



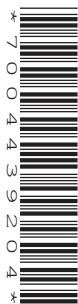
Oxford Cambridge and RSA

AS Level Chemistry B (Salters)

H033/02 Chemistry in depth

Friday 25 May 2018 – Morning

Time allowed: 1 hour 30 minutes



You must have:

- the Data Sheet for Chemistry B (Salters)
(sent with general stationery)

You may use:

- a scientific calculator



First name										
Last name	StemUp Model Solution									
Centre number						Candidate number				

INSTRUCTIONS

- Use black ink. HB pencil may be used for graphs and diagrams only.
- Complete the boxes above with your name, centre number and candidate number.
- Answer **all** the questions.
- Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.
- Do **not** write in the barcodes.

INFORMATION

- The total mark for this paper is **70**.
- The marks for each question are shown in brackets [].
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **16** pages.

Answer **all** the questions.

- 1 Chemists have arranged the elements into a Periodic Table which allows them to make predictions about the behaviour of the elements and their compounds.

(a) Many properties, such as first ionisation enthalpy, show a gradual change across a **period**.

- (i) Write an equation representing the first ionisation enthalpy of sodium.

Show state symbols.



[2]

- (ii) Explain the **general** increase in first ionisation enthalpy across Period 3 (sodium to argon).

...Across the period the electrons are removed from the same shell, so the
...shielding stays about the same.
...The nuclear charge (number of protons) increases, so the outer electron is
...more strongly attracted and held more tightly. [2]

(b) Elements in a **group** often show similar properties.

The Group 2 element calcium reacts with water to produce a solution of calcium hydroxide and bubbles of hydrogen gas.

Predict a chemical equation for the reaction of radium, Ra, with water.
Include state symbols.



[1]

- (c) Mendeleev first proposed his Periodic Table in 1869. He left gaps for elements which he predicted would be discovered later.

One such element was in a gap immediately below silicon and he called it 'eka-silicon'.

Predict the formula of the oxide of eka-silicon, giving a reason.
Use **X** as the symbol for eka-silicon.

Formula XO_2

Reason $\text{X (like Si) has 4 electrons in its outer shell, so it}$
...has an oxidation state of +4, like Si in SiO_2 . [2]

(d)* A student is asked to identify a solid Group 2 compound, **A**.

The student carries out the following tests.

1. A very small amount of the solid is added to 2 cm depth of water in a test tube. Compound **A** partly dissolves. A couple of drops of universal indicator are added which show a pH of 11.
2. The student carries out a titration to calculate the M_r of the compound and hence identify the Group 2 element present.

0.092 g of compound **A** is dissolved in water and made up to 250 cm³. 25.0 cm³ samples of this solution are titrated with 0.0100 mol dm⁻³ hydrochloric acid giving a mean titre of 24.80 cm³.

Identify compound **A**, giving reasons in full for your choice and including a chemical equation for the reaction in the titration.

Test 1: A only partly dissolves, so it is sparingly soluble; this suggests the metal is near the top of Group 2. A is not a carbonate, because Group 2 carbonates are insoluble and would not give an alkaline solution. pH 11 shows an alkali, so A is an oxide or a hydroxide.

Equation: $X(OH)_2 + 2HCl \rightarrow XCl_2 + 2H_2O$ (or $XO + 2HCl \rightarrow XCl_2 + H_2O$)

$n(HCl) = 24.80/1000 \times 0.0100 = 2.48 \times 10^{-4} \text{ mol}$

$n(A) \text{ in } 25.0 \text{ cm}^3 = 2.48 \times 10^{-4} / 2 = 1.24 \times 10^{-4} \text{ mol}$

mass of A in 25.0 cm³ = $0.092 / 10 = 0.0092 \text{ g}$

$M_r(A) = 0.0092 / 1.24 \times 10^{-4} = 74.2$

If A is an oxide, $A_r(X) = 74.2 - 16.0 = 58.2$; no Group 2 metal. If A is a hydroxide, $A_r(X) = 74.2 - 2(17.0) = 40.2$, which is calcium (40.1).

So A is calcium hydroxide, $Ca(OH)_2$: $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$. This fits test 1, as $Ca(OH)_2$ is sparingly soluble and alkaline.

