

**NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2**

CANDIDATE
NAME

SUBJECT
CLASS

REGISTRATION
NUMBER

CHEMISTRY

Paper 1 Multiple Choice

9729/01
15 September 2022
1 hour

Additional Materials:

Optical Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

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

Write your name, