Surname	StemUp Model Solution	Centre Number	Candidate Number
Other Names			2

GCE A LEVEL

A410U10-1

S19-A410U10-1

TUESDAY, 4 JUNE 2019 – AFTERNOON

CHEMISTRY – A level component 1
Physical and Inorganic Chemistry

2 hours 30 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1. to 8.**	**15**	
Section B	**9.**	**22**	
	10.	**17**	
	11.	**15**	
	12.	**16**	
	13.	**23**	
	14.	**12**	
	Total	**120**	

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ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:
- calculator;
- **Data Booklet** supplied by WJEC.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **all** questions in the spaces provided.

Candidates are advised to allocate their time appropriately between **Section A (15 marks)** and **Section B (105 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 120.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The assessment of the quality of extended response (QER) will take place in **Q.9***(a)*(iii) and **Q.11***(b)*(ii).

If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

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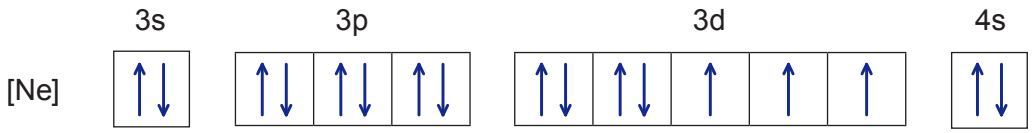
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SECTION A

Answer **all** *questions in the spaces provided.*

1. Complete the diagram below, using arrows to represent electrons, to show the electron arrangement for an atom of cobalt. [1]

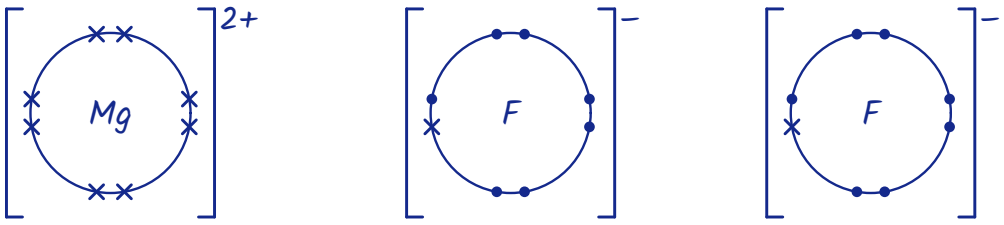


2. Complete the definition below.

Relative atomic mass is the average mass of an atom of an element compared to

$^{1}/_{12}$th of the mass of an atom of carbon-12 . [1]

3. Draw a dot-and-cross diagram to show the bonding of the compound magnesium fluoride. [2]



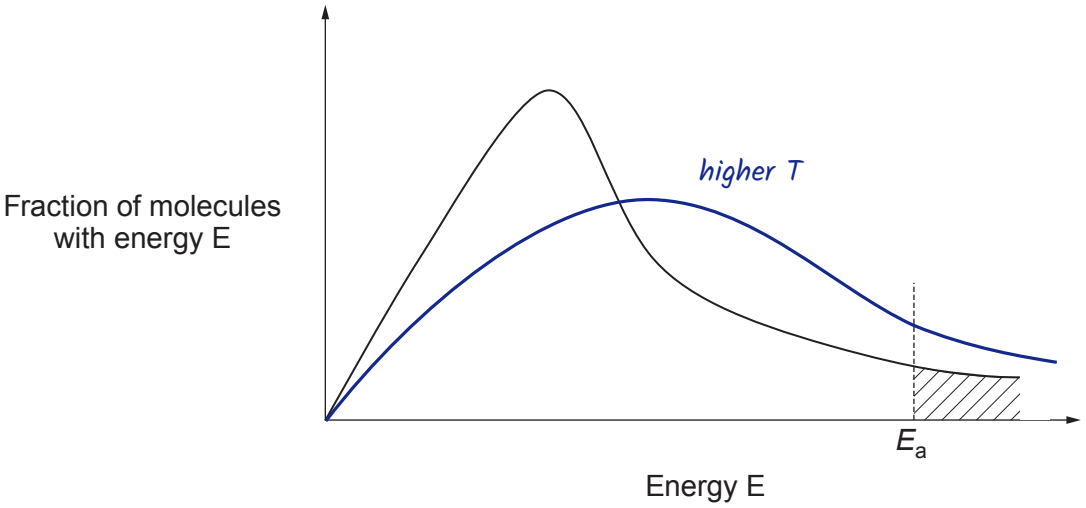
x = Mg electron · = F electron

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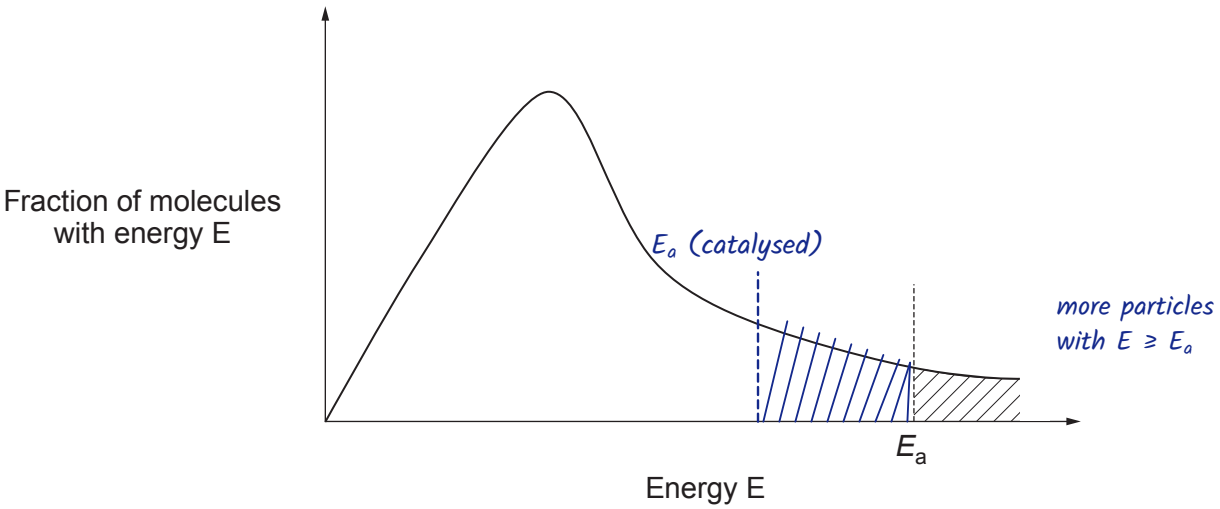
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4. *(a)* The graph below shows the energy distribution of particles at a temperature of 298 K.

Sketch the distribution at a higher temperature on the same axes. [1]



(b) Use the diagram below to show how a catalyst can affect the number of particles with sufficient energy to react. [1]



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5. Both iodine and diamond contain covalent bonding. Explain why their melting temperatures are very different. [2]

Iodine: to melt it only the weak van der Waals forces between I_2 molecules must be broken, so it has a low melting temperature.

Diamond: giant covalent, so strong covalent bonds between atoms must be broken, so a very high melting temperature.

6. When blue crystals of $CuSO_4.5H_2O$ are heated they form a white solid. Upon addition of water they return to their original blue colour.

Explain these observations. [2]

Copper(II) ions are only coloured when water ligands are bonded to them.

Heating removes the water ligands (white $CuSO_4$); adding water replaces the ligands, so it turns blue again.

7. A sample of the element boron contains 22.10 % boron-10 and 77.90 % boron-11.

Calculate the relative atomic mass of this sample, giving your answer to **four** significant figures. [2]

$A_r = ((22.10 \times 10) + (77.90 \times 11)) \div 100$

$= (221.0 + 856.9) \div 100 = 1077.9 \div 100$

A_r = 10.78

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8. Potassium manganate(VII) can be used to oxidise Fe^{2+} ions to Fe^{3+} ions in a redox titration. The following reaction occurs.

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

In an experiment 25.00 cm^3 portions of $Fe^{2+}(aq)$ were titrated against a standard acidified potassium manganate(VII) solution of concentration 0.0200 mol dm^{-3}.

The results were as follows.

	Titration 1	Titration 2	Titration 3	Titration 4
Volume of acidified potassium manganate(VII) solution added / cm^3	27.20	27.10	27.30	26.80

(a) Calculate the mean volume of acidified potassium manganate(VII) solution added. [1]

(27.20 + 27.10 + 27.30) ÷ 3 (titration 4 not concordant)

Mean volume = ... 27.20 ..... cm^3

(b) Calculate the number of moles of Fe^{2+} present in each 25.00 cm^3 portion. [2]

$n(MnO_4^-) = 27.20 \times 0.0200 \div 1000 = 5.44 \times 10^{-4}$ mol

$n(Fe^{2+}) = 5 \times 5.44 \times 10^{-4}$

Number of moles = ... 2.72×10^{-3} ..... mol

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SECTION B

Answer **all** *questions in the spaces provided.*

9. Many common acids donate one hydrogen ion during chemical reactions, however others can donate two or more hydrogen ions.

(a) Hydrochloric acid, HCl, and ethanoic acid, CH_3COOH, are examples of monobasic acids – these are acids that can donate only one hydrogen ion in chemical reactions.

Hydrochloric acid is a strong acid and ethanoic acid is a weak acid.

(i) Define pH. [1]

$pH = -\log_{10}[H^+]$

(ii) Write an expression for the acid dissociation constant, K_a, for ethanoic acid. [1]

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

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(iii) A student makes the following statements:

- when the concentration of any monobasic acid is doubled, the concentration of H^+ ions is also doubled; this applies to both strong acids and weak acids
- each time the concentration of an acid is doubled, the pH value increases by 0.3

Is the student correct? Explain your answer.

You should refer to both statements and the difference(s) between strong acids and weak acids in your answer. [6 QER]

The student is only partly correct: statement 1 is true for strong acids but not weak acids, and statement 2 is wrong.

Strong acids (HCl) fully dissociate, not reversibly: $HCl \rightarrow H^+ + Cl^-$.

Weak acids (ethanoic acid) only partially dissociate, reversibly: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$.