[6]

- (e) Calculate the volume of gas (in cm^3 at RTP) produced when 0.493 g of barium carbonate, BaCO_3 , is reacted with an excess of hydrochloric acid. (M_r of $\text{BaCO}_3 = 197.2$)



$$n(\text{BaCO}_3) = 0.493 / 197.2 = 2.50 \times 10^{-3} \text{ mol} = n(\text{CO}_2)$$

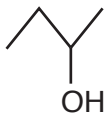
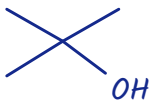
$$V = 2.50 \times 10^{-3} \times 24\,000 = 60.0 \text{ cm}^3$$

volume of gas = ...60.0..... cm^3 [1]

- 2 Bioethanol is a well-known biofuel. Biobutanol is another biofuel and can be used in some combustion engines. Biobutanol can be produced in the UK from sugar beet.

- (a) Butanol has the molecular formula, $C_4H_{10}O$. There are four structural isomers with this formula that contain the $-OH$ functional group.

Complete the table below to show **one** other structural isomer of $C_4H_{10}O$ that contains an $-OH$ group.

skeletal formula			
name	butan-1-ol	butan-2-ol	2-methylpropan-2-ol

[2]

- (b) Explain why the combustion of butan-1-ol is exothermic, using ideas about bond-breaking and bond-making.
You do not need to list the specific bonds broken and made.

Bond breaking is endothermic (energy is absorbed) and bond making is exothermic (energy is released).
In the combustion of butan-1-ol, more energy is released in making the bonds in the products (CO_2 and H_2O) than is absorbed in breaking the bonds in the reactants, so overall the reaction is exothermic.

[2]

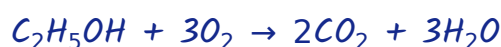
- (c) One disadvantage of butan-1-ol as a fuel is that it requires a higher oxygen to fuel ratio for complete combustion when compared to ethanol.

Write equations to show that butan-1-ol requires a higher oxygen to fuel ratio than ethanol for complete combustion.

combustion of butan-1-ol:



combustion of ethanol:



(6 mol O_2 per mol butan-1-ol, but only 3 for ethanol)

[1]

- (d) In a simple laboratory experiment, the combustion of 1.00 g of a biofuel compound raised the temperature of 500 g of water by 16.0 °C.

Calculate a value for the enthalpy change of combustion of the biofuel compound.
(M_r of the biofuel compound = 214)

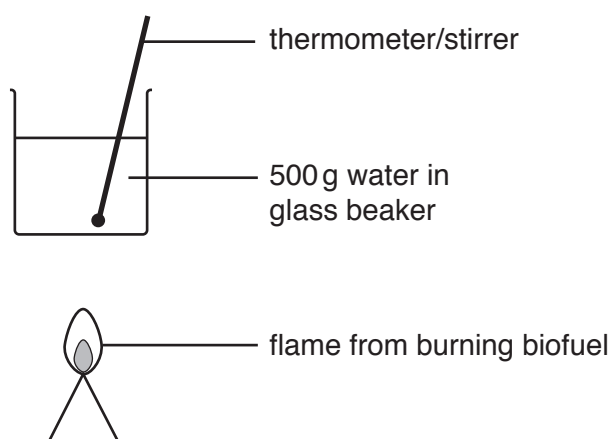
$$q = mc\Delta T = 500 \times 4.18 \times 16.0 = 33\,440\text{ J} = 33.44\text{ kJ}$$

$$n(\text{biofuel}) = 1.00 / 214 = 4.67 \times 10^{-3}\text{ mol}$$

$$\Delta_c H = -33.44 / 4.67 \times 10^{-3} = -7160\text{ kJ mol}^{-1}$$

$$\Delta_c H = \dots\dots\dots -7160 \dots\dots\dots \text{kJ mol}^{-1} \text{ [3]}$$

- (e) The laboratory set-up used to obtain the data in part (d) is shown below.



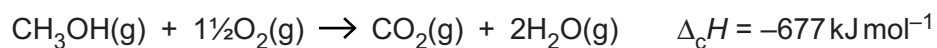
This set-up can be modified to improve the accuracy of the value for the enthalpy change.

Suggest and explain **one** simple modification that could improve the accuracy.

Use a copper (metal) can instead of the glass beaker, because copper is a better thermal conductor than glass, so more of the heat is transferred to the water. [1]

- (f) Another alcohol that is used in some fuels is methanol, CH₃OH.

An equation for the complete combustion of methanol is shown below.



Use this information and the data in the table below to calculate a value for the bond enthalpy of the C–O bond.

