



Oxford Cambridge and RSA

Tuesday 5 October 2021 – Afternoon

A Level Chemistry A

H432/01 Periodic table, elements and physical chemistry

Time allowed: 2 hours 15 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 **100**.
- 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 **32** pages.

ADVICE

- Read each question carefully before you start your answer.

2
SECTION A

You should spend a maximum of 20 minutes on this section

Write your answer to each question in the box provided.

Answer **all** the questions.

- 1** Which statement describes electronegativity?
- A** A measure of the reactivity of an element.
 - B** The ability of an atom to attract an electron to become a 1– ion.
 - C** The attraction of a bonded atom for the electrons in a covalent bond.
 - D** The attraction of an atom for a lone pair of electrons.

Your answer

C

[1]

- 2** A chlorate(VII) ion has a 1– charge.
- What is the formula for sodium chlorate(VII)?

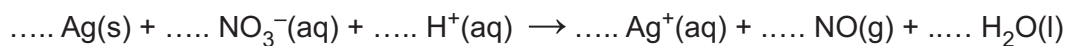
- A** NaClO_3
- B** NaClO_4
- C** NaClO_7
- D** NaClO_8

Your answer

B

[1]

- 3 The unbalanced equation for the reaction of silver with concentrated nitric acid is shown below.



Which numbers for Ag and H₂O will balance the equation?

	Ag(s)	H ₂ O(l)
A	1	2
B	2	3
C	3	1
D	3	2

Your answer

D

[1]

- 4 Which sample contains the greatest number of molecules?

- A** 140.0g C₂H₂
B 180.0g C₂H₆
C 240.0g C₄H₁₀
D 400.0g C₆H₆

Your answer

B

[1]

- 5 Chromium(III) oxide, Cr₂O₃, is reduced to chromium by heating with magnesium.

What is the minimum mass of Mg required to reduce 11.4 g of chromium(III) oxide?

- A** 0.61g
B 0.91g
C 3.65g
D 5.47g

Your answer

D

[1]

- 6 A student is supplied with 100.0 cm^3 of a solution of 0.400 mol dm^{-3} magnesium iodide, MgI_2 .
A student plans to dilute this solution so that the iodide concentration is 0.250 mol dm^{-3} .
What volume of water, in cm^3 , does the student need to add?

- A 60.0
B 160.0
C 220.0
D 320.0

Your answer

C

[1]

- 7 Which row shows elements in order of increasing first ionisation energy?

- A $\text{Ca} < \text{Si} < \text{P} < \text{N}$
B $\text{N} < \text{P} < \text{Si} < \text{Ca}$
C $\text{Ca} < \text{N} < \text{P} < \text{Si}$
D $\text{C} < \text{Si} < \text{P} < \text{Ca}$

Your answer

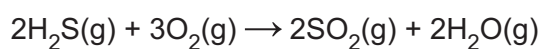
A

[1]

- 8 Bond enthalpies are given in the table.

Bond	H-S	O=O	S=O	O-H
Bond enthalpy / kJ mol^{-1}	+346	+498	+531	+464

What is the enthalpy change, in kJ mol^{-1} , for the reaction below?



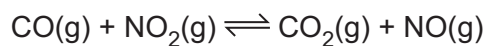
- A -174
B -1102
C -1794
D -2098

Your answer

B

[1]

- 9 An equilibrium system is shown below.



Different amounts of CO, NO₂, CO₂ and NO are added to four containers, as shown below.

Container	CO/mol	NO ₂ /mol	CO ₂ /mol	NO/mol
A	1	1	0	0
B	1	0	1	1
C	1	1	1	0
D	0	1	1	1

Which container would have the largest concentration of CO(g) at equilibrium?

Your answer

B

[1]

- 10 An aqueous solution of ethanoic acid, CH₃COOH, has a concentration of 0.50 mol dm⁻³.
pK_a for CH₃COOH = 4.76 at 25 °C.

What is the pH of the ethanoic acid solution at 25 °C?

- A** 2.53
B 2.68
C 4.91
D 5.06

Your answer

A

[1]

- 11 The feasibility of a chemical reaction depends on the temperature and the signs of ΔH and ΔS .

Which row has signs for ΔH and ΔS for a reaction that is feasible at high temperatures but is **not** feasible at low temperatures?

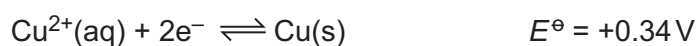
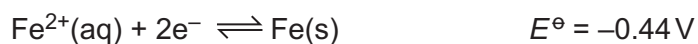
	ΔH	ΔS
A	+	+
B	+	–
C	–	+
D	–	–

Your answer

A

[1]

- 12 Two redox systems are shown below.



Which species in the two redox systems is the strongest oxidising agent?

- A** $\text{Fe}^{2+}(\text{aq})$
B $\text{Fe}(\text{s})$
C $\text{Cu}^{2+}(\text{aq})$
D $\text{Cu}(\text{s})$

Your answer

C

[1]

13 Which statement(s) explain(s) the trend in boiling points down the halogens group?

- 1:** The induced dipole–dipole interactions (London forces) become stronger.
- 2:** The covalent bonds become stronger.
- 3:** The permanent dipole–dipole interactions become stronger.

- A** 1, 2 and 3
- B** Only 1 and 2
- C** Only 2 and 3
- D** Only 1

Your answer

D

[1]

14 Which statement(s) about a molecule of Cl-N=O is/are correct?

- 1:** It is a polar molecule.
- 2:** It contains 6 lone pairs of electrons.
- 3:** It has a bond angle of 180° .