Doubling the concentration of a strong acid doubles $[H^+]$ as all H^+ ions are released. Doubling a weak acid's concentration does not double $[H^+]$: $[H^+] = \sqrt{(K_a[HA])}$, so it rises by only about $\sqrt{2}$ (1.41), less than 2.

$pH = -\log[H^+]$, so when more H^+ is present the pH decreases, not increases.

Strong acid: doubling the concentration lowers the pH by log 2 = 0.30, e.g. 0.100 mol dm^{-3} HCl pH 1.00, 0.200 mol dm^{-3} HCl pH 0.70.

Weak acid: the pH decreases by less than 0.30 (about 0.15).

So the student is correct in part for strong acids but incorrect for weak acids, and the pH falls.

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(b) Sulfuric acid is a dibasic acid as it can donate up to two hydrogen ions during chemical reactions.

When a small amount of sodium hydroxide is present the following reaction can occur.

$$H_2SO_4(aq) + NaOH(aq) \longrightarrow NaHSO_4(aq) + H_2O(l)$$

When more sodium hydroxide is present the following reaction can occur.

$$NaHSO_4(aq) + NaOH(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l)$$

(i) The soluble salt $NaHSO_4$ can be prepared as a white solid using the first reaction above. Briefly outline how this preparation would be undertaken.

A detailed experimental procedure is not required. [4]

Titrate a known volume of sulfuric acid with sodium hydroxide solution using an indicator.

Record the volume of NaOH needed to reach the first end point (when the indicator changes colour).

Add the same volume of sodium hydroxide to a fresh sample of the same volume of sulfuric acid not containing indicator.

Evaporate the solution (partially, then leave to crystallise) to obtain the solid $NaHSO_4$.

(ii) The $NaHSO_4$ formed in this preparation is hydrated and has the formula $NaHSO_4.xH_2O$.

In an experiment a sample of $NaHSO_4.xH_2O$ was heated to constant mass. The sample lost 37.5 % of its mass.

Calculate the value of x in the formula $NaHSO_4.xH_2O$. [3]

$M_r(NaHSO_4) = 120.11$ and $M_r(H_2O) = 18.02$

$NaHSO_4 : H_2O = 62.5/120.11 : 37.5/18.02$

$= 0.520 : 2.08 = 1 : 4.00$

x = 4

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(iii) $NaHSO_4$ can also be formed by reaction of concentrated sulfuric acid with sodium halides such as sodium chloride, sodium bromide or sodium iodide.

When concentrated sulfuric acid is added to **one** of these halides several changes are observed, including a smell of rotten eggs.

Identify the halide used and explain why the smell is observed with this halide but not with the others. [2]

The halide is iodide (sodium iodide).

Iodide is a stronger reducing agent than chloride or bromide, so it can reduce the sulfuric acid (S from +6 to −2) to form H_2S, which smells of rotten eggs; Cl^- and Br^- are not strong enough reducing agents.

(c) Many reactions of acids produce hydrogen gas. When an electrical discharge is passed through this gas certain frequencies of energy are emitted.

(i) Explain why this energy is emitted. [2]

Electrons are excited to higher energy levels by absorbing energy equal to the difference between energy levels.

They then drop to lower energy levels, emitting light whose frequency corresponds only to the difference between the energy levels.

(ii) The first ionisation energy of hydrogen is 1316 kJ mol^{-1}.

Calculate the wavelength of the convergence limit of the Lyman series for hydrogen in nm. [3]

energy per atom = $1316 \times 1000 \div 6.02 \times 10^{23} = 2.186 \times 10^{-18}$ J

$f = E \div h = 2.186 \times 10^{-18} \div 6.63 \times 10^{-34} = 3.297 \times 10^{15}$ Hz

$\lambda = c \div f = 3.00 \times 10^{8} \div 3.297 \times 10^{15} = 9.10 \times 10^{-8}$ m

Wavelength = 91.0 nm

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10. The green mineral atacamite contains three different ions, $M_a(OH)_bX_c$. It is insoluble in water but can form a solution when added to acid.

A student planned to analyse a sample of atacamite using the following method.

STEP 1: Add 1.00 g of atacamite to 150 cm^3 of strong acid of concentration 0.100 mol dm^{-3}, and then make this up to exactly 250 cm^3 with more of the same acid.

STEP 2: Take exactly 25.0 cm^3 of the solution from step 1 and add excess silver nitrate solution. If any precipitate forms, filter it off and dry completely. Record its colour and the mass formed.

STEP 3: Take exactly 25.0 cm^3 of the solution from step 1 and add excess barium chloride solution. If any precipitate forms, filter it off and dry completely. Record its colour and the mass formed.

STEP 4: Take exactly 25.0 cm^3 of the solution from step 1 and add excess sodium hydroxide solution. If any precipitate forms, filter it off and dry completely. Record its colour and the mass formed.

STEP 5: To find the amount of acid remaining in the solution, use a pH probe to find the precise pH of the solution prepared in step 1.

(a) The student had to select an appropriate strong acid from the common laboratory reagents.

Suggest an appropriate acid to use. Explain your choice. [2]

Nitric acid, because all nitrates are soluble, so its anion will not cause a precipitate in steps 2 and 3.