Bond	Bond enthalpy / kJ mol ⁻¹
C–H	+413
O=O	+498
O–H	+464
C=O	+805

$$\text{bonds broken: } 3(\text{C-H}) + (\text{C-O}) + (\text{O-H}) + 1\frac{1}{2}(\text{O=O})$$

$$= 3(413) + 464 + 1\frac{1}{2}(498) + (\text{C-O}) = 2450 + (\text{C-O})$$

$$\text{bonds made: } 2(\text{C=O}) + 4(\text{O-H}) = 2(805) + 4(464) = 3466$$

$$\Delta_c H = \Sigma(\text{broken}) - \Sigma(\text{made})$$

$$-677 = 2450 + (\text{C-O}) - 3466$$

$$(\text{C-O}) = -677 + 3466 - 2450 = +339 \text{ kJ mol}^{-1}$$

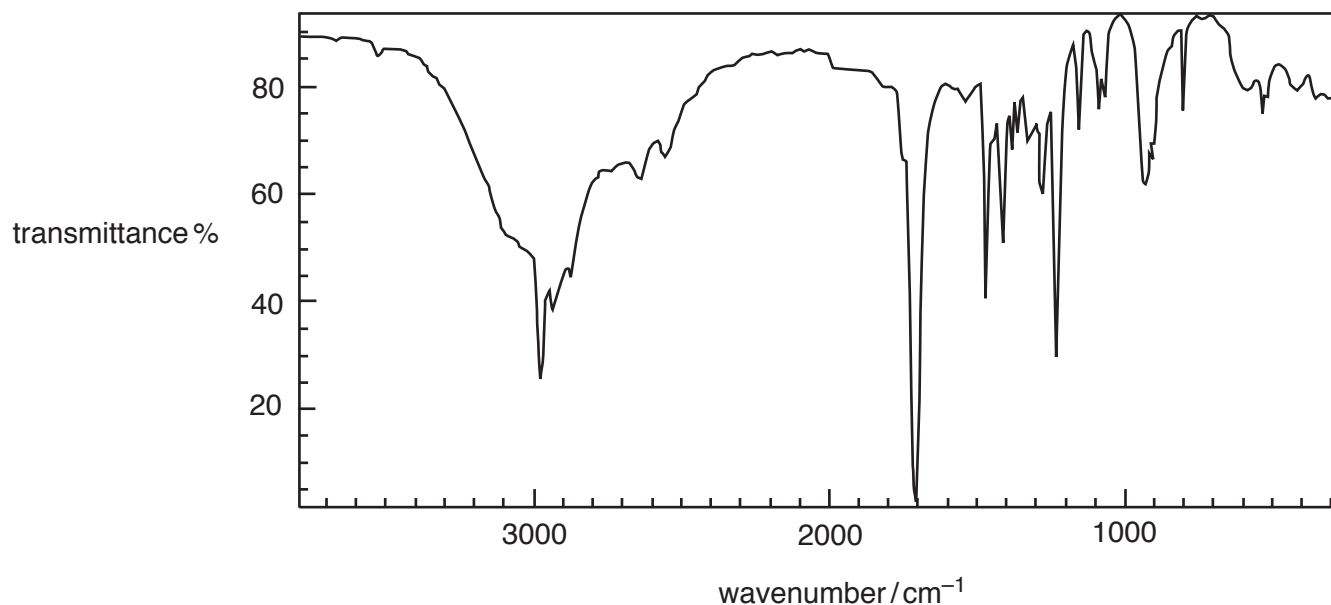
bond enthalpy of C–O bond = ...+339..... kJ mol⁻¹ [3]

(g)* Apart from being used in fuels, alcohols are also important in the preparation of other organic chemicals.

Alcohol **A**, $C_4H_{10}O$, is an isomer of butanol.