- A** 1, 2 and 3
- B** Only 1 and 2
- C** Only 2 and 3
- D** Only 1

Your answer

B

[1]

15 $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is a hydrated 'double salt'.

A student analyses this double salt using test tube tests.

Which row(s) gives/give correct result(s) for the stated test?

	Test	Results
1	Reaction with cold $\text{NaOH}(\text{aq})$	Green precipitate
2	Reaction with $\text{Ba}(\text{NO}_3)_2(\text{aq})$	White precipitate
3	Reaction with warm $\text{NaOH}(\text{aq})$	Red-brown precipitate and an alkaline gas

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer

C

[1]

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SECTION B

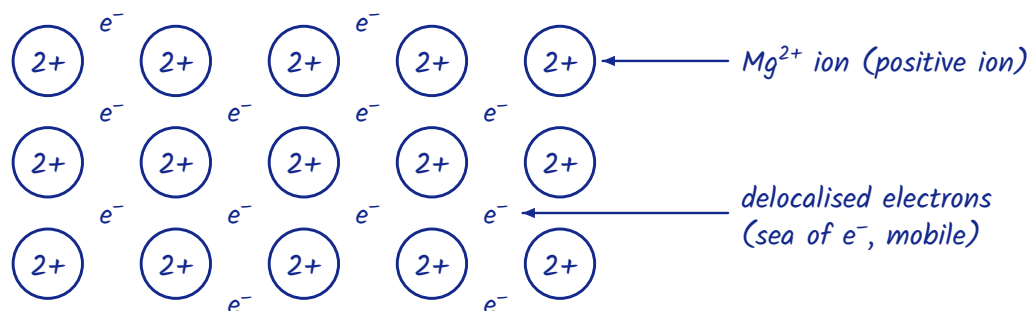
Answer **all** the questions.

16 This question is about magnesium and magnesium halides.

(a) Magnesium has metallic bonding and is a good conductor of electricity.

Describe, with the aid of a labelled diagram, the metallic bonding in magnesium and explain why magnesium conducts electricity.

Include the correct charges on the particles in your diagram.



Metallic bonding: attraction between Mg^{2+} ions and delocalised electrons.

Mg conducts as the delocalised electrons can move.

[3]

(b) The 12 successive ionisation energies of magnesium are shown in **Table 16.1**.

Ionisation number	Ionisation energy/ kJ mol^{-1}
1	738
2	1451
3	7733
4	10 541
5	13 629
6	17 995
7	21 704
8	25 657
9	31 644
10	35 463
11	169 996
12	1 893 711

Table 16.1

- (i) Write an equation to represent the **fourth** ionisation energy of magnesium.

Include state symbols.



- (ii) Explain how the successive ionisation energies provide evidence that magnesium is in Group 2 of the periodic table.

There is a big jump (large difference) in ionisation energy between the 2nd and 3rd ionisation energies (1451 to 7733 kJ mol⁻¹), so the 3rd electron is removed from an inner shell: Mg has 2 outer electrons, so it is in Group 2. [1]

- (iii) Electrons occupy orbitals.

In **Table 16.2** below, add a tick (✓) below the ionisation numbers that are responsible for removing an electron from a full orbital in a magnesium atom.

Ionisation number	1	2	3	4	5	6	7	8	9	10	11	12
	✓		✓	✓	✓				✓		✓	

Table 16.2

[1]

- (c) The enthalpy change of solution for magnesium fluoride, MgF_2 , can be determined indirectly using an energy cycle based on the enthalpy changes below.

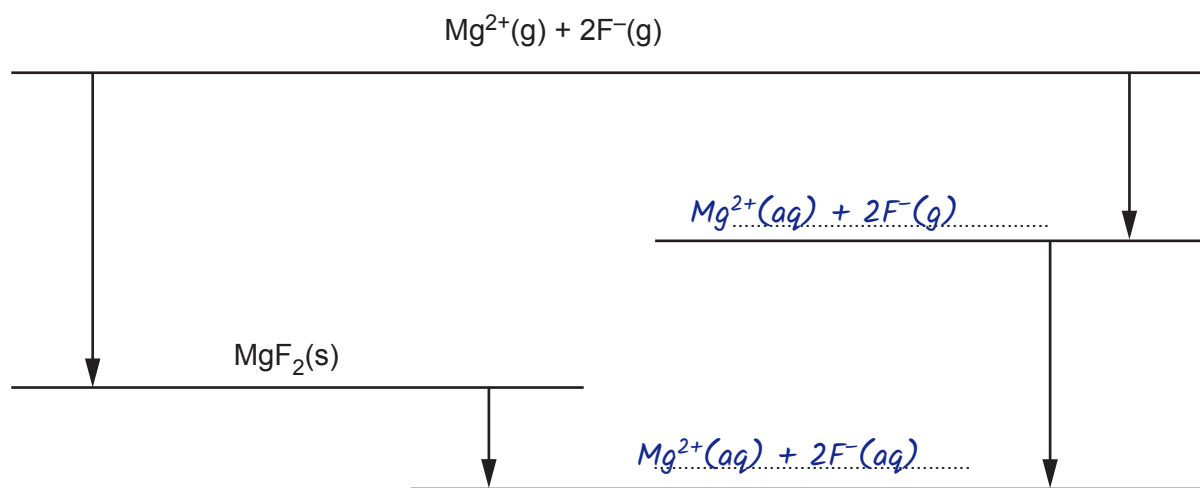
Enthalpy change	Energy / kJ mol^{-1}
Lattice enthalpy of magnesium fluoride	-2926
Hydration of magnesium ions	-1920
Hydration of fluoride ions	-506

- (i) Explain what is meant by **enthalpy change of solution**.