HCl cannot be used as it reacts with $AgNO_3$, and H_2SO_4 cannot be used as it reacts with $BaCl_2$.

(b) In step 2 a white precipitate of mass 0.0672 g was produced.

State which ion this step identifies and calculate the number of moles of this ion present in the original 250 cm^3 of solution. [3]

Ion chloride (Cl^-)

moles AgCl in 25.0 cm^3 = 0.0672 ÷ 143.5 = 4.68×10^{-4} mol

moles Cl^- in 250 cm^3 = $4.68 \times 10^{-4} \times 10$

Number of moles = 4.68×10^{-3} mol

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(c) After completing step 2, the student decides that he does not need to carry out step 3.

Is he correct? Give a reason for your answer. [2]

Yes, he is correct. Two of the three ions (OH^- and Cl^-) are already identified as anions, so there cannot be another anion such as sulfate; the remaining ion must be a cation.

(d) A pale blue precipitate is formed in step 4.

(i) Give the **formula** of the **ion** identified from this observation. [1]

Cu^{2+}

(ii) When the student heats the precipitate to ensure it is dry, a colour change is seen with some of the solid turning black but most of it remaining blue. He did not record a mass for the sample.

Suggest why he would not have been able to use the mass of the solid to calculate the number of moles of the ion in the original compound. [1]

The sample is impure / not homogeneous: it is a mixture of $Cu(OH)_2$ and black CuO, so the mass is not of a single compound.

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(e) In step 5, the pH of a 25.0 cm^3 portion of the remaining solution was found to be 1.36.

(i) Calculate the number of moles of acid remaining in 25.0 cm^3 of the solution. [2]

$[H^+] = 10^{-1.36} = 0.04365$ mol dm^{-3}

moles = $0.04365 \times 25.0 \div 1000$

Number of moles = 1.091×10^{-3} mol

(ii) Calculate the number of moles of hydroxide ion present in the original 1.00 g of atacamite. [3]

acid remaining in 250 cm^3 = $1.091 \times 10^{-3} \times 10 = 1.091 \times 10^{-2}$ mol

original acid = $250 \times 0.100 \div 1000 = 2.50 \times 10^{-2}$ mol

moles OH^- = $2.50 \times 10^{-2} - 1.091 \times 10^{-2}$

Number of moles = 1.41×10^{-2} mol

(f) Deduce the formula of atacamite. [3]

$OH^- : Cl^- = 1.41 \times 10^{-2} : 4.68 \times 10^{-3} = 3 : 1$

Cu^{2+} balances the charges: $2\ Cu^{2+} = 3\ OH^- + 1\ Cl^-$

Formula of atacamite $Cu_2(OH)_3Cl$

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11. *(a)* Selenium is an element in the p-block of the Periodic Table.

What information regarding the electronic structure of the selenium atom can be deduced from this statement? [1]

Its outer (highest energy) electrons are in a p-orbital (p sub-shell).

(b) The illustration below gives some information about the elements surrounding selenium in the Periodic Table.

S
Sulfur
electronegativity = 2.58
boiling temperature = 445
first ionisation energy = 1000
standard electrode potential for S(+6) → S(+4) = +0.16 V

As
Arsenic
electronegativity = 2.18
boiling temperature = 603
first ionisation energy = 947

Se
Selenium
electronegativity = ?
boiling temperature = 685
first ionisation energy = ?
standard electrode potential for Se(+6) → Se(+4) = ?

Br
Bromine
electronegativity = 2.96
boiling temperature = 60

Te
Tellurium
electronegativity = 2.10
boiling temperature = 990
standard electrode potential for Te(+6) → Te(+4) = +1.18 V

All ionisation energies are given in kJ mol^{-1} and all temperatures in °C

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(i) Both sulfur and selenium have molecules containing rings of eight atoms.

Explain the difference in their boiling temperatures. [2]

Selenium atoms have more electrons than sulfur atoms, so there are stronger (more) van der Waals forces between the Se_8 molecules, which need more energy to overcome, giving a higher boiling temperature.

(ii) Suggest values for the missing properties of selenium. Use the ideas you have studied to explain the values you have chosen. [6 QER]

Electronegativity of Se = 2.48 (between S 2.58 and As 2.18 / Te 2.10, and less than Br 2.96). Electronegativity increases across a period, as the nuclear charge increases with the same shielding, and decreases down a group, as the outer shell is further from the nucleus and more shielded.

First ionisation energy of Se = 940 kJ mol^{-1}, slightly lower than arsenic (947). It decreases down a group (Se is lower than S, 1000). Across a period the general trend is an increase, but there is a slight dip from Group 5 to Group 6: the outer p electrons in arsenic are all unpaired, but in selenium one p orbital contains a pair of electrons, and the extra electron-electron repulsion in selenium outweighs the slight increase in nuclear charge, so the electron is easier to remove.

Standard electrode potential for Se(+6) → Se(+4) = +0.67 V, between S (+0.16 V) and Te (+1.18 V). The stability of the +4 oxidation state increases down the group due to the inert pair effect, so the +6 state is more easily reduced to +4 and the electrode potential becomes more positive down the group as electrons are more easily gained.

