(aq)}$. The initial rate is $9.52 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$.
- The student dilutes a different sample of $0.680 \text{ mol dm}^{-3} \text{ HCl(aq)}$ with water. The pH of this diluted acid is 1.50.
- The student repeats the reaction using the same volume of this diluted acid.

Determine the initial rate using this diluted acid.

$$[\text{H}^+] \text{ in diluted acid} = 10^{-1.50} = 0.0316 \text{ mol dm}^{-3} = [\text{HCl}]$$

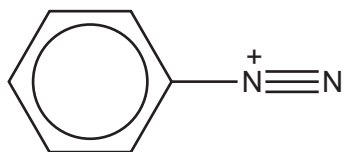
$$\text{1st order: rate} = k[\text{HCl}]$$

$$k = 9.52 \times 10^{-4} \div 0.680 = 1.40 \times 10^{-3} \text{ s}^{-1}$$

$$\text{initial rate} = 1.40 \times 10^{-3} \times 0.0316 = 4.43 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\text{initial rate} = \dots\dots\dots 4.43 \times 10^{-5} \dots\dots\dots \text{mol dm}^{-3} \text{ s}^{-1} \quad [3]$$

(c) The benzenediazonium ion, shown below, is stable at temperatures below 10 °C.



Benzenediazonium

Above 10 °C, the benzenediazonium ion reacts with water to form phenol.

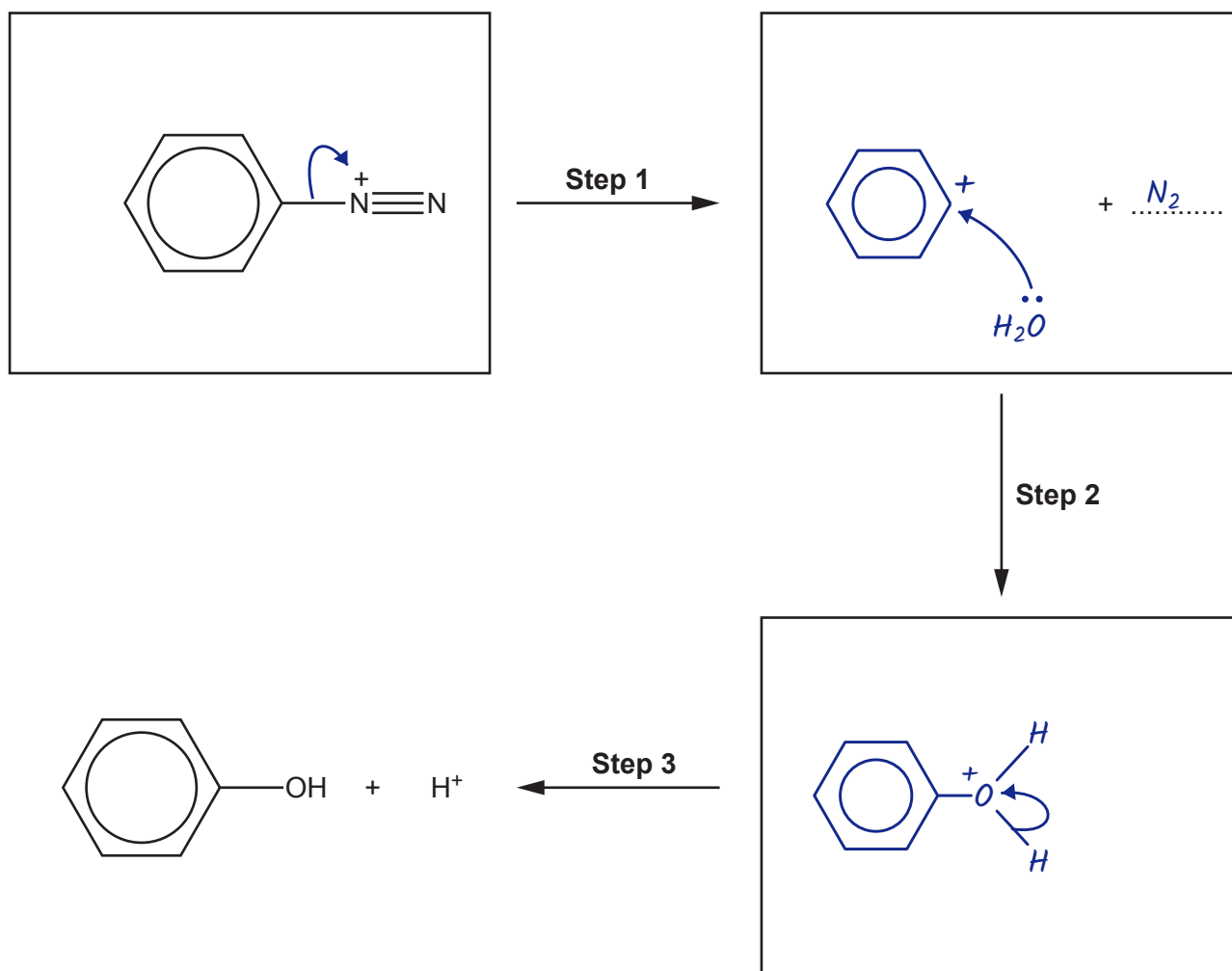
The reaction proceeds in a three-step mechanism.

Step 1 Elimination of nitrogen gas to form a carbocation.

Step 2 Nucleophilic attack by water.

Step 3 Proton loss to form the organic product.

Complete the boxes below with intermediates and curly arrows to show the mechanism for this reaction.

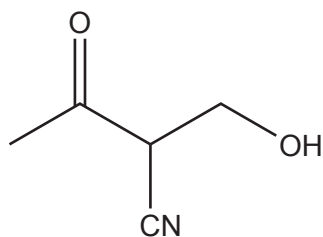


[4]

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Turn over for the next question

- 3* A chemist is investigating compound **A**, shown below, as a potential organic intermediate.



Compound A

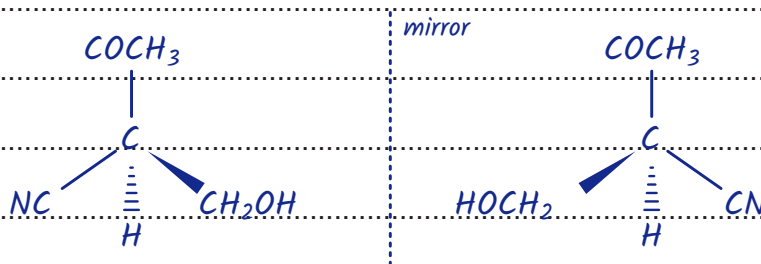
Describe the type of stereoisomerism shown by compound **A** and suggest **three** reactions of compound **A**, one for each of the three functional groups using reagents of your choice.

In your answer, show stereoisomers of compound **A**, your chosen reactants and conditions, and the structures for the organic products produced.

Mechanisms and equations are **not** required.

[6]

Compound A shows optical isomerism. The carbon bonded to H, CN, COCH₃ and CH₂OH is a chiral centre (four different groups), so A has two enantiomers, non-superimposable mirror images:



Ketone (C=O): reduce with NaBH₄ in aqueous solution (water/methanol) at room temperature. Product is a secondary alcohol, a diol:

CH₃CH(OH)CH(CN)CH₂OH.

Primary alcohol (CH₂OH): heat under reflux with excess acidified potassium dichromate(VI), K₂Cr₂O₇/H₂SO₄ (orange to green). It is oxidised to a carboxylic acid: CH₃COCH(CN)COOH.

Nitrile (C≡N): heat under reflux with dilute acid, e.g. HCl(aq) (hydrolysis). The CN becomes COOH: CH₃COCH(COOH)CH₂OH (+ NH₄Cl).

So each of the three functional groups can be converted separately, and the products still contain the chiral centre.

Additional answer space if required.

4 Tutton's salts are 'double salts' with the formula $\text{X}_2\text{Y}(\text{Z}\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$.

A Tutton's salt contains two cations: X^+ and Y^{2+} .

- X^+ can be an ion of the Group 1 elements K, Rb, Cs or Fr, or an ammonium ion.
- Y^{2+} can be a 2+ ion of magnesium or an ion of most of the transition elements in Period 4.
- Z can be S or Cr.

$(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is an example of a Tutton's salt.

(a) Predict the formula of a Tutton's salt containing different ions from $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

$\text{K}_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ [1]

(b) A student prepares a sample of the Tutton's salt, $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ using the method shown below.

Step 1 Dissolve 0.025 mol of ammonium sulfate and 0.025 mol of hydrated copper(II) sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, in water and make up to 50 cm^3 .