The enthalpy change when 1 mole of a solid compound dissolves completely in water (forming aqueous ions).

..... [1]

- (ii) On the dotted lines, add the species present, including state symbols.



[2]

- (iii) Calculate the enthalpy change of solution of MgF_2 .

$$\begin{aligned}\Delta_{\text{sol}}H &= -(\text{lattice enthalpy}) + \Delta_{\text{hyd}}H(\text{Mg}^{2+}) + 2\Delta_{\text{hyd}}H(\text{F}^-) \\ &= -(-2926) + (-1920) + 2(-506) = 2926 - 1920 - 1012\end{aligned}$$

enthalpy change of solution = ... -6 kJ mol^{-1} [1]

- (iv) The enthalpy changes of solution of the magnesium halides show a trend from MgF_2 to MgI_2 .

Explain why it is difficult to predict whether the enthalpy change of solution becomes more exothermic or less exothermic down the group from MgF_2 to MgI_2 .

Down the group the halide ion gets larger (ionic radius $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$).

So the halide ion has less attraction for Mg^{2+} ; lattice enthalpy becomes less exothermic.

The halide ion also has less attraction for H_2O ; its hydration enthalpy becomes less exothermic.

Both decrease, so it is difficult to predict whether lattice enthalpy or hydration enthalpy has the bigger effect. [4]

17 This question is about d-block elements.

(a) Most d-block elements are also classified as transition elements.

Explain why scandium and zinc are classified as d-block elements but are **not** also transition elements.

Your explanations should include full electron configurations.

Sc: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$ Zn: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

Both are d-block elements because the 3d sub-shell is being filled (highest energy sub-shell).

A transition element has an ion with an incomplete (partially filled) d sub-shell.

Sc forms only Sc^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6$, so the 3d sub-shell is empty.

Zn forms only Zn^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$, so the 3d sub-shell is full.

Neither forms an ion with an incomplete d sub-shell, so they are not transition elements.

[4]

(b) Compound **A** is a hydrated chromium(III) salt with a molar mass of 608.3 g mol^{-1} and the following percentage composition by mass:

Cr, 17.10%; H, 3.94%; O, 63.13%; S, 15.83%.

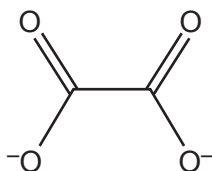
A student dissolves compound **A** in water.

The resulting solution contains the complex ion $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.

The student mixes this solution with aqueous sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$.

A ligand substitution reaction takes place forming a solution containing three stereoisomers of a complex ion **B** of chromium(III).

Complex ion **B** is six-coordinate and contains two ethanedioate ligands and two water ligands. The ethanedioate ion is the bidentate ligand shown below.



Ethanedioate ligand

(i) What is meant by a **bidentate ligand**?

A ligand that donates two lone pairs of electrons to a metal ion, forming two coordinate (dative covalent) bonds.

[1]

- (ii)* Determine the formulae of **A** and **B**. Write the ionic equation for the ligand substitution and show 3D structures for the three stereoisomers of **B**.

$$Cr : H : O : S = 17.10/52.0 : 3.94/1.0 : 63.13/16.0 : 15.83/32.1 =$$

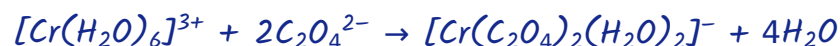
$$0.329 : 3.94 : 3.95 : 0.493 = 1 : 12 : 12 : 1.5 = 2 : 24 : 24 : 3$$

$$Cr_2H_{24}O_{24}S_3: M = 104.0 + 24.0 + 384.0 + 96.3 = 608.3 \text{ g mol}^{-1},$$

equal to the molar mass, so $A = Cr_2(SO_4)_3 \cdot 12H_2O$ ($Cr_2H_{24}O_{24}S_3$).

B: Cr^{3+} with two $C_2O_4^{2-}$ (4-) and two neutral H_2O ligands, so overall

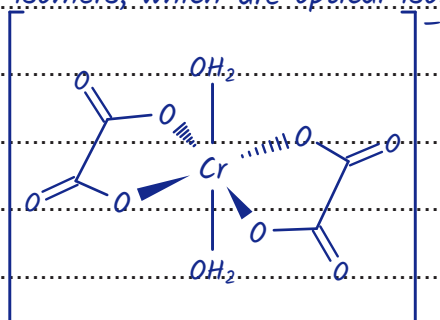
charge 1-: $B = [Cr(C_2O_4)_2(H_2O)_2]^-$