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(c) One radioactive isotope of selenium is selenium-75. It can be used as a medical tracer to identify cartilaginous tumours.

(i) The half-life of selenium-75 is 120 days. Samples are provided that have eight times higher concentration of selenium-75 atoms than the minimum needed for use as a tracer.

Find the maximum time a sample can be stored before the concentration of selenium-75 becomes too low to use. [2]

number of half-lives: 8 → 4 → 2 → 1 = 3 half-lives

3 × 120 days

Time = 360 days

(ii) Selenium-75 does not emit alpha particles when it decays.

Explain why this is important for its use as a medical tracer. [2]

Alpha particles are very (highly) ionising, so they would damage DNA / cause mutations and cancer in the patient's cells.

Alpha particles also could not be detected outside the body, as they are very poorly penetrating.

(d) Selenium dioxide, SeO_2, is a foul smelling solid, with a smell resembling rotting horseradish. It can be used to oxidise alkenes.

$$SeO_2 + C_3H_6 + H_2O \longrightarrow H_2SeO_2 + C_3H_6O$$

In an oxidation experiment, 2.70 g of C_3H_6 produced a yield of 62 % of C_3H_6O.

Calculate the mass of C_3H_6O formed. [2]

moles C_3H_6 = 2.70 ÷ 42.06 = 0.0642 mol

moles C_3H_6O = 0.0642 × 0.62

mass = 0.0642 × 0.62 × 58.06 = 2.31 g

Mass = 2.31 g

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12. Chlorine is one of the most widely used elements, and compounds containing chlorine atoms have a huge range of uses in the home and in industry.

(a) Give **one** large scale use of the **element** chlorine. [1]

Treatment (chlorination) of water supplies to kill bacteria.

(b) Chlorine reacts with hot concentrated sodium hydroxide solution to form two chlorine-containing products. Write the equation for this reaction. [1]

$3Cl_2 + 6NaOH \rightarrow NaClO_3 + 5NaCl + 3H_2O$

(c) Chlorine can be used to produce bromine from the bromide ions present in seawater. An excess of chlorine is usually used in this process.

In one experiment, a volume of 2.00 dm^3 of chlorine gas was bubbled into seawater at 298 K under 1 atm pressure. A mass of 9.4 g of bromine was produced.

Calculate the percentage of chlorine that remains unreacted at the end of the experiment, giving your answer to an **appropriate** number of significant figures. [3]

moles Cl_2 = 2.00 ÷ 24.5 = 0.0816 mol

moles Br_2 = 9.4 ÷ 159.8 = 0.0588 mol = moles Cl_2 reacted

$(Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2)$

% unreacted = 100 − (0.0588 × 100 ÷ 0.0816) = 100 − 72.1

Percentage of chlorine unreacted = 28 %

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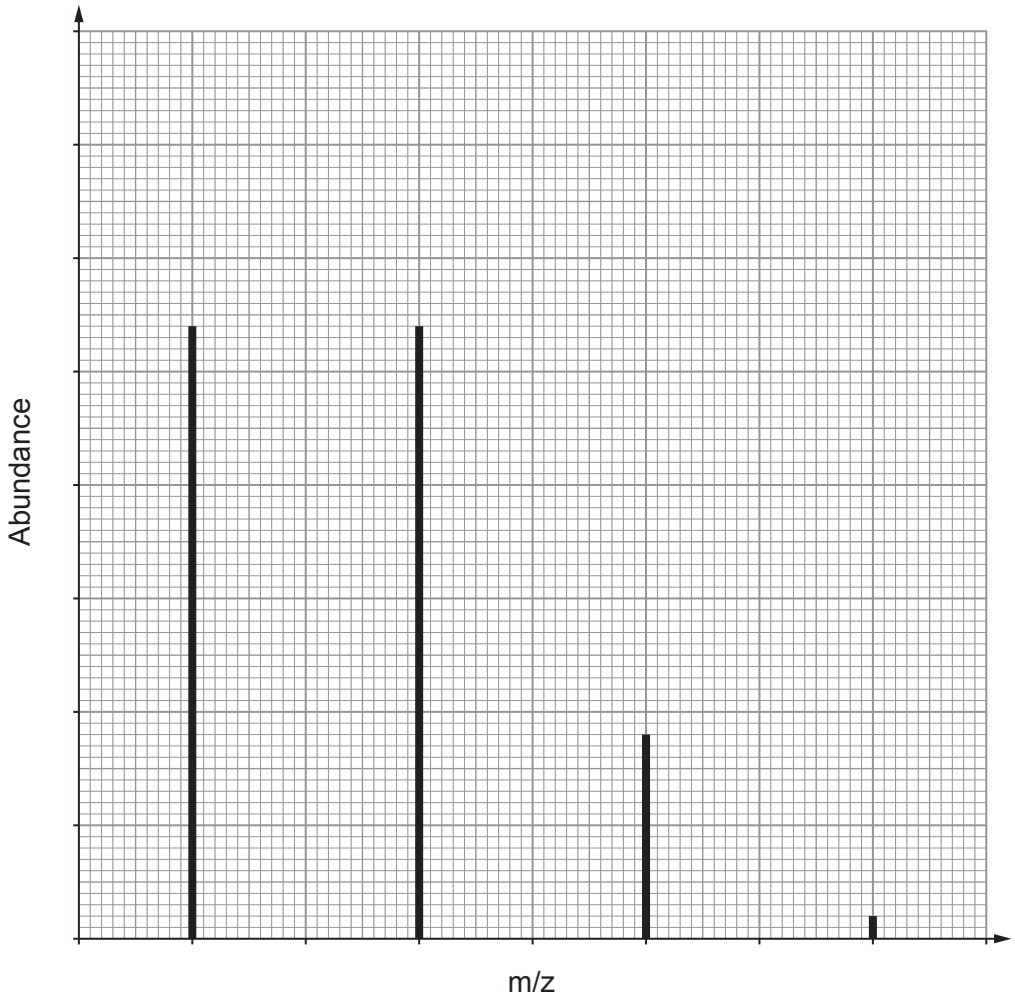
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(d) Chlorine-containing compounds can be studied using mass spectrometry.