Step 2 Boil the resulting mixture for 2 minutes and allow to cool.

Step 3 Allow the solvent to evaporate slowly. Pale blue crystals of the Tutton's salt form.

(i) What masses are needed of ammonium sulfate and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$?

mass of ammonium sulfate $0.025 \times 132.1 = 3.30$ g

mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $0.025 \times 249.6 = 6.24$ g
[2]

(ii) In **Step 3**, why does the student allow the solvent to evaporate and **not** boil off all the solvent in **Step 2**?

*Boiling off all the solvent would also remove the water of
crystallisation (dehydration), forming the anhydrous salt instead of the
hydrated crystals.* [1]

- (c) The student dissolves their Tutton's salt in water. A pale blue solution forms.

The student carries out two tests on this aqueous solution.

- (i) The student adds an excess of aqueous ammonia to their aqueous solution of Tutton's salt. A deep blue solution forms.

The complex ion responsible for the deep blue solution has a molar mass of 167.5 g mol^{-1} .

Suggest the formula of this complex ion.

$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ [1]

- (ii) The student adds $\text{NaOH}(\text{aq})$ to the aqueous solution of Tutton's salt and warms the mixture.

A precipitate and a gas are formed.

Write the formulae of the precipitate and gas and suggest a test that could confirm the identity of the gas.

Formula of precipitate $\text{Cu}(\text{OH})_2$

Formula of gas NH_3

Test to confirm the identity of the gas *hold damp red litmus paper at the mouth of the test tube:*
it turns blue (alkaline gas). [3]

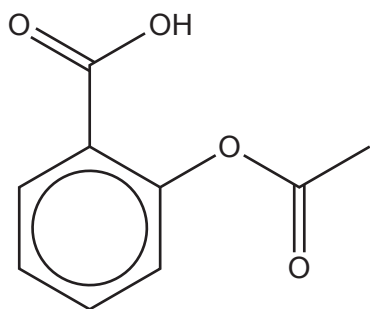
- (iii) How could the student carry out a test-tube test to confirm the anion in the Tutton's salt?

Add a few drops of dilute hydrochloric acid and then aqueous barium chloride, $\text{BaCl}_2(\text{aq})$, to a sample of the solution in a test tube.
A white precipitate of BaSO_4 forms, confirming sulfate ions, SO_4^{2-}

..... [2]

5 Aspirin tablets are used for pain relief.

The structure of aspirin is shown below.



Aspirin

- (a) A student uses the reaction of aspirin with cold NaOH(aq) to determine the mass of aspirin in **one** tablet.

In this reaction, 1 mol of aspirin reacts with 1 mol of cold NaOH(aq).

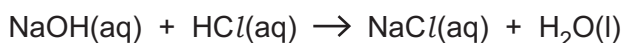
The student's method is outlined below.

Step 1 The student reacts **three** aspirin tablets with 100 cm³ of 0.500 mol dm⁻³ NaOH(aq). The NaOH is in excess. A colourless solution forms.

Step 2 The colourless solution from **Step 1** is made up to 250.0 cm³ with distilled water.

Step 3 A 25.00 cm³ sample of the diluted solution from **Step 2** is titrated with 0.200 mol dm⁻³ HCl(aq) in the burette.

The HCl(aq) reacts with excess NaOH(aq) that remains in **Step 1**:



The student repeats the titration to obtain concordant (consistent) titres.

Titration results

The trial titre has been omitted.

The burette readings have been read to the nearest 0.05 cm³.

	1	2	3
Final reading / cm³	23.10	45.40	27.40
Initial reading / cm³	0.00	23.10	5.00

Analysis of results

From the results, the student can determine the following.

1. The amount, in mol, of excess NaOH(aq) that remains after the reaction of aspirin with NaOH(aq).
2. The amount, in mol, of NaOH(aq) that reacted with the aspirin.

