

TEMASEK JUNIOR COLLEGE
2024 JC2 PRELIMINARY EXAMINATION
Higher 2



CANDIDATE
NAME

H2 MARK SCHEME

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INDEX
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Chemistry

9729/02

Paper 2 Structured Questions

21 August 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in bracket [] at the end of each question or part question.

For Examiner's Use		
Paper 1		/30
Paper 2	Q1	
	Q2	
	Q3	
	Q4	
	Q5	
	Total	/75
Paper 3		/80
TOTAL (%)		/100

This document consists of **23** printed pages and **1** blank page.

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

- 1 (a) Table 1.1 shows the successive ionisation energies of an element **A**.

Table 1.1

ionisation energies / kJ mol^{-1}	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	8 th	9 th	10 th
element A	945	1794	2735	4839	6056	11690	14180	17370	20550	23830

- (i) Explain why the successive ionisation energies of an element always increase. [1]

[1] As electrons are removed, **number of electrons decrease** while **nuclear charge remains the same**. Hence, there are **stronger electrostatic forces of attraction between the nucleus and the remaining electrons** and more energy is required for subsequent removal of electrons.

- (ii) Element **A** is in Period 4.

Using information from Table 1.1 and the *Data Booklet*, identify element **A**.

Explain your answer clearly. [2]

[1] There is a **significant increase** in the values of the **5th and 6th ionisation energies**. This means that the **6th electron is removed** from an **inner principal quantum / electron shell** which is **closer to the nucleus**, and hence experiences stronger electrostatic forces of attraction.

[1] This means that there are **5 valence electrons** in element **A**, which puts it in **Group 15, A is arsenic**.

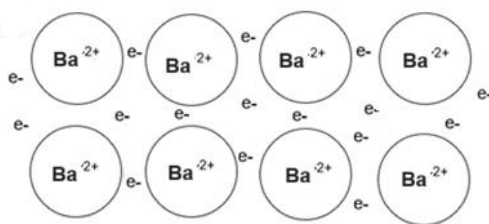
- (iii) State and explain how the first ionisation energy of element **A** will compare to that of the element to its right in the Periodic Table. [2]

[1] Element **A** will have a **higher** first ionisation energy as the electron to be removed from element **A** is **unpaired** ($4s^2 4p^3$).

[1] While the electron removed from the element to its right in the periodic table is **paired** ($4s^2 4p^4$). Less energy is required to remove this electron due to **inter-electronic repulsion between the paired electrons in the same orbital**.

ECF from (ii)

- (b) (i) With the aid of a labelled diagram, describe the structure and bonding of barium. [2]



[1]

[1] Ba^{2+} cations are arranged in a giant metallic structure held by strong electrostatic forces of attraction between the sea of delocalised electrons and the Ba^{2+} metal cations.

- (ii) Explain the trend in atomic radii down Group 2. [2]

Down the group,

[✓] number of protons increases, nuclear charge increases.

[✓] Number of electron shell increases

[✓] valence electrons are further away from the nucleus.

[✓] atomic radii increase.

2[✓] = [1]

- (iii) The density of magnesium and barium is 1.7 g cm^{-3} and 3.6 g cm^{-3} respectively. Explain why the density of barium is significantly greater than that of magnesium. [1]

[✓] Both atomic mass and atomic radius $\text{\textcircled{R}}$ of Ba atom are larger than Mg atom due to higher number of protons, neutrons and electrons in Ba.

Atomic volume (V) $\propto r^3$

Since density = mass/volume,

[✓] The increase in mass is more significant / greater than the increase in volume, hence the mass of Ba per unit volume is larger, therefore higher density.

2[✓] = [1]

- (iv) When magnesium is burned in air, a mixture of the ionic solids magnesium oxide and magnesium nitride, Mg_3N_2 , is formed. Adding water to Mg_3N_2 produces an alkaline gas and a white insoluble solid.

Suggest an equation for the reaction between Mg_3N_2 and water, and use it to calculate the mass of white insoluble solid that would be formed from 2.0g of Mg_3N_2 . [2]

[1] $\text{Mg}_3\text{N}_2 + 3\text{H}_2\text{O} \rightarrow 3\text{MgO} + 2\text{NH}_3$

OR $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$

M_r of $\text{Mg}_3\text{N}_2 = 100.9$, M_r of $\text{Mg}(\text{OH})_2 = 58.3$

Amt of $\text{Mg}(\text{OH})_2 = 3 \times (2/100.9) = 0.0595 \text{ mol}$

[1] Mass of $\text{Mg}(\text{OH})_2 = 0.0595 \times 58.3 = 3.47\text{g}$

(If the white solid is MgO : ans is 2.40 g)

- (c) The scientific community was shocked at the recent claim of the discovery of an isotope of a new element, *unbibium*, with a mass number of 292. This is over 50 mass units higher than uranium, the heaviest known naturally-occurring element. There is a possibility that there is an 'island of stability' beyond the known Periodic Table at some very high atomic numbers.

- (i) The scientists suggested that the atomic number of *unbibium* is 122. How many neutrons are there in this isotope? [1]

[1] $292 - 122 = 170$

- (ii) If *unbibium* really exists then it will require a new block of the Periodic Table, corresponding to the occupancy of another type of subshell, beyond the **s**, **p**, **d** and **f**. This would be a **g** subshell, which is predicted to be found in the 5th shell of an atom, i.e. the **5g** subshell.

Based on the sequence of subshells in the Periodic Table, **s**, **p**, **d**, **f**, predict how many orbitals there are in a **g** subshell. [1]

[1] 9

[Total: 14]

2 (a) The halogens and their compounds have many applications.

(i) Explain, in terms of structure and bonding, the trend in the volatility of the halogens. [2]

- ✓ The halogens have simple molecular structures. Down the group, size of electron cloud of X_2 increases and is more easily distorted.
- ✓ The strength of the instantaneous dipole-induced dipole attractions increases.
- ✓ Hence requiring more energy to overcome the intermolecular forces.
- ✓ The boiling point increases and volatility decreases down the group.