(i) Explain how ions are formed and separated in the mass spectrometer. [2]

Ions are formed by bombarding the sample with high energy electrons from an electron gun, knocking out an electron. They are deflected by a magnetic field (electromagnet) according to their mass and charge (m/z).

(ii) The diagram below shows **part** of the mass spectrum of a chlorine-containing compound. There are no other significant peaks near this group of peaks and adjacent peaks are two atomic mass units apart.



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I. State how many chlorine atoms are present in these ions, giving a reason for your answer. [2]

Three chlorine atoms.

There are 4 peaks, each 2 apart: three Cl atoms give 4 possible isotope combinations (35,35,35 to 37,37,37), the heaviest and lightest differing by 6.

II. The height of the first peak is 54 and the height of the final peak is 2.

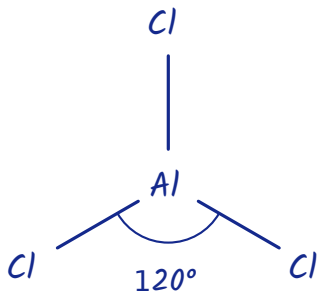
Explain the ratio of these peak heights. [2]

The ratio of isotopes is three ^{35}Cl to one ^{37}Cl.

With three chlorines, the chance of all ^{35}Cl : all ^{37}Cl = 3 × 3 × 3 : 1 × 1 × 1 = 27 : 1, which is 54 : 2.

(e) Chlorine can form many compounds of general formula AB_3, for example $AlCl_3$ and ClF_3.

(i) Draw the shape of the $AlCl_3$ molecule, giving its bond angle(s). [1]



trigonal planar, bond angles 120°

(ii) Explain why the molecule $AlCl_3$ often forms dimers. [2]

The aluminium atom is electron deficient (only 6 outer electrons) and the chlorine atoms have lone pairs, so a Cl lone pair forms a coordinate (dative) bond to Al in another $AlCl_3$, removing the electron deficiency.

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(iii) Use the principles of valence shell electron pair repulsion theory to explain why the shape of ClF_3 is not the same as that of BF_3.

You do not need to identify the shape of the ClF_3 molecule. [2]

ClF_3 has five pairs of outer electrons (3 bonding and two lone pairs) but BF_3 has three pairs (no lone pairs). Electron pairs repel as far apart as possible and lone pairs repel more than bonded pairs, so ClF_3 is based on a trigonal bipyramid, not trigonal planar.

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13. Ammonia, NH_3, and hydrazine, NH_2NH_2, are both compounds containing only nitrogen and hydrogen.

(a) The production of ammonia in the Haber process uses nitrogen and hydrogen gases as starting materials, a pressure of 200 atm and a temperature of 400 °C. The reaction occurring is shown below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -94\,kJ\,mol^{-1}$$

(i) Explain fully why a pressure of 200 atm is used for this reaction. [3]

Fewer gas molecules on the product side (2 vs 4), so higher pressure shifts the equilibrium right, giving more ammonia. Higher pressure also gives a greater rate of formation. Higher pressures need more expensive equipment and more energy, and are a greater safety risk.

(ii) The enthalpy change value given above is not the standard enthalpy change of formation for ammonia. Give **one** reason why this is not the standard enthalpy change of formation. [1]

It is not under standard conditions (400 °C and 200 atm), and it produces 2 moles of ammonia, not one.

(iii) Write an expression for the equilibrium constant, K_c, for this reaction. [1]

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

(iv) State the effect (if any) of increasing temperature on the value of K_c. Give a reason for your answer. [2]

K_c decreases. The forward reaction is exothermic, so increasing the temperature shifts the equilibrium in the endothermic direction (to the left), decreasing the amount of products.

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(v) A mixture of nitrogen and hydrogen has an initial concentration of 0.020 mol dm^{-3} of each gas. The mixture is allowed to come to equilibrium in a fixed volume.