Use the results to determine the mass, in mg, of aspirin in **one** aspirin tablet.

titres: 23.10, 22.30, 22.40 cm³; concordant titres are 22.30 and 22.40 cm³

mean titre = (22.30 + 22.40) ÷ 2 = 22.35 cm³

n(HCl) = 0.200 × 22.35 ÷ 1000 = 4.47 × 10⁻³ mol

n(NaOH) remaining in 25.00 cm³ = n(HCl) = 4.47 × 10⁻³ mol

1. n(NaOH) in excess in 250.0 cm³ = 4.47 × 10⁻³ × 10 = 4.47 × 10⁻² mol

n(NaOH) at start = 0.500 × 100 ÷ 1000 = 0.0500 mol

2. n(NaOH) reacted with aspirin = 0.0500 - 0.0447 = 5.30 × 10⁻³ mol

n(aspirin) in three tablets = 5.30 × 10⁻³ mol (1 : 1 ratio)

M(aspirin, C₉H₈O₄) = 180.0 g mol⁻¹

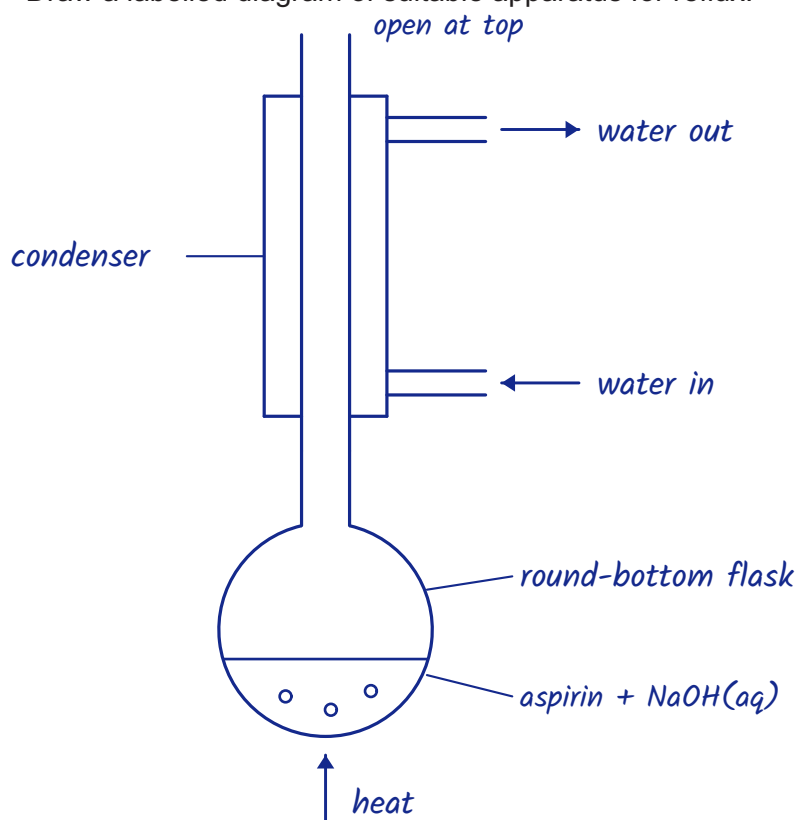
mass in three tablets = 5.30 × 10⁻³ × 180.0 = 0.954 g

mass in one tablet = 0.954 ÷ 3 = 0.318 g = 318 mg

mass of aspirin in **one** tablet = ... **318** mg [6]

(b) Aspirin reacts with hot NaOH(aq) , under reflux.

(i) Draw a labelled diagram of suitable apparatus for reflux.