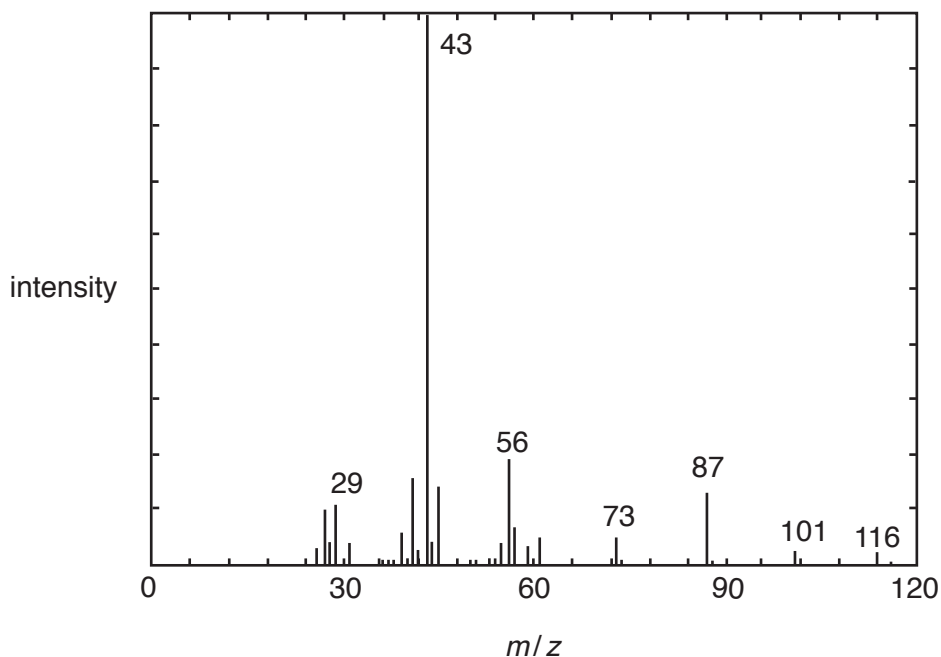
Alcohol **A** can be oxidised to compound **C** using acidified potassium dichromate(VI).

The infrared spectrum of compound **C** is shown below.



Alcohol **A** reacts with a carboxylic acid **D** to give compound **E**.

The mass spectrum of compound **E** is shown below.



Working shown on this page will not be marked

Using the information on page 8, determine the formulae of the **two** possible compounds that could be alcohol **A**. Determine the corresponding formulae for compounds **C** and **E**, and the formula of **D**.

Give full reasoning for all compounds.

The IR spectrum of C has a strong absorption at about 1710 cm^{-1} ($\text{C}=\text{O}$) and a very broad absorption from about 2500 to 3300 cm^{-1} , centred near 2980 cm^{-1} ($\text{O}-\text{H}$ in a carboxylic acid). So C is a carboxylic acid.

An alcohol oxidised by acidified dichromate(VI) to a carboxylic acid must be a primary alcohol, so A is either $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (butan-1-ol) or $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ (2-methylpropan-1-ol).

The corresponding C is $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ or $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$.

An alcohol reacts with a carboxylic acid to form an ester, so E is a butyl ester. The peak at the largest m/z , 116, is the molecular ion, so $M_r(\text{E}) = 116$. The butyl part, C_4H_9 , is 57, so the acid part is $116 - 57 = 59 = \text{CH}_3\text{COO}$. So D is ethanoic acid, CH_3COOH ; the peak at 43 (CH_3CO^+) supports this.

E is $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3\text{COOCH}_2\text{CH}(\text{CH}_3)\text{CH}_3$ ($\text{C}_6\text{H}_{12}\text{O}_2$, $M_r = 116$).

[6]

3 Bromomethane is a gas that is used as a fumigant to protect young plants against insects and rodents.

(a) It is possible to make bromomethane by reacting methane with bromine in the presence of light. This takes place by a radical chain reaction.

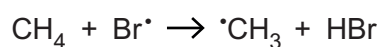
(i) Write an equation to show the effect of light on bromine in the initiation stage of this reaction.



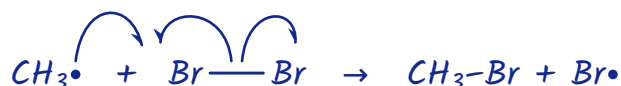
[1]

(ii) The initiation stage is followed by the propagation stage which involves two steps.

The equation for the **first** propagation step is shown below.



Write the mechanism for the **second** propagation step using 'half curly arrows'. Indicate radicals with dots as above.



[2]

(iii) Bromomethane can also be made by treating methanol with hydrogen bromide.

Is this method or the reaction of methane and bromine preferable?

Give a reason for your answer.