2✓ = 1m

Note: Volatility depends on the boiling point and covalent bonds are not broken.

(ii) When heated in chlorine, phosphorous form phosphorus pentachloride, PCl_5 .

Explain the reaction of PCl_5 with water. Include the pH value of the resulting solution and write equation for the reaction that occurs. [2]

- ✓ PCl_5 undergoes hydrolysis due to energetically accessible vacant 3d orbitals for dative bonding with water.
- ✓ It forms strongly acidic solution, pH = 1.

2✓ = 1m



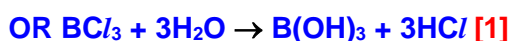
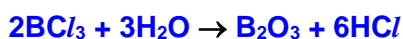
Note:

- Be familiar with the state symbols.
- In limited water: $PCl_5(s) + H_2O(l) \rightarrow POCl_3(l) + 2HCl(g)$
 $POCl_3(l) + 3H_2O(l) \rightarrow H_3PO_4(aq) + 3HCl(aq)$

There is said to be a diagonal relationship between elements of the second and third periods of the Periodic Table.

(iii) By analogy with the reaction of $SiCl_4$, suggest a balanced equation for the hydrolysis of BCl_3 . [1]

Deduce the equation by inferring from $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$



- (iv) Explain why BCl_3 can undergo hydrolysis like SiCl_4 . [1]

The B atom in BCl_3 is electron deficient / has (energetically accessible) vacant 2p orbital to accept the lone pair of electrons from oxygen of water to form a dative bond. [1]

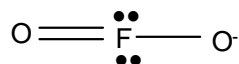
Note: BCl_3 is a covalent chloride, not ionic chloride. Explanation using charge density and polarising power is for ionic chloride and not application to BCl_3 .

- (b) Oxoanions of Group 17 elements have the general formula XO_m^- , where $m = 1, 2, 3$ or 4 . These oxoanions are strong oxidising agents.

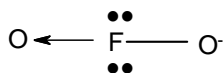
- (i) Suggest why fluorine does not form higher oxoanions where $m \geq 2$. [1]

Fluorine is in Period 2 of the Periodic Table, hence unable to expand its octet structure to form more than 1 covalent bond. [1]

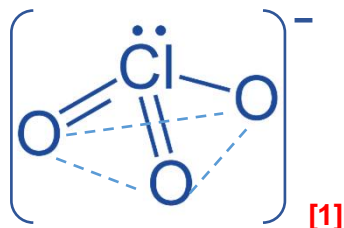
Eg FO_2^- , there would be 10 electrons around central atom, F if the structure is



As F is very electronegative, it is less likely to form dative bonds in the structure of



- (ii) Draw the structure of the C/O_3^- ion to show its shape. [1]



1.25×10^{-3} mol of an aqueous bromate salt containing the BrO_3^- anion was added to excess potassium iodide. The resulting mixture was washed with hexane to dissolve the iodine, and the aqueous and organic layers were separated. Silver nitrate solution was added to the aqueous layer, a yellow precipitate and a pale cream precipitate were obtained.

- (iii) Identify the two precipitates formed. [1]

AqBr (redox product) and AqI (excess KI) [1]

- (iv) The iodine collected in the organic layer was titrated against $0.500 \text{ mol dm}^{-3}$ sodium thiosulfate. 14.90 cm^3 of titrant was required to discharge the blue-black colour of the starch indicator.

Calculate the number of moles of electrons transferred per mole of BrO_m^- .

Hence, determine the value of m .

[2]

Reaction: $\text{BrO}_m^- + \text{I}^- \rightarrow \text{I}_2 + \text{Br}^-$ (not balanced)



$$n_{\text{thiosulfate}} = \frac{14.90}{1000} \times 0.500 = 7.45 \times 10^{-3} \text{ mol}$$

$$n_{\text{iodine}} = \frac{1}{2} n_{\text{thiosulfate}} = 3.725 \times 10^{-3} \text{ mol} \quad [\checkmark]$$

$$\frac{n_{\text{iodine}}}{n_{\text{bromate}}} = \frac{3.725 \times 10^{-3}}{1.25 \times 10^{-3}} = 3 \text{ (nearest whole number)} \quad [\checkmark] \text{ i.e.}$$

3 mol of I_2 produced from 1 mol of BrO_m^- reacting with 6 mol of I^-



Therefore, BrO_m^- gained 6 mol of electrons to form Br^- . $[\checkmark]$

Original oxidation state of Br in $\text{BrO}_m^- = -1 + 6 = +5$

$$5 + m(-2) = -1$$

$$\underline{m = 3} \quad [\checkmark] \quad 2\checkmark = 1\text{m}$$

- (c) Fig. 2.1 shows two cells connected in series. **Cell 1** and **Cell 2** involve the electrolysis of saturated solution of CuBr_2 and concentrated HX respectively, where X is one of the Group 17 elements.

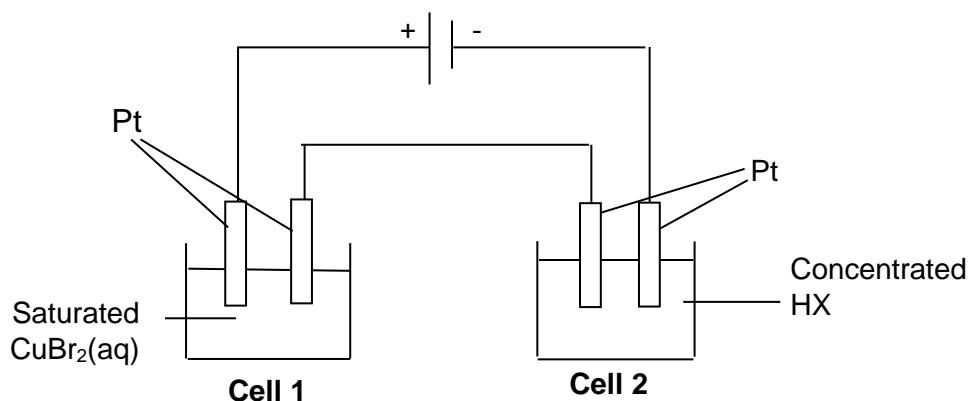
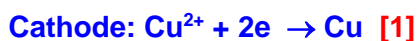


Fig. 2.1

- (i) Write ion-electron equations for the reactions occurring at the cathode and anode in **Cell 1** during electrolysis. [2]

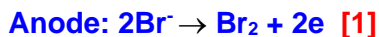
Cathode: consider reduction of the cation and water.