In the equilibrium mixture 20 % of the nitrogen gas had been converted into ammonia. Calculate the value of K_c under these conditions. [3]

at equilibrium: $[N_2] = 0.020 \times 0.80 = 0.016$ mol dm^{-3}

$[H_2] = 0.020 - 3(0.004) = 0.008$ mol dm^{-3}, $[NH_3] = 2(0.004) = 0.008$

$K_c = 0.008^2 \div (0.016 \times 0.008^3)$

$= 6.4 \times 10^{-5} \div 8.192 \times 10^{-9}$

K_c = 7813 mol^{-2} dm^6

(b) The standard enthalpy change of formation for ammonia is −46 kJ mol^{-1} and for hydrazine it is +51 kJ mol^{-1}.

(i) State what information these values provide about the stability of these molecules. [1]

Ammonia is stable with respect to its elements, whereas hydrazine is unstable relative to its elements.

(ii) One method of producing hydrazine is to oxidise ammonia using an appropriate oxidising agent, such as hydrogen peroxide.

$2NH_3(g) + H_2O_2(l) \longrightarrow NH_2NH_2(l) + 2H_2O(l)$ $\quad \Delta H^\theta = -241$ kJ mol^{-1}

Substance	Standard enthalpy change of formation, $\Delta_f H^\theta$ / kJ mol^{-1}	Standard entropy, S^θ / J K^{-1} mol^{-1}
$NH_3(g)$	−46	193
$NH_2NH_2(l)$	+51	122
$H_2O_2(l)$		102
$H_2O(l)$	−286	70

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I. Calculate the standard enthalpy change of formation of hydrogen peroxide, H_2O_2. [2]

$\Delta H = \Sigma\Delta_f H(\text{products}) - \Sigma\Delta_f H(\text{reactants})$

$-241 = [51 + 2(-286)] - [2(-46) + \Delta_f H(H_2O_2)]$

$\Delta_f H(H_2O_2) = 51 - 572 + 92 + 241$

$\Delta_f H^\theta$ = −188 kJ mol^{-1}

II. Calculate the temperature at which the value of ΔG^θ is equal to zero. [3]

$\Delta S = [122 + 2(70)] - [2(193) + 102] = -226$ J K^{-1} mol^{-1}

$\Delta G = 0$ when $T = \Delta H \div \Delta S$

$T = -241\,000 \div -226$

T = 1066 K

III. A student states that the temperature calculated in part II is the minimum temperature required for the reaction to occur. Is the student correct? Give a reason for your answer. [2]

No, the student is not correct. ΔG must be negative for the reaction to occur; since ΔH and ΔS are both negative, $\Delta G = \Delta H - T\Delta S$ becomes positive above 1066 K, so this is the maximum temperature, not the minimum.

(iii) An alternative route for producing hydrazine starts with the molecule urea, which is produced in biological systems.

$$(NH_2)_2CO + NaOCl + 2NaOH \longrightarrow N_2H_4 + H_2O + NaCl + Na_2CO_3$$

Give **one** disadvantage of this route over the production of hydrazine from ammonia. [1]

The route produces more waste materials ($NaCl$, Na_2CO_3), so it has a lower atom economy.

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(iv) Hydrazine can undergo both oxidation and reduction reactions. Electrochemical potentials for both processes are included in the table below.

	Standard electrode potential, E^{θ} / V
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	+1.82
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$N_2H_4(aq) + 4H_2O(l) + 2e^- \rightleftharpoons 2NH_4^+(aq) + 4OH^-(aq)$	+0.11
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26
$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$	–0.42
$N_2(g) + 4H_2O(l) + 4e^- \rightleftharpoons N_2H_4(aq) + 4OH^-(aq)$	–1.15

I. Suggest whether addition of sodium hydroxide to a hydrazine solution will favour its use as a reducing agent. Give a reason for your answer. [2]

Yes. Adding OH^- favours the reverse reaction of the N_2/N_2H_4 half-equation (oxidation of hydrazine to N_2) to remove the OH^-, so it makes hydrazine a stronger reducing agent.

II. Identify which of these four M^{3+} ions (if any) can be reduced by hydrazine under standard conditions. Give a reason for your answer. [2]

All four (Co^{3+}, Fe^{3+}, V^{3+} and Cr^{3+}) can be reduced. The electrode potential for hydrazine acting as a reducing agent (–1.15 V) is more negative than the electrode potentials for all four metal ions.

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14. It is possible to study the concentration dependence of rate by finding how the rate of a reaction changes over time. This is because the concentrations of the reactants change over time.