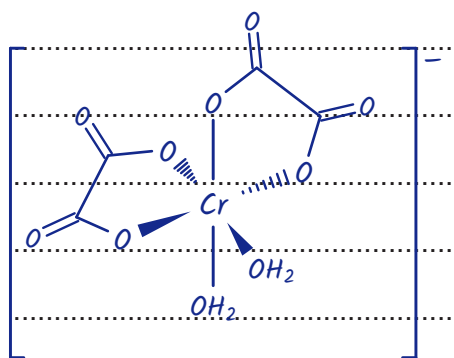
Each $C_2O_4^{2-}$ forms 2 coordinate bonds, so **B** is octahedral (90°). The 3

stereoisomers are the trans isomer (H_2O ligands opposite) and two cis

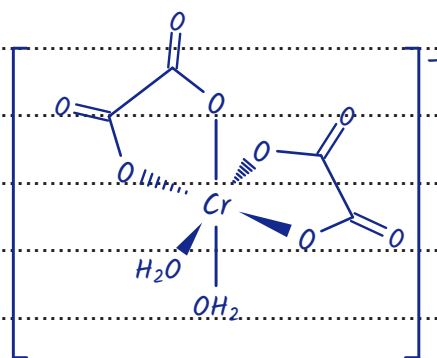
isomers, which are optical isomers (non-superimposable mirror images):



trans isomer (left): H_2O ligands at 180°
cis isomers (below): optical isomers



cis isomer



cis isomer (mirror image)

[6]

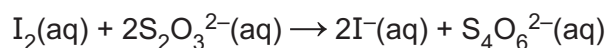
Additional answer space if required.

- 18** A student carries out an experiment to determine the percentage by mass of copper in an ore containing copper in its +2 oxidation state.

The student is provided with a sample of the copper ore, 1 mol dm^{-3} potassium iodide, KI(aq) , and $0.0200 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$.

The student's method is outlined below.

- Step 1** Add an excess of warm nitric acid to 2.50 g of the ore.
The copper(II) compounds in the ore react, forming aqueous copper(II) nitrate.
- Step 2** Filter the mixture to remove the unreacted rock. Neutralise the filtrate.
- Step 3** Add an excess of aqueous potassium iodide, KI(aq) .
A precipitate of copper(I) iodide and a solution of iodine, $\text{I}_2(\text{aq})$, forms.
- Step 4** Titrate the mixture from **Step 3** using $0.0200 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$ in the burette.



26.55 cm^3 of $0.0200 \text{ mol dm}^{-3}$ $\text{Na}_2\text{S}_2\text{O}_3$ are required to reach the end point.

- (a) In **Step 1**, the student observed that bubbles of gas were produced.

Suggest the formula of the copper(II) compound which reacted with HNO_3 to form the gas, and write a full equation for the reaction.

Formula: CuCO_3

Equation: $\text{CuCO}_3 + 2\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + \text{CO}_2 + \text{H}_2\text{O}$ [2]

- (b) Write an **ionic** equation, including state symbols, for the reaction in **Step 3**.

$2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^{-}(\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{I}_2(\text{aq})$ [1]

- (c) Suggest a suitable indicator for this titration and state the colour change at the end point in **Step 4**.

Indicator: starch (solution)

Colour from blue-black to colourless [1]

- (d) Determine the percentage, by mass, of copper in the copper ore.
Give your answer to an **appropriate** number of significant figures.

$$n(S_2O_3^{2-}) = 0.0200 \times 26.55 \div 1000 = 5.31 \times 10^{-4} \text{ mol}$$

$$n(I_2) = 5.31 \times 10^{-4} \div 2 = 2.655 \times 10^{-4} \text{ mol}$$

$$2Cu^{2+} \equiv I_2, \text{ so } n(Cu^{2+}) = 2 \times 2.655 \times 10^{-4} = 5.31 \times 10^{-4} \text{ mol}$$

$$\text{mass of Cu} = 5.31 \times 10^{-4} \times 63.5 = 0.03372 \text{ g}$$

$$\text{percentage} = 0.03372 \div 2.50 \times 100 = 1.35\% \text{ (3 s.f.)}$$

percentage = ...1.35..... % [4]

- (e) Explain whether the calculated percentage by mass of copper would be higher, lower or the same if the following changes were made to the method.

- (i) The potassium iodide was not in excess, in **Step 3**.

Lower: not all the Cu^{2+} reacts, so less I_2 forms and a smaller titre is needed. [1]

- (ii) The burette readings were read from the top of the meniscus, in **Step 4**.

The same: the titre is measured by difference, so the error cancels out. [1]

- (f) The student then modifies the method in order to obtain a more accurate value for the percentage by mass of copper in the ore. The student decides to use 25.00 g of the copper ore in **Step 1**.

What further modifications should the student make to produce a more accurate value for the percentage by mass of copper in the ore?

Make the neutralised filtrate from Step 2 up to 250.0 cm³ in a volumetric flask (standard solution) and titrate 25.0 cm³ portions measured by pipette.
Repeat the titrations until concordant titres (within 0.10 cm³) are obtained and take the mean of the concordant titres. [2]