Since $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$ is more positive than $E^\circ_{\text{H}_2\text{O}/\text{H}_2} = -0.83 \text{ V}$, copper ions are preferentially reduced.



Anode: consider oxidation of the anion and water.

Since $E^\ominus_{\text{Br}_2/\text{Br}^-} = +1.07 \text{ V}$ is less positive than $E^\ominus_{\text{O}_2/\text{H}_2\text{O}} = +1.23 \text{ V}$, copper ions are preferentially oxidised.



- (ii) A current of 22.8 A was passed through the saturated solution of CuBr_2 in **Cell 1**.

After 10 minutes, a halogen is formed at one of the electrodes in **Cell 2** and is collected by a syringe. It is found that the mass of the syringe increased by 5.04 g.

Identify X by calculating the M_r of the halogen produced. [2]

Since two half cells are connected in series, the current passed through the Cell 2 is also 22.8 A.

No. of moles of electrons transferred = $(I \times t) / F$

$$= (22.8 \times 10 \times 60) / 96500$$

$$= 0.142 \text{ mol [1]}$$

From $2\text{X}^- \rightarrow \text{X}_2 + 2\text{e}^-$,

no. of moles of the X_2 gas produced in Cell 2

$$= \frac{1}{2} \times 0.142 = 0.0710 \text{ mol (note: mole ratio)}$$

M_r of the gas, $\text{X}_2 = 5.04 / 0.0710$

$$= 71.0$$

Hence, X is Cl. [1]

[Total: 15]

- 3 Table 3.1 shows the enthalpy change of combustion and hydrogenation of some substances.

Table 3.1

Substances	$\Delta H_{\text{combustion}} / \text{kJ mol}^{-1}$	$\Delta H_{\text{hydrogenation}} / \text{kJ mol}^{-1}$
but-1-ene (g)	-2717	-127
buta-1,3-diene (g)	-3187	-239
cyclopentadiene (g)	-2800	x
hydrogen (g)	-286	

- (a) Use of the Data Booklet is relevant to this question.

0.422 g of but-1-ene, C_4H_8 , was used to heat up 500 cm^3 of water from its initial temperature of 30°C .

- (i) Calculate the expected maximum temperature of the water. [2]

$$\text{no. of moles of but-1-ene} = \frac{0.422}{4 \times 12 + 8} = 7.54 \times 10^{-3} \text{ mol}$$

$$7.54 \times 10^{-3} \times 2717 \times 10^3 = 500 \times 4.18 \times (T_{\text{max}} - 30) \quad [1]$$

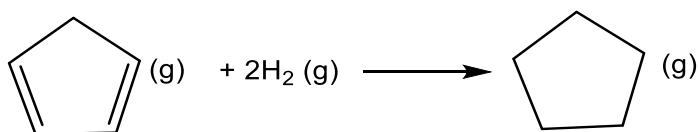
$$T_{\text{max}} = 39.8^\circ\text{C} \quad [1]$$

- (ii) When the experiment was conducted in the laboratory, the maximum temperature of the water was found to be lower.

Suggest an explanation for this. [1]

Heat loss to surroundings/incomplete combustion of but-1-ene [1]

- (b) Cyclopentadiene undergoes catalytic hydrogenation to form cyclopentane.



- (i) Using data from the Data Booklet, calculate x , the enthalpy change of hydrogenation of gaseous cyclopentadiene. [2]

Bonds broken: 3 C-C, 2 C=C, 6 C-H, 2 H-H

Bonds formed: 5 C-C, 10 C-H

$\Delta H_{\text{hydrogenation}}$ (gaseous cyclopentadiene)

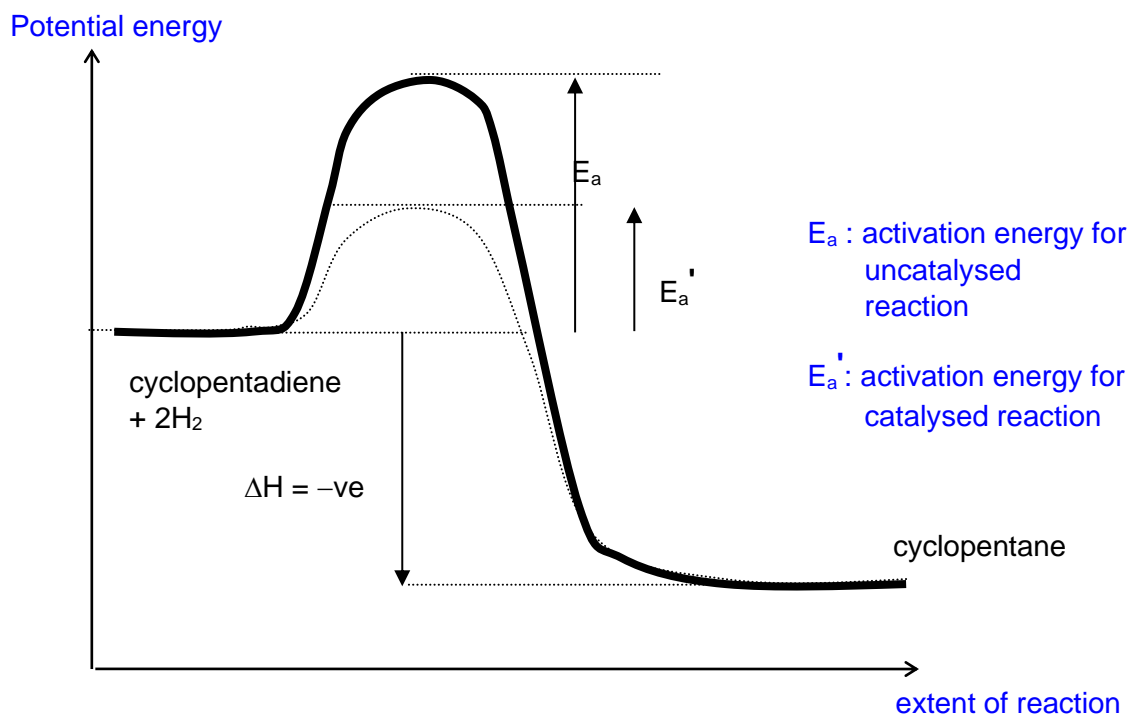
$$= [3(+350) + 2(+610) + 6(+410) + 2(+436)] + [5(-350) + 10(-410)] \quad [1]$$