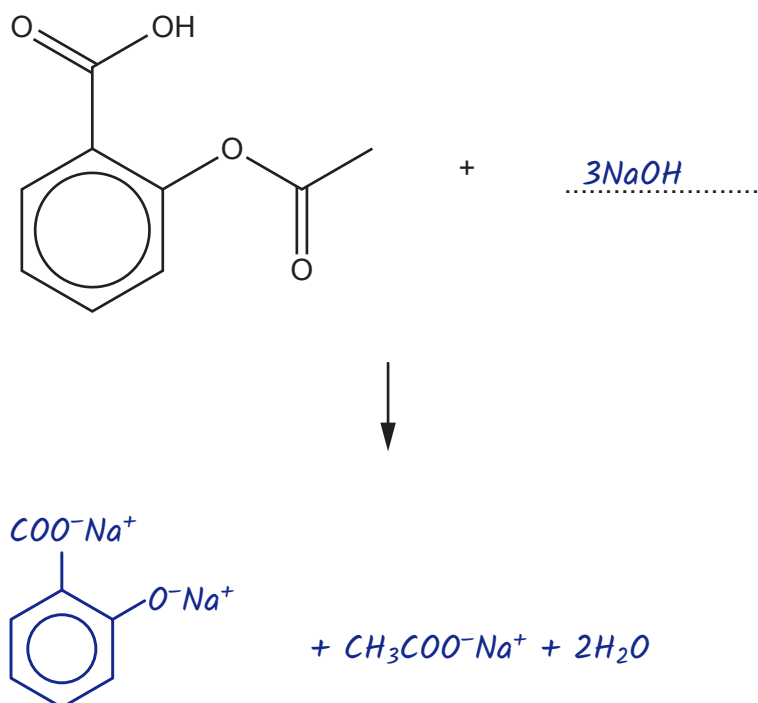


[2]

(ii) In this reaction, 1 mol of aspirin reacts with 3 mol of hot NaOH(aq).

Complete the equation for the reaction of aspirin with an excess of hot NaOH(aq).

Show structures for organic compounds.



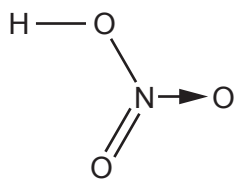
[3]

16
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6 This question is about nitric acid, hydrochloric acid and sulfuric acid.

- (a) Nitric acid has 2 single covalent bonds, 1 double covalent bond and 1 dative covalent bond as shown below.



Nitric acid

Predict the H–O–N and O–N–O bond angles in nitric acid.

Explain your reasoning.

H–O–N: 104.5°. The O has 2 bonded pairs and 2 lone pairs; lone pairs repel more than bonded pairs, so the angle is less than 109.5°.

O–N–O: 120°. The N has 3 bonded regions (no lone pairs), which repel equally and get as far apart as possible (trigonal planar).

[4]

- (b) Dilute nitric acid reacts with aluminium oxide to form a solution of aluminium nitrate.

- (i) Write an equation for this reaction.

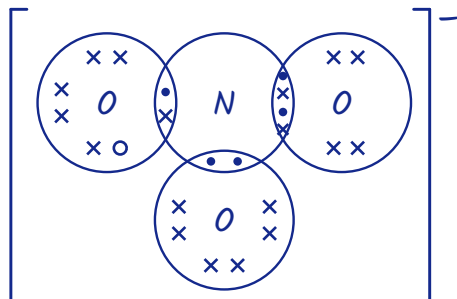


[2]

- (ii) The solution contains nitrate ions, NO_3^- .

Draw a 'dot-and-cross' diagram for the NO_3^- ion.

Use a different symbol for the extra electron.



• = N electron
× = O electron
○ = extra electron

[2]

- (c) A mixture of concentrated nitric and hydrochloric acid is called 'aqua regia'. Aqua regia can dissolve gold.

The reaction of aqua regia with gold is a redox reaction which forms chlorauric acid, HAuCl_4 .

- (i) Balance the half-equation for the oxidation process in this reaction.



[1]

- (ii) In the reduction process in this reaction, HNO_3 and H^+ react together to form 2 oxides: **X** ($M_r = 30$) and **Z** ($M_r = 18$).

Determine the formulae of **X** and **Z** and write the half-equation for this reduction.

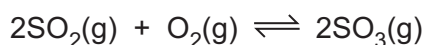
X = $\dots \text{NO} \dots$

Z = $\dots \text{H}_2\text{O} \dots$

half-equation $\dots \text{HNO}_3 + 3\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O} \dots$ [3]

(d) In the UK, most sulfuric acid, H_2SO_4 , is manufactured by the Contact process.

One stage in the Contact process involves the equilibrium between sulfur dioxide, oxygen and sulfur trioxide.



This equilibrium is investigated:

Step 1 $5.82 \times 10^{-2} \text{ mol}$ of SO_2 is mixed with $7.40 \times 10^{-2} \text{ mol}$ of O_2 in a 2.00 dm^3 container.

Step 2 The container is sealed and allowed to reach equilibrium at constant temperature.

Step 3 At equilibrium, $5.20 \times 10^{-2} \text{ mol}$ of SO_3 is formed.