19 Storage cells and fuels cells are types of electrochemical cell.

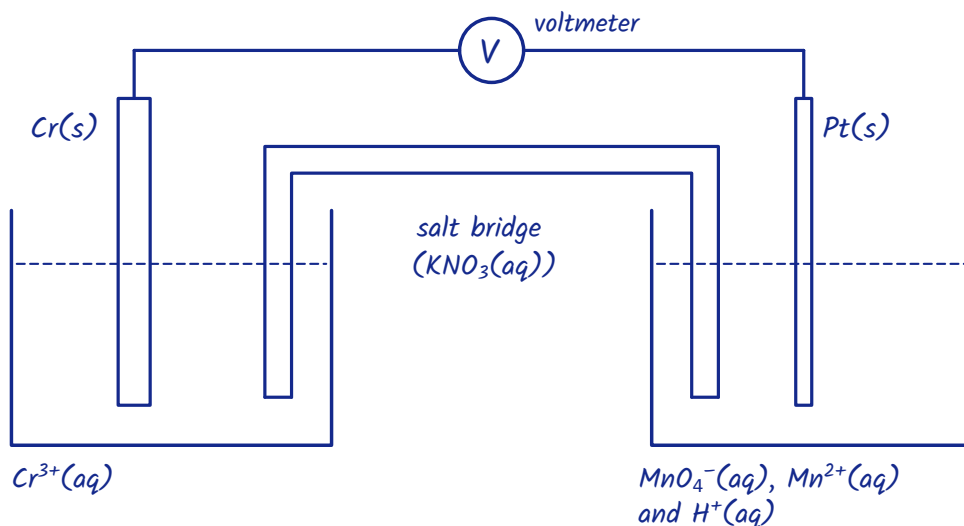
The electrode potentials for five redox systems are shown in **Table 19.1**.

Redox system	Half-equation	$E^{\ominus}/V$
1	$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^{-} \rightleftharpoons \text{Cr}(\text{s})$	-0.74
2	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^{-} \rightleftharpoons 4\text{OH}^{-}(\text{aq})$	+0.40
3	$\text{MnO}_4^{-}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{MnO}_4^{2-}(\text{aq})$	+0.56
4	$\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) + 5\text{e}^{-} \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
5	$\text{MnO}_4^{2-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	+1.70

Table 19.1

(a) A student sets up an electrochemical cell based on redox systems 1 and 4 in **Table 19.1**.

(i) Draw a labelled diagram to show how this cell could be set up in the laboratory.



[3]

(ii) Construct the equation for the overall cell reaction.



(b) In acid conditions, $\text{MnO}_4^{2-}(\text{aq})$ disproportionates to form $\text{MnO}_2(\text{s})$ and $\text{MnO}_4^{-}(\text{aq})$.

(i) Explain, in terms of oxidation numbers, why disproportionation has taken place.

Mn is oxidised from +6 in MnO_4^{2-} to +7 in MnO_4^{-} .

Mn is reduced from +6 in MnO_4^{2-} to +4 in MnO_2 .

The same element is both oxidised and reduced at the same time.

[2]

(ii) Explain, in terms of electrode potentials and equilibrium shifts why $\text{MnO}_4^{2-}(\text{aq})$ disproportionates in acid conditions. Use the information in **Table 19.1**.

$E^{\ominus}$ of system 3 ($\text{MnO}_4^{-}/\text{MnO}_4^{2-}$, +0.56 V) is less positive than $E^{\ominus}$ of

system 5 ($\text{MnO}_4^{2-}/\text{MnO}_2$, +1.70 V), $E_{\text{cell}} = +1.14 \text{ V}$.

So system 3 shifts to the left (MnO_4^{2-} oxidised to MnO_4^{-}) and

system 5 shifts to the right (MnO_4^{2-} reduced to MnO_2), which needs

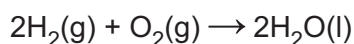
H^{+} :

$3\text{MnO}_4^{2-} + 4\text{H}^{+} \rightarrow 2\text{MnO}_4^{-} + \text{MnO}_2 + 2\text{H}_2\text{O}$

[2]

(c) An **alkaline** hydrogen-oxygen fuel cell is set up.

The overall equation for the cell reaction is shown below.



Redox system **2** in **Table 19.1** is the positive electrode of this cell.

(i) Write the half-equation at the negative electrode.

$\text{H}_2(\text{g}) + 2\text{OH}^{-}(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^{-}$

[1]

(ii) The cell potential is 1.23 V.

Calculate the electrode potential of the negative electrode.

$$E_{\text{cell}} = E(\text{positive}) - E(\text{negative})$$

$$E(\text{negative}) = 0.40 - 1.23$$

electrode potential = *...-0.83...* V [1]

(iii) State **one** important feature of a fuel cell that is different from a conventional storage cell.

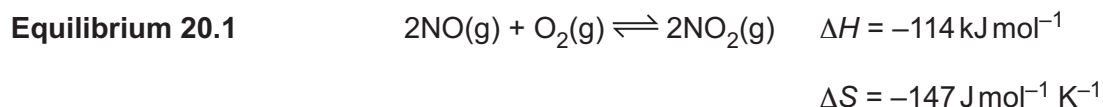
The fuel (H_2) reacts with oxygen to give electrical energy; it works

continuously as long as fuel and O_2 are supplied.

[1]

20 This question is about chemical equilibrium.

Nitrogen monoxide, NO, and oxygen, O₂, react to form nitrogen dioxide, NO₂, in the reversible reaction shown in **Equilibrium 20.1**.



(a) A dynamic equilibrium exists in a closed system.

State **one** other feature of a dynamic equilibrium.

The rate of the forward reaction equals the rate of the reverse reaction
(concentrations stay constant). [1]

(b) (i) Show that the formation of NO₂ in **Equilibrium 20.1** is feasible at 25 °C.

$$T = 25 + 273 = 298 \text{ K}; \Delta S = -147 \text{ J mol}^{-1} \text{ K}^{-1} = -0.147 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = -114 - (298 \times -0.147)$$

$$\Delta G = -114 + 43.8 = -70.2 \text{ kJ mol}^{-1}$$

$\Delta G < 0$ (negative), so the formation of NO₂ is feasible at 25 °C.