$$= -248 \text{ kJ mol}^{-1} \quad [1]$$

- (ii) The hydrogenation reaction is thermodynamically favourable but it will not proceed without a catalyst.

Construct a labelled reaction pathway diagram to show how the addition of the catalyst speeds up the hydrogenation of cyclopentadiene.

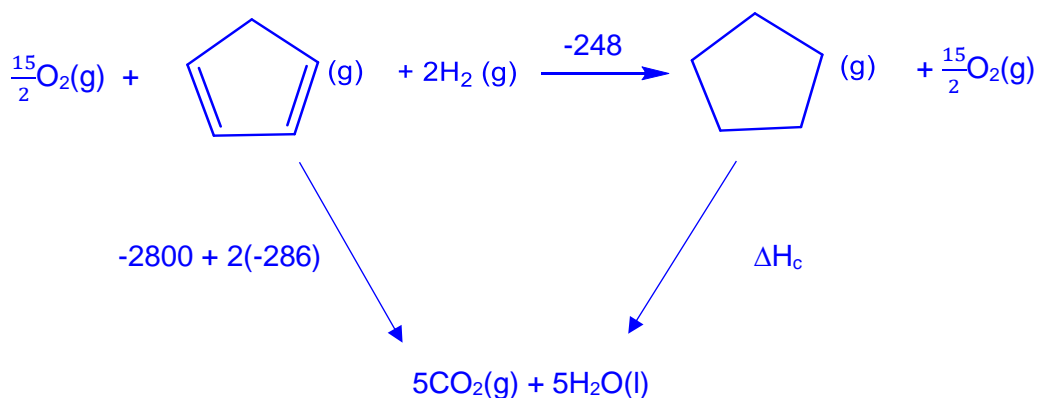
Assume the hydrogenation of cyclopentadiene takes place via a one-step reaction. [2]



[1] labelled axes, activation energy, enthalpy changes, reactants and products

[1] shape of curve for both catalysed and uncatalysed reaction

- (iii) Use data from Table 3.1 and the answer in (b)(i) to construct an energy cycle to calculate the enthalpy change of combustion of gaseous cyclopentane. [3]



By Hess' law,

$$-248 + \Delta H_c = -2800 + 2(-286) \quad [1]$$

$$\Delta H_c = -3120 \text{ kJ mol}^{-1} \quad [1]$$

[1] energy cycle with balanced equations and state symbols

- (c) Alkadienes, such as buta-1,3-diene, are thermodynamically more stable due to conjugation where the π system exists over a series of atoms.

This extra stability can be shown by comparing the enthalpy change of hydrogenation of but-1-ene and buta-1,3-diene. Using data in Table 3.1, calculate the energy that is associated with the conjugated effect. [1]

$$\begin{aligned}\text{Energy} &= 2 \times 127 - (239) \\ &= 15 \text{ kJ mol}^{-1} \quad [1]\end{aligned}$$

- (d) Buta-1,3-diene undergoes an equimolar addition reaction with HBr to produce a mixture of 1,2-addition and 1,4-addition products.

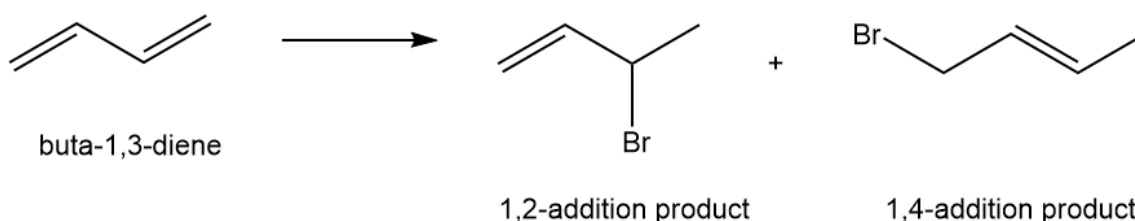


Fig. 3.1 shows the synthesis of compound **Q** from buta-1,3-diene. The first step involves a similar reaction to the above addition reaction between buta-1,3-diene and HBr.