Determine the equilibrium concentrations and calculate K_c , including units.

$$n(\text{SO}_2)_{\text{reacted}} = n(\text{SO}_3)_{\text{formed}} = 5.20 \times 10^{-2} \text{ mol}$$

$$n(\text{O}_2)_{\text{reacted}} = 5.20 \times 10^{-2} \div 2 = 2.60 \times 10^{-2} \text{ mol}$$

$$\text{at equilibrium: } n(\text{SO}_2) = 5.82 \times 10^{-2} - 5.20 \times 10^{-2} = 6.20 \times 10^{-3} \text{ mol}$$

$$n(\text{O}_2) = 7.40 \times 10^{-2} - 2.60 \times 10^{-2} = 4.80 \times 10^{-2} \text{ mol}$$

$$[\text{SO}_2] = 6.20 \times 10^{-3} \div 2.00 = 3.10 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{O}_2] = 4.80 \times 10^{-2} \div 2.00 = 2.40 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{SO}_3] = 5.20 \times 10^{-2} \div 2.00 = 2.60 \times 10^{-2} \text{ mol dm}^{-3}$$

$$K_c = [\text{SO}_3]^2 \div ([\text{SO}_2]^2 [\text{O}_2])$$

$$K_c = (2.60 \times 10^{-2})^2 \div ((3.10 \times 10^{-3})^2 \times 2.40 \times 10^{-2}) = 2931$$

$$K_c = \dots\dots\dots 2931 \dots\dots\dots \text{units } \text{dm}^3 \text{ mol}^{-1} \dots\dots\dots [5]$$

TURN OVER FOR QUESTION 6 PART (e)

(e)* Three reactions involving sulfuric acid are shown below.

Reaction 1

Dilute sulfuric acid is reacted with nickel(II) hydroxide to form a green solution.

The solvent is allowed to evaporate leaving hydrated crystals of compound **D**, with the percentage composition by mass: Ni, 22.33%; S, 12.20%; O, 60.87%; H, 4.60%.

Reaction 2

Concentrated sulfuric acid is reacted with hydrogen bromide, HBr, to form three products:

- an element which exists as diatomic molecules
- a gaseous compound **E**
- a liquid.

At RTP, 1.00 dm³ of compound **E** has a mass of 2.67 g.

Reaction 3

Concentrated sulfuric acid acts as a catalyst when 2-hydroxypropanoic acid reacts to form compound **F** ($M_r = 144$).

In this reaction, 2 mol of 2-hydroxypropanoic acid forms 1 mol of compound **F** and 2 mol of water.

Identify compounds **D**, **E** and **F** and construct equations for the reactions.

Show structures for any organic compounds.

[6]

D: Ni : S : O : H = 22.33/58.7 : 12.20/32.1 : 60.87/16.0 : 4.60/1.0 =

0.380 : 0.380 : 3.80 : 4.60 = 1 : 1 : 10 : 12, so NiSO₄·10H₂O.

D is hydrated nickel(II) sulfate, NiSO₄·6H₂O.

H₂SO₄ + Ni(OH)₂ + 4H₂O → NiSO₄·6H₂O

E: M = 2.67 × 24.0 = 64.1 g mol⁻¹, so E is sulfur dioxide, SO₂. The

diatomic element is bromine, Br₂, and the liquid is water. HBr is oxidised to

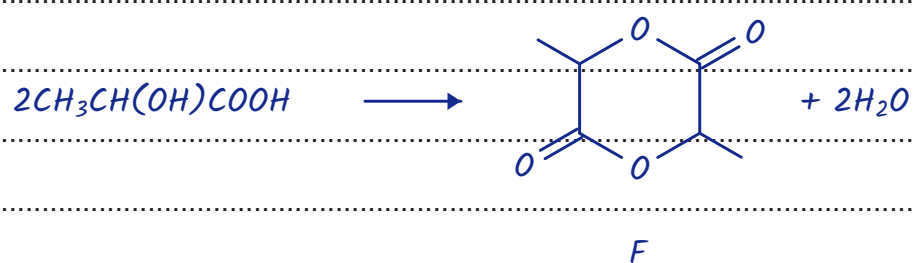
Br₂ and the H₂SO₄ is reduced (S from +6 to +4).

H₂SO₄ + 2HBr → Br₂ + SO₂ + 2H₂O

F: 2 × C₃H₆O₃ (2 × 90.0) – 2 × H₂O (36.0) = 144, so F is C₆H₈O₄. The

OH of each molecule forms an ester with the COOH of the other, so F is

a cyclic diester:



Additional answer space if required.

END OF QUESTION PAPER

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