...Methanol and HBr: CH_3Br is the only organic product; with Br_2 further
...substitution occurs (CH_2Br_2 etc.)... [1]

- (b) A student predicts incorrectly that chloromethane will have a higher boiling point than bromomethane. The student's reason is that chlorine is more electronegative than bromine and thus the carbon to chlorine bond is more polar than the carbon to bromine bond. This will cause stronger permanent dipole-permanent dipole bonds.

Discuss the student's reasoning and give the correct chemistry where necessary.

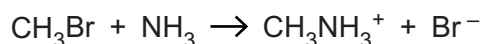
The student is correct that Cl is more electronegative than Br, so the C-Cl bond is more polar than the C-Br bond and pd-pd bonds in chloromethane are stronger.

However, bromomethane is a bigger molecule with more electrons than chloromethane, so it has stronger instantaneous dipole-induced dipole (id-id) bonds.

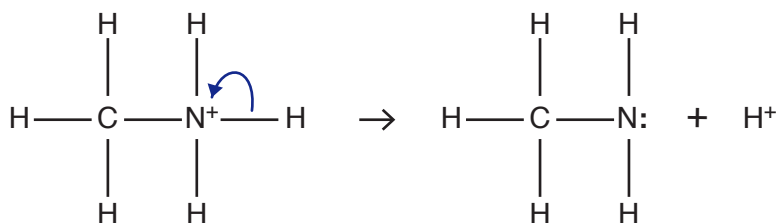
The increase in id-id bonds is greater than the decrease in pd-pd bonds, so bromomethane has the higher boiling point. [4]

- (c) Haloalkanes react with ammonia under suitable conditions.

- (i) The first step in the mechanism of the reaction of bromomethane with ammonia involves the following reaction.



Draw a 'curly arrow' to show the electron movement in the second step in the mechanism below.



[1]

- (ii) Name the mechanism for the reaction of bromomethane with ammonia.

nucleophilic substitution

[1]

- (iii) Name the functional group in the organic product of the reaction.

amine

[1]

- (d) A student investigates the rate of hydrolysis of haloalkanes.

Two test tubes, each containing aqueous silver nitrate and ethanol, are placed in a water bath at 60 °C. Five drops of each of chlorobutane and iodobutane are added separately to each of the two test tubes.

- (i) Describe what the student would see as the reactions progress that would show that iodobutane reacts faster.

A (yellow) precipitate (cloudiness) forms first, in the shortest time, with iodobutane and last with chlorobutane. [1]

- (ii) Suggest why ethanol is used in the mixture.

Ethanol is a solvent, so the haloalkane and the aqueous silver nitrate can mix. [1]

- (iii) Use the following data to explain whether bond enthalpy or bond polarity is the more important in determining the order of the rate of hydrolysis of haloalkanes.

Electronegativity Cl = 3.2 I = 2.7 C = 2.6

Bond enthalpy/kJ mol⁻¹ C–Cl = +346 C–I = +228

The C–Cl bond is the most polar, so on polarity alone chlorobutane would react fastest.

The C–I bond is the weakest (+228 kJ mol⁻¹). Iodobutane reacts fastest, so bond enthalpy is more important than bond polarity. [3]

- (e) When bromomethane, CH₃Br, gets into the Earth's atmosphere, a C–Br bond may be broken by ultraviolet radiation from the Sun. However, the ultraviolet radiation may not have high enough energy to break the bond.

Suggest what other effect it may have on the molecule.

It increases the electronic energy (excites the electrons in the molecule). [1]

- (f) The minimum frequency of radiation needed to break one C–Br bond is 7.14×10^{14} Hz.

Calculate the bond enthalpy of the C–Br bond, in kJ mol⁻¹.

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

$$\begin{aligned}
 E &= h\nu N_A = 6.63 \times 10^{-34} \times 7.14 \times 10^{14} \times 6.02 \times 10^{23} \\
 &= 2.85 \times 10^5 \text{ J mol}^{-1} \\
 &= 285 \text{ kJ mol}^{-1} \text{ (3 s.f.)}
 \end{aligned}$$

bond enthalpy = ...+285..... kJ mol⁻¹ [3]

(g) Ozone is present in both the troposphere (lower atmosphere) and the stratosphere (upper atmosphere).

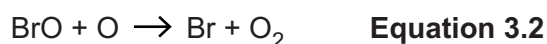
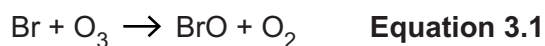
(i) The ozone percentage concentration in the stratosphere is 0.000021% by volume.