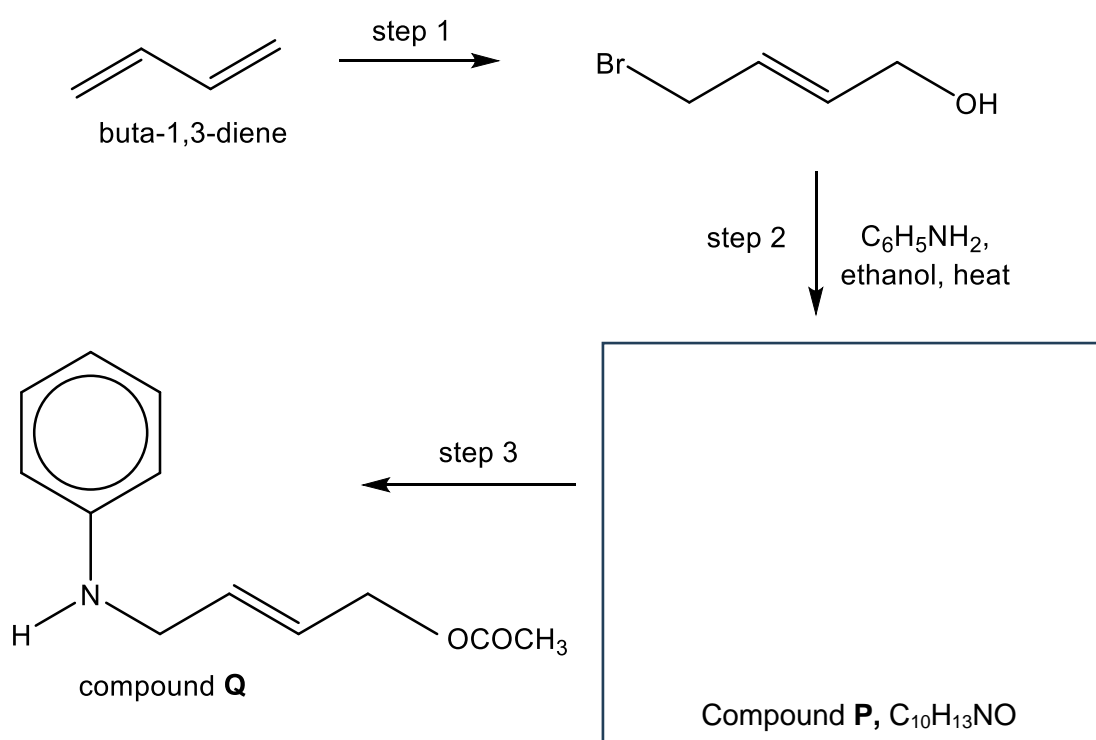


Fig. 3.1

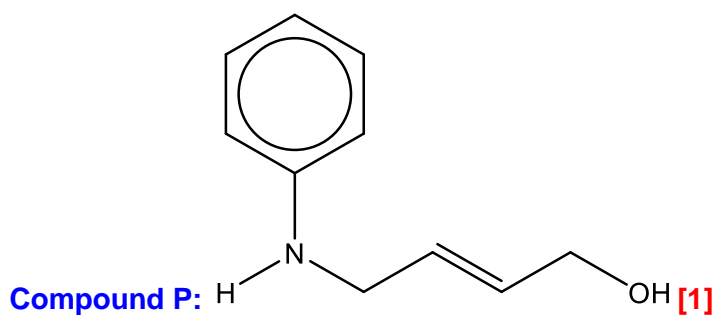
- (i) State the reagents and conditions for steps 1 and 3. [2]

Step 1: Br₂(aq) [1]

Step 3: CH₃CO₂H, conc. sulfuric acid, heat [1]

- (ii) Draw the structure of compound **P** in the box in **Fig 3.1**.

[1]



- (iii) Suggest a chemical test between buta-1,3-diene and compound **Q**.

[2]

✓ Heat both compounds with dilute hydrochloric acid.

To the hydrolysed products of **Q**, ✓ add sodium metal/sodium carbonate/ PCl_5 .
 ✓ Effervescence of hydrogen gas/carbon dioxide gas/white fumes of HCl would be observed.

✓ No hydrogen gas/carbon dioxide/white fumes are observed for but-1,3-diene.

2 ✓: **[1]**

Alternative answers:

Heat both compounds with acidified KMnO_4 . **[1]** Both compounds decolourise purple KMnO_4 . Buta-1,3-diene gives CO_2 due to the terminal alkenes while compound **Q** does not give off CO_2 . **[1]**

Add $\text{Br}_2(\text{aq})$ to both compounds. **[1]** Both compounds decolourise orange bromine water. Compound **Q** forms a white ppt while buta-1,3-diene does not form white ppt. **[1]**

Note: $\text{Br}_2(\text{l})$ should not be used as it is corrosive.

[Total: 16]

- 4 (a) The use of the *Data Booklet* is relevant to this question.

Iron is a transition element in Period 4 of the Periodic Table. The reaction scheme in Fig. 4.1 shows the chemistry of some iron-containing species.

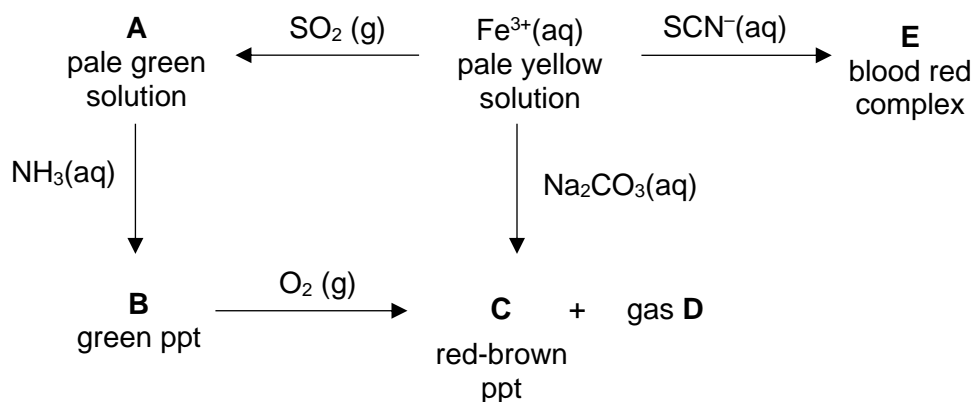


Fig. 4.1

- (i) Define the term *transition element*. [1]

Transition element is a d-block element forming one or more stable ions with partially filled d subshell. [1]

- (ii) State the full electronic configuration of an iron(III) ion. [1]

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ [1]

- (iii) State the role of $\text{NH}_3(\text{aq})$ in the reaction of **A** to form **B**.