[2]

(ii) Determine the maximum temperature, in K, for feasibility.

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

Feasible when $\Delta G \leq 0$; at the maximum temperature $\Delta G = 0$,

$$\text{so } T = \Delta H \div \Delta S = -114 \div -0.147 = 775.5 \text{ K} = 776 \text{ K (3 s.f.)}$$

maximum temperature = ...776..... K [1]

- (c) A chemist investigates the equilibrium shown in **Equilibrium 20.1**.

The chemist mixes together 1.60 mol of NO(g) and 1.50 mol of O₂(g) in a container and the mixture is allowed to reach equilibrium.

At equilibrium:

- 75% of the NO(g) has been converted to NO₂(g)
- the total pressure is 1.21 MPa.

- (i) Calculate K_p , in MPa⁻¹, for **Equilibrium 20.1**.

Give your answer to **3** significant figures.

$$n(\text{NO}_2) = 0.75 \times 1.60 = 1.20 \text{ mol}; \quad n(\text{NO}) = 1.60 - 1.20 = 0.40 \text{ mol}$$

$$n(\text{O}_2) = 1.50 - 1.20 \div 2 = 0.90 \text{ mol}; \quad \text{total} = 0.40 + 0.90 + 1.20 = 2.50 \text{ mol}$$

$$p(\text{NO}) = 0.40/2.50 \times 1.21 = 0.1936 \text{ MPa}; \quad p(\text{O}_2) = 0.90/2.50 \times 1.21 = 0.4356 \text{ MPa}$$

$$p(\text{NO}_2) = 1.20/2.50 \times 1.21 = 0.5808 \text{ MPa}$$

$$K_p = p(\text{NO}_2)^2 \div (p(\text{NO})^2 \times p(\text{O}_2)) = 0.5808^2 \div (0.1936^2 \times 0.4356)$$

$$K_p = 0.3373 \div 0.01633 = 20.7 \text{ MPa}^{-1}$$

$$K_p = \dots\dots\dots 20.7 \dots\dots\dots \text{MPa}^{-1} \text{ [4]}$$

- (ii) The chemist then repeats the experiment three times. In each experiment, the chemist makes **one** change but uses the same initial amounts of NO and O₂.

Complete the table to show the predicted effect of each change compared with the original experiment.

Only use the words **greater**, **smaller** or **same**.

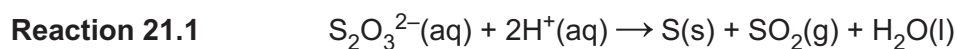
Change	K_p	Equilibrium amount of NO ₂ (g)	Initial rate
Temperature increase	<i>smaller</i>	<i>smaller</i>	<i>greater</i>
Pressure increase	<i>same</i>	<i>greater</i>	<i>greater</i>
Catalyst added	<i>same</i>	<i>same</i>	<i>greater</i>

[3]

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21 This question is about how the rate of reaction is affected by changes in conditions.

A student carries out two investigations using the reaction between aqueous thiosulfate ions, $\text{S}_2\text{O}_3^{2-}(\text{aq})$, and aqueous hydrogen ions, $\text{H}^+(\text{aq})$.



(a) In **Investigation 1**, the student determines how the rate of **Reaction 21.1** is affected by changes in concentration.

The results are shown in the table.

Experiment	$[\text{S}_2\text{O}_3^{2-}(\text{aq})]$ / mol dm^{-3}	$[\text{H}^+(\text{aq})]$ / mol dm^{-3}	initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.16	1.00	0.0120
2	0.08	1.00	0.0060
3	0.02	0.50	0.0015

From the results, the student concludes that the rate equation is
 $\text{rate} = k [\text{S}_2\text{O}_3^{2-}(\text{aq})]$

(i) Explain how the student's results support this rate equation.

Experiments 1 and 2: $[\text{H}^+]$ is constant and $[\text{S}_2\text{O}_3^{2-}]$ halves; the rate also halves (0.0120 to 0.0060), so the reaction is first order with respect to $\text{S}_2\text{O}_3^{2-}$.

Experiments 2 and 3: $[\text{S}_2\text{O}_3^{2-}]$ is quartered (0.08 to 0.02) and $[\text{H}^+]$ halves; the rate quarters (0.0060 to 0.0015), so $[\text{H}^+]$ has no effect: zero order with respect to H^+ .