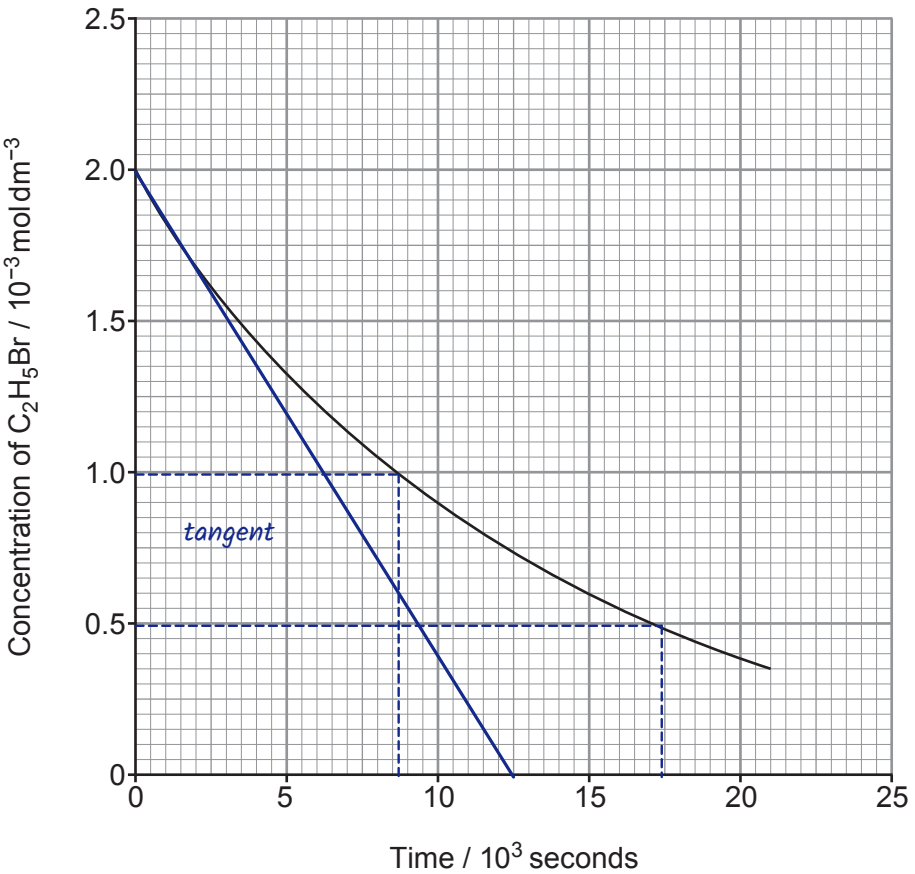
The reaction below occurs in non-aqueous solution in the presence of a small amount of water.

$$C_2H_5Br + OH^- + H_2O \longrightarrow C_2H_5OH + Br^- + H_2O$$

Three students carried out experiments to find how the concentration of each reactant affects the rate. Each one changed the concentration of a different reactant. They used the initial concentrations shown below and an automated sampling device to take measurements every 10 minutes for 6 hours.

	Initial concentration of each reactant / mol dm^{-3}		
	$[C_2H_5Br]$	$[OH^-]$	$[H_2O]$
George's experiment: Finding the effect of $[C_2H_5Br]$ on rate	2.00×10^{-3}	2.00	2.00
Hannah's experiment: Finding the effect of $[H_2O]$ on rate	2.00	2.00	2.00×10^{-3}
Jamal's experiment: Finding the effect of $[OH^-]$ on rate	2.00	2.00×10^{-3}	2.00

(a) The results obtained in George's experiment are shown on the graph below.



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(i) Calculate the initial rate for the reaction, stating its unit. [3]

gradient of tangent at $t = 0$: $2.00 \times 10^{-3} \div 12.5 \times 10^{3}$

rate = 1.60×10^{-7} mol dm^{-3} s^{-1}

Initial rate = 1.60×10^{-7}

Unit mol dm^{-3} s^{-1}

(ii) Use the graph to show that the reaction is first order with respect to C_2H_5Br. [2]

Half-life 2.00 to 1.00 is 8700 s; 1.00 to 0.50 is 17 400 − 8700 = 8700 s.

Constant half-life (8700 s), so first order with respect to C_2H_5Br.

(b) Suggest why this method uses much lower concentrations of the reactants being studied than those of the other reactants involved. [1]

So that changes in the concentrations of the other reactants are negligible and do not affect the rate.

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(c) Hannah finds that the concentration of water does not change during her experiment.

(i) Give a reason why the concentration of water does not change. [1]

One molecule of water is used but one is produced, so there is no change in the number of water molecules.

(ii) The order of the reaction with respect to water is zero. Suggest how Hannah could confirm this. [1]

Repeat the experiment with a different concentration of water, keeping all the other concentrations the same; the rate (graph) should be unchanged.

(d) Jamal carried out his experiment at a slightly different temperature from George.

He found that the reaction is first order with respect to hydroxide ions. The final rate equation is therefore as follows.

$$\text{rate} = k[C_2H_5Br][OH^-]$$

The value of the rate constant is 4.07×10^{-5}.

(i) Give the unit of the rate constant. [1]

$mol^{-1}\ dm^3\ s^{-1}$

(ii) The activation energy for this reaction is $89.5\,kJ\,mol^{-1}$ and its frequency factor, A, has a value of 4.30×10^{11}.

Calculate the temperature used for Jamal's experiment.

You **must** show your working. [3]

$E_a = 89\,500\ J\ mol^{-1}$; $k = Ae^{-Ea/RT}$ so $T = -E_a \div [R \ln(k/A)]$

$\ln(4.07 \times 10^{-5} \div 4.30 \times 10^{11}) = \ln(9.465 \times 10^{-17}) = -36.90$

$T = -89\,500 \div (8.31 \times -36.90)$

Temperature = *292* K

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