Hence, explain the reactions taking place when $\text{NH}_3(\text{aq})$ is added to **A**. Include equations and the formula of all iron-containing species. [2]

NH_3 acts as a base. [✓]

$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ [✓]

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$ [✓]

OR $\text{Fe}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{OH})_2(\text{s})$

[✓] identity of A or B shown in answer

2 ticks = 1 mark

- (iv) Identify compound **C** and gas **D**. [1]

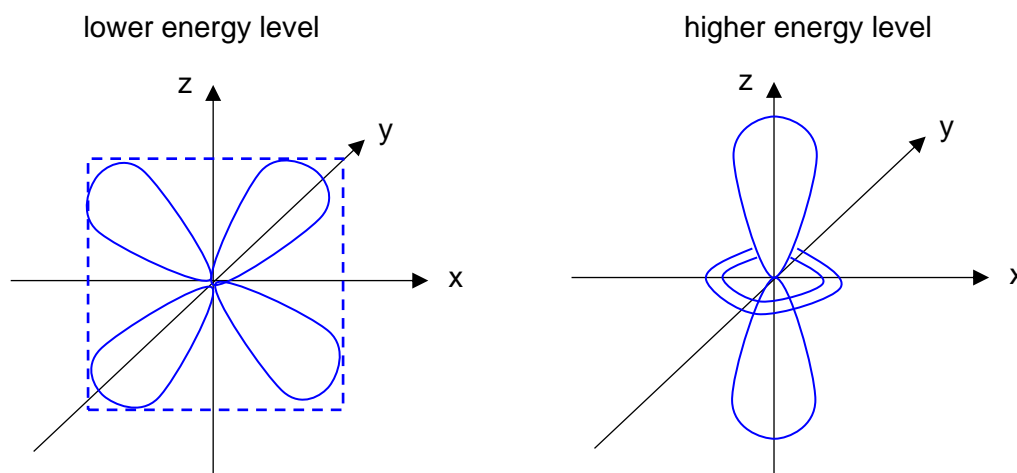
C: $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$ or $\text{Fe}(\text{OH})_3$ [✓] D: CO_2 [✓]

- (v) When thiocyanate ions, SCN^- , is added to a solution of $\text{Fe}^{3+}(\text{aq})$, an octahedral complex is formed.

Using the axes provided, sketch the shape of two d orbitals.

- One d orbital from the lower energy level in the octahedral complex.
- One d orbital from the higher energy level in the octahedral complex.

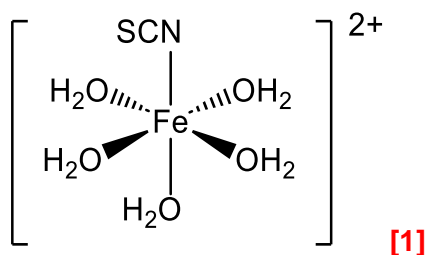
[2]



[2]

- (vi) When SCN^- is added to $\text{Fe}^{3+}(\text{aq})$, one water molecule of $\text{Fe}^{3+}(\text{aq})$ is replaced by one SCN^- ion.

Draw a diagram to show the three-dimensional structure of the complex ion in **E**. Assume the SCN^- ligand coordinates via the N atom. [1]

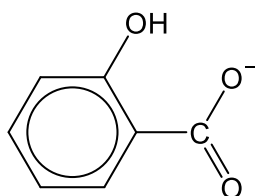


[1]

- (b) Transition metal complex ions are coloured. The formula of a complex ion can be determined using colorimetry.

In colorimetry, the colorimeter is set to use the wavelength of light that is absorbed most strongly by the complex ion. The more concentrated the complex ion solution, the more intense its colour and so the higher the absorbance.

A purple complex is formed when salicylate, $\text{C}_6\text{H}_4(\text{OH})\text{CO}_2^-$, is added to iron(III) ions, $\text{Fe}^{3+}(\text{aq})$. A student carried out an experiment to determine the formula of complex ion formed between $\text{Fe}^{3+}(\text{aq})$ and salicylate. Salicylate acts as a bidentate ligand, and has the structure shown below.

salicylate, $\text{C}_6\text{H}_4(\text{OH})\text{CO}_2^-$

- (i) State a colour in the visible spectrum from which a suitable wavelength of light might be chosen to test for the iron(III) complex formed with salicylate. [1]

Yellow [1]

- (ii) Explain what is mean by the term *bidentate ligand*. [1]

One ligand donates 2 lone pair of electrons to central metal ion (or atom)

OR one ligand forms 2 dative bonds with central metal ion (or atom). [1]

The student prepared solutions containing different volumes of $0.025 \text{ mol dm}^{-3} \text{ Fe}^{3+}(\text{aq})$ and $0.050 \text{ mol dm}^{-3}$ salicylate, and tested the absorbance of the solutions in the colorimeter.

Fig. 4.2 shows the relationship between absorbance and the volumes of $\text{Fe}^{3+}(\text{aq})$ and aqueous salicylate used.