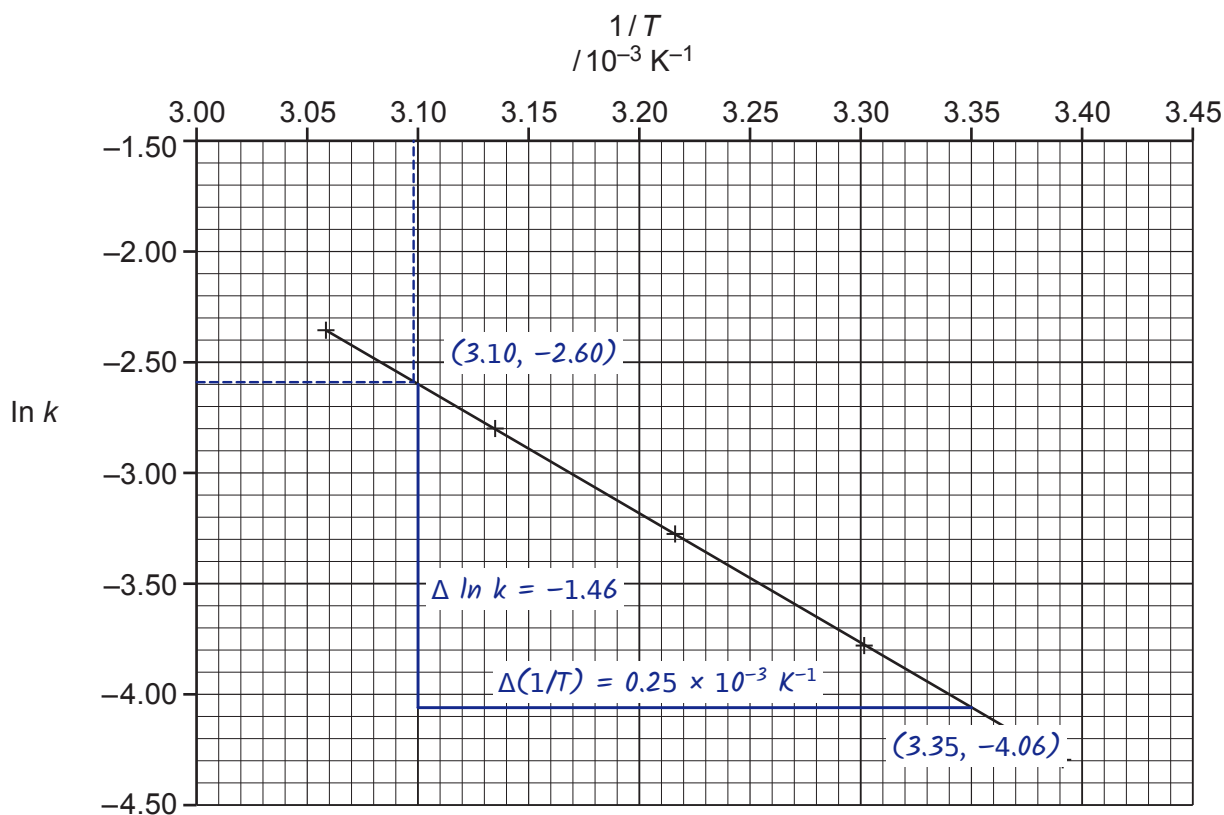
[2]

(ii) Predict a possible two-step mechanism for **Reaction 21.1**.
 The first step is the rate-determining step.



- (b) In **Investigation 2** the student determines the rate constant k of **Reaction 21.1** at different temperatures, T .

From the results, the student plots a graph of $\ln k$ against $1/T$ as shown below.



Graph 21.2

- (i) Calculate the activation energy, E_a , for **Reaction 21.1**, in kJ mol^{-1} .

Give your answer to **3** significant figures.

$$\text{gradient} = (-4.06 - (-2.60)) \div ((3.35 - 3.10) \times 10^{-3})$$

$$= -1.46 \div 2.5 \times 10^{-4} = -5840 \text{ K}$$

$$\text{gradient} = -E_a/R, \text{ so } E_a = 5840 \times 8.314 = 48\,554 \text{ J mol}^{-1}$$

$$E_a = 48.6 \text{ kJ mol}^{-1} \text{ (3 s.f.)}$$

$$E_a = \dots\dots\dots 48.6 \dots\dots\dots \text{ kJ mol}^{-1} \text{ [3]}$$

- (ii) From the graph the student estimates the value of $\ln A$ as -2.00 .
(A is the pre-exponential factor.)

Explain what mistake the student has made.

*$\ln A$ is the intercept when $1/T = 0$, but the graph's axis starts at $1/T$
 $= 3.00 \times 10^{-3} \text{ K}^{-1}$, so -2.00 is not the intercept at $1/T = 0$.*

..... [1]

- (iii) The student calculates the value of k in **Investigation 1** as 0.075 s^{-1} .

Using **Graph 21.2**, determine the temperature, in $^{\circ}\text{C}$, at which **Investigation 1** was carried out.

$$\ln k = \ln 0.075 = -2.59$$

$$\text{From the graph, at } \ln k = -2.59, 1/T = 3.10 \times 10^{-3} \text{ K}^{-1}$$

$$T = 1 \div (3.10 \times 10^{-3}) = 322.6 \text{ K}$$

$$\text{temperature} = 322.6 - 273 = 49.6 \text{ }^{\circ}\text{C}$$

temperature = ... *49.6* $^{\circ}\text{C}$ [2]

22 This question is about acids, bases and buffers.

(a) Sodium hydroxide, NaOH, is a strong base.

Calculate the pH of $0.140 \text{ mol dm}^{-3}$ NaOH(aq) at 298 K.

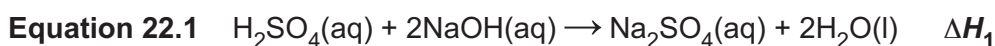
Give your answer to 2 decimal places.

$$[H^+] = K_w \div [OH^-] = 1.00 \times 10^{-14} \div 0.140 = 7.14 \times 10^{-14} \text{ mol dm}^{-3}$$

$$pH = -\log(7.14 \times 10^{-14}) = 13.15$$

$$pH = \dots\dots\dots 13.15 \dots\dots\dots [2]$$

(b) Sulfuric acid reacts with sodium hydroxide as shown in **Equation 22.1**.



This is a neutralisation reaction.