Calculate the concentration of ozone in ppm (parts per million).

$$\begin{aligned} 0.000021\% &= 0.000021 \text{ parts per } 100 \text{ parts} \\ &= 0.21 \text{ parts per } 1\,000\,000 \text{ parts} = 0.21 \text{ ppm} \end{aligned}$$

ozone concentration = ...0.21..... ppm [1]

(ii) The process by which Br reacts with ozone in the stratosphere is represented in the following equations.



Combine **equations 3.1** and **3.2** to produce the overall equation for the process.



[1]

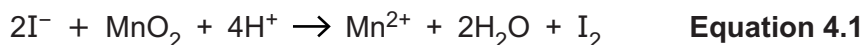
(iii) Explain how **equations 3.1** and **3.2** show that Br could be a catalyst for the breakdown of ozone.

.....Br is used up in equation 3.1 but reformed in equation 3.2, so it is
.....chemically unchanged and not used up overall..... [1]

(iv) Give **one** disadvantage of a build-up of **tropospheric** ozone.

.....It causes photochemical smog, which causes breathing problems..... [1]

- 4 Iodine can be extracted from the ash of burnt seaweed. The ash is washed with water. The washed ash is heated with manganese(IV) oxide, MnO_2 , and concentrated sulfuric acid, forming iodine.

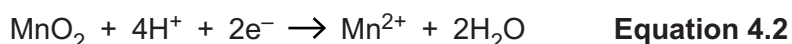


- (a) Complete the table below to show the oxidation states for manganese and iodine in the reaction shown in **equation 4.1**.

Element	Initial oxidation state	Final oxidation state
Mn	+4	+2
I	-1	0

[1]

- (b) The half-equation for the conversion of MnO_2 to Mn^{2+} ions is shown below.



Explain, in terms of electrons, why the manganese is said to be reduced.

It gains electrons. (MnO_2 gains 2e^- as Mn goes from +4 to +2). [1]

- (c) A student extracts iodine from seaweed ash in the laboratory. The student suspects that the water used to wash the ash contains a mixture of salts, including sodium chloride.

The student tests this water to see if it contains chloride ions by adding silver nitrate solution.

- (i) Give the result of the test for chloride ions.

A white precipitate forms. [1]

- (ii) Suggest why the student might not get this result.

*The concentration of chloride ions may be too low, so no precipitate forms;
or the water may contain iodide ions, which give a yellow precipitate.* [2]

- (d) Iodine and chlorine are both members of the halogen group.

- (i) Write the electron configuration for the highest energy sub-shell for an **iodide ion**.

5p^6 [1]

- (ii) A student carries out a displacement reaction to show that chlorine is more reactive than iodine.

Describe the experiment the student would do and the expected result.

*..Add..chlorine..water..to..potassium..iodide..solution..The..solution..turns..from.....
..colourless..to..brown..... [2]*

- (iii) Write an ionic equation for the reaction in (ii).



[1]

- (iv) Describe and explain, in terms of electrons, why chlorine is more reactive than iodine.

*..A..chlorine..atom..is..smaller..than..an..iodine..atom..(fewer..electron..shells),..so.....
..its..outer..shell..is..closer..to..the..nucleus..with..less..shielding.....
..So..the..electron..gained..to..form..the..halide..ion..is..attracted..and..held..more.....
..tightly..by..chlorine, and chlorine gains an electron more readily..... [2]*

- (e) The student collected 0.92 g of impure iodine, I_2 , and decided to determine its purity.

The student dissolved the impure iodine in potassium iodide solution.
This iodine solution was then titrated with sodium thiosulfate solution.
The equation for the reaction is shown below.



The titration required 28.40 cm³ of 0.200 mol dm⁻³ sodium thiosulfate solution.

Calculate the percentage purity of the iodine.

$$n(\text{S}_2\text{O}_3^{2-}) = 28.40/1000 \times 0.200 = 5.68 \times 10^{-3} \text{ mol}$$

$$n(\text{I}_2) = 5.68 \times 10^{-3} / 2 = 2.84 \times 10^{-3} \text{ mol}$$

$$\text{mass } \text{I}_2 = 2.84 \times 10^{-3} \times 253.8 = 0.721 \text{ g}$$

$$\text{purity} = 0.721 / 0.92 \times 100 = 78 \%$$

purity of iodine = ...78..... % [3]

END OF QUESTION PAPER

[illegible]

stemup.co.uk