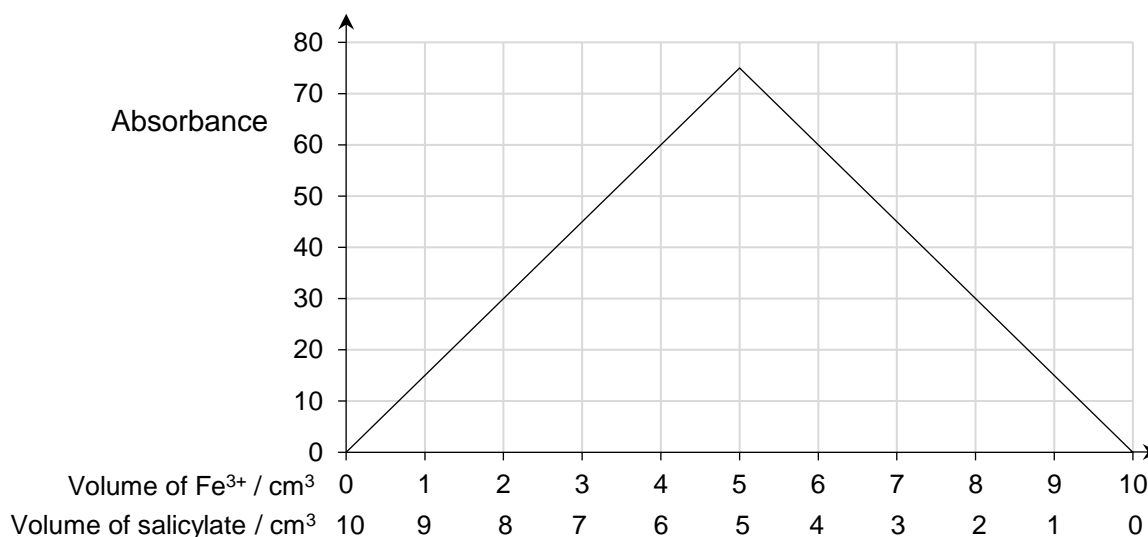


Fig. 4.2

- (iii) The sample of $\text{Fe}^{3+}(\text{aq})$ was prepared from solid hydrated iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Determine the mass of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ needed to prepare 250 cm^3 of a standard solution of $0.025 \text{ mol dm}^{-3} \text{ Fe}^{3+}(\text{aq})$. [2]

Number of moles of Fe^{3+} in 250 cm^3 solution = $250/1000 \times 0.025$

= 0.00625 mol [1]

$$\text{Mr of Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} = 55.8 + 3(14.0) + 9(16.0) + 9(18.0) = 403.8$$

$$\text{Mass of Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} = 0.00625 \times 403.8 = 2.52 \text{ g [1]}$$

- (iv) Using Fig. 4.2, determine the number of moles of salicylate that forms a complex with 1 mole of Fe^{3+} ion. [2]

$$\text{Number of moles of salicylate} = (5/1000) \times 0.050 = 2.50 \times 10^{-4} \text{ mol}$$

$$\text{Number of moles of Fe}^{3+} = (5/1000) \times 0.025 = 1.25 \times 10^{-4} \text{ mol}$$

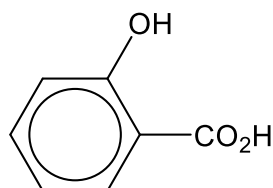
Working [1]

Hence, 2 moles [1] of salicylate forms a complex with 1 mole of Fe^{3+} .

- (v) Given that the iron(III) complex formed has a coordination number of 6, determine the formula of the complex ion formed between $\text{Fe}^{3+}(\text{aq})$ and salicylate, $\text{C}_6\text{H}_4(\text{OH})\text{CO}_2^-$. [1]

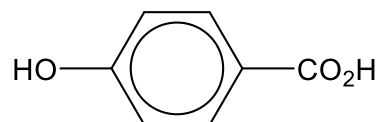
$$[\text{Fe}(\text{H}_2\text{O})_2(\text{C}_6\text{H}_4(\text{OH})\text{CO}_2)_2]^+ \text{ [1] Allow ecf from (iv)}$$

- (c) The structures of salicylic acid and its isomer, **T**, are shown below.



salicylic acid

$$\text{pK}_a = 2.98$$



T

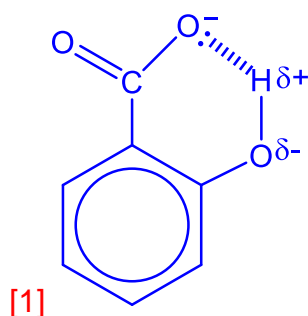
$$\text{pK}_a = 4.58$$

- (i) With the aid of a suitable diagram, explain why the pK_a of salicylic acid is **much** lower than pK_a of **T**. [2]

Analysis: "much lower" implies that there is another stabilisation effect other than electron withdrawing effect.

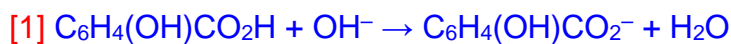
[✓] salicylic acid is a stronger acid / dissociates to a greater extent

[✓] anion of salicylic acid is stabilised by internal / intramolecular hydrogen bonding



Aqueous sodium hydroxide is added to salicylic acid to form a buffer containing salicylic acid $\text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{H}$ and sodium salicylate, $\text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{Na}$.

- (ii) Construct an equation to illustrate how this buffer can regulate the pH change when a small amount of alkali is added. [1]



- (iii) Calculate the volume of $0.200 \text{ mol dm}^{-3}$ NaOH solution needed to mix with 15.0 cm^3 of a $0.100 \text{ mol dm}^{-3}$ solution of salicylic acid to obtain a pH of 3.5. [2]

Let $v \text{ dm}^3$ be the volume of NaOH added.

	NaOH	RCO_2H	\rightarrow	RCO_2Na
Initial / mol	$0.2v$	0.0015		0
Change / mol	$-0.2v$	$-0.2v$		$+0.2v$
Final / mol	0	$0.0015 - 0.2v$		$0.2v$

Final amt of RCO_2H and salt produced [1]