A student carries out an experiment to determine the enthalpy change ΔH_1 and uses this value to deduce the enthalpy change of neutralisation, $\Delta_{\text{neut}}H$.

The student measures out two solutions:

- 25.0 cm^3 of 1.60 mol dm^{-3} $\text{H}_2\text{SO}_4(\text{aq})$
- 55.0 cm^3 of 1.50 mol dm^{-3} $\text{NaOH}(\text{aq})$ (an excess).

The temperature of each solution is the same.

The student mixes the two solutions. The temperature increases by 13.0°C .

(i) Show that NaOH is in excess.

$$n(\text{H}_2\text{SO}_4) = 1.60 \times 25.0 \div 1000 = 0.0400 \text{ mol}$$

$$n(\text{NaOH}) = 1.50 \times 55.0 \div 1000 = 0.0825 \text{ mol}$$

$1 \text{ mol H}_2\text{SO}_4$ reacts with 2 mol NaOH , so 0.0400 mol needs 0.0800 mol NaOH

$0.0825 > 0.0800$, so NaOH is in excess.

[2]

- (ii) Calculate the enthalpy change, ΔH_1 , for **Equation 22.1**, and deduce the value for the enthalpy change of neutralisation, $\Delta_{\text{neut}}H$, in kJ mol^{-1} .

Assume that the densities of all solutions and the specific heat capacity, c , of the reaction mixture are the same as for water.

$$q = mc\Delta T = (25.0 + 55.0) \times 4.18 \times 13.0 = 4347.2 \text{ J} = 4.3472 \text{ kJ}$$

$$\Delta H_1 = -q \div n(\text{H}_2\text{SO}_4) = -4.3472 \div 0.0400 = -108.68 \text{ kJ mol}^{-1}$$

Equation 22.1 forms 2 mol H_2O , so

$$\Delta_{\text{neut}}H = \Delta H_1 \div 2 = -108.68 \div 2 = -54.34 \text{ kJ mol}^{-1}$$

enthalpy change, $\Delta H_1 = \dots\dots\dots -108.7 \dots\dots\dots \text{ kJ mol}^{-1}$

enthalpy change of neutralisation, $\Delta_{\text{neut}}H = \dots\dots\dots -54.3 \dots\dots\dots \text{ kJ mol}^{-1}$ [4]

- (iii) The student repeats the experiment using 50.0 cm^3 of 1.60 mol dm^{-3} H_2SO_4 and 110.0 cm^3 of 1.50 mol dm^{-3} NaOH .

Predict the increase in temperature.

Explain your reasoning.

The same, 13.0 °C.

Double the moles react, so double the energy is released, but it is

spread over double the volume (mass) of solution, so the temperature

rise is unchanged.

[2]

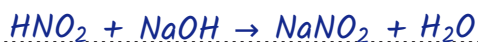
- (c)* Nitrous acid, HNO_2 , is a weak Brønsted–Lowry acid with a $\text{p}K_{\text{a}}$ value of 3.34 at room temperature.

HNO_2 can be prepared by reacting N_2O_3 with water.
 HNO_2 is the only product.

A chemist makes up a buffer solution by the following method.

- Step 1** The chemist weighs a sample of N_2O_3 .
 Water is then added to form 100 cm^3 of 0.500 mol dm^{-3} $\text{HNO}_2(\text{aq})$.
- Step 2** The chemist adds 100 cm^3 of 0.150 mol dm^{-3} $\text{NaOH}(\text{aq})$ to the 100 cm^3 solution of 0.500 mol dm^{-3} solution of $\text{HNO}_2(\text{aq})$.
 The resulting solution is made up to 1.00 dm^3 .

Explain why a buffer solution forms in **Step 2**. Determine the pH of this buffer solution and the mass of N_2O_3 that was used in **Step 1**.



$$n(\text{HNO}_2) = 0.500 \times 100 \div 1000 = 0.0500\text{ mol}; \quad n(\text{NaOH}) = 0.150 \times 100 \div 1000 = 0.0150\text{ mol}$$

HNO_2 is in excess, so it is only partially neutralised: 0.0150 mol NO_2^-

(NaNO_2) forms and $0.0500 - 0.0150 = 0.0350\text{ mol HNO}_2$ remains.

The solution contains both the weak acid HNO_2 and its conjugate base

NO_2^- , so it is a buffer: $\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$.

$$K_{\text{a}} = 10^{-3.34} = 4.57 \times 10^{-4}\text{ mol dm}^{-3}$$

Total volume 1.00 dm^3 , so $[\text{HNO}_2] = 0.0350$ and $[\text{NO}_2^-] = 0.0150\text{ mol dm}^{-3}$

$$[\text{H}^+] = K_{\text{a}} \times [\text{HNO}_2] \div [\text{NO}_2^-] = 4.57 \times 10^{-4} \times 0.0350 \div 0.0150 = 1.07 \times 10^{-3}\text{ mol dm}^{-3}$$

$$\text{pH} = -\log(1.07 \times 10^{-3}) = 2.97$$



$$n(\text{N}_2\text{O}_3) = 0.0500 \div 2 = 0.0250\text{ mol}; \quad M(\text{N}_2\text{O}_3) = 2(14.0) + 3(16.0) = 76.0\text{ g mol}^{-1}$$

$$\text{mass of N}_2\text{O}_3 = 0.0250 \times 76.0 = 1.90\text{ g}$$

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..... [6]

Additional answer space if required.

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END OF QUESTION PAPER

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