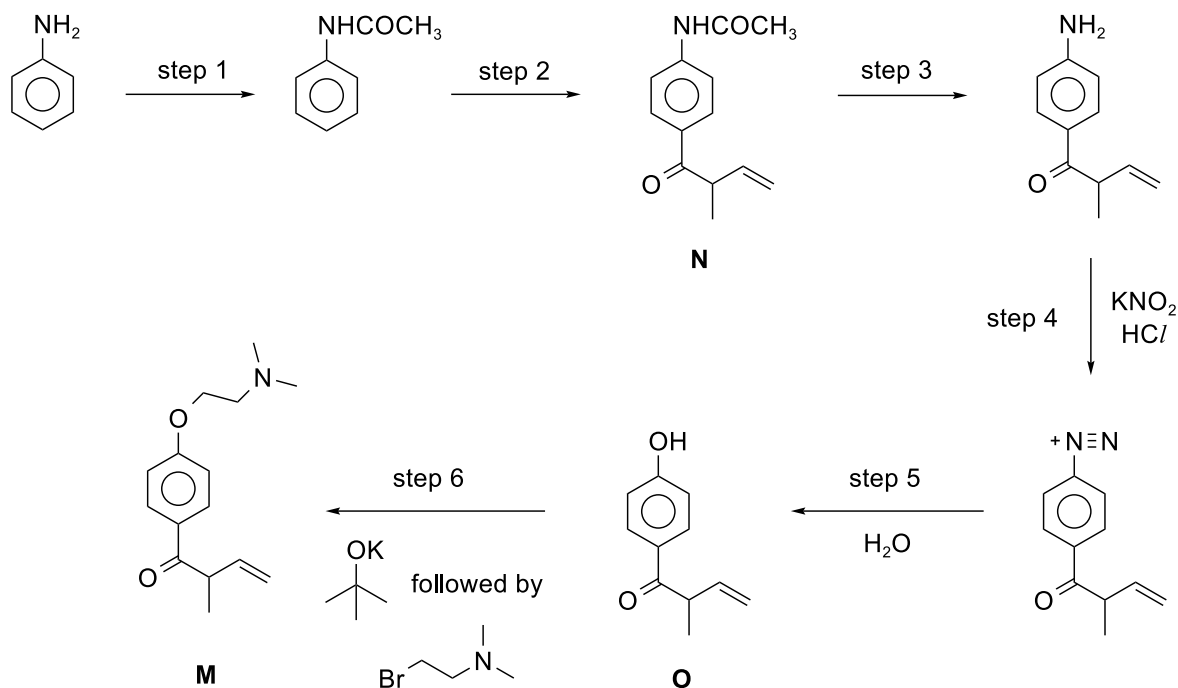
$$\text{pH} = \text{pK}_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

$$3.5 = 2.98 + \lg \frac{0.2v}{0.0015 - 0.2v}$$

$$v = 5.76 \text{ cm}^3 \text{ [1]}$$

[Total: 20]

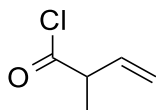
- 5 Phenylamine undergoes the following reaction scheme to produce compound **M**.



- (a) (i) Suggest the reagent in step 1. [1]

[1] anhydrous CH_3COCl

(ii)



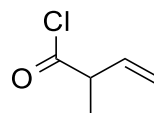
functions as an *electrophile* in step 2.

Explain the term *electrophile*. [1]

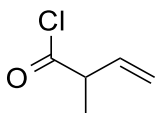
Electron pair acceptor / electron deficient species which can accept a pair of electrons from electron rich species.

- (iii) A student claimed that he was able to obtain compound **N** by carrying out step 2 directly on phenylamine.

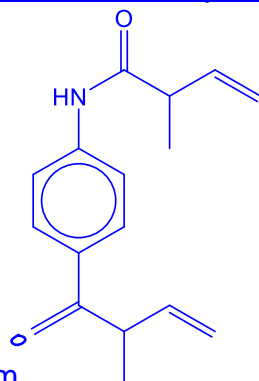
Explain whether the student's claim is valid or not. [1]



Analysis: step 2 is electrophilic sub using and anhydrous AlCl_3



[1] Invalid as _____ reacts readily / undergoes condensation very readily



with phenylamine to form
generated for electrophilic substitution.

reducing the amount of electrophile

- (iv) Identify the oxidation states of the N atoms in the organic compounds before and after step 4. [1]

Before step 4, oxidation state of N is -3

After step 4, oxidation state of N is 0.

[1] both correct OS

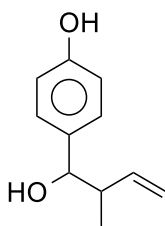
- (v)

With reference to the role of , explain why step 6 would not occur in the

absence of .

[1] acts as a base / removes H⁺ from phenol / deprotonates phenol to generate phenoxide which is a stronger nucleophile / more reactive

- (b) (i) Compound **O** reacts with sodium borohydride to give **P**.
Deduce the structure of **P**. [1]



[1]

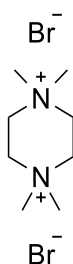
- (ii) Explain the difference in reactivity between the alkene and the ketone functional groups towards sodium borohydride. [2]

[1] The carbonyl carbon is electron deficient as it is bonded to an electronegative oxygen atom. Hence the carbonyl carbon reacts readily with nucleophilic reagents (such as sodium borohydride).

[1] The π bond of $C=C$ of the alkene is electron-rich, hence it cannot react with nucleophilic reagents.

- (c) After step 6 is completed, by-product **Q** is produced alongside **M**. Further analysis revealed that **Q** is $C_8H_{20}N_2Br_2$.

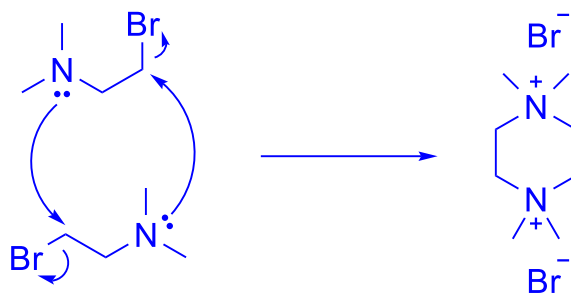
Draw the structure of **Q** and explain how it is formed as a by-product. [2]



[1] **Q** is

[1] The N atom in 1 molecule of $Br-CH_2-CH_2-N(CH_3)_2$ acts as a nucleophile which undergo nucleophilic substitution / reacts with the Br of another molecule.

For info:



[Total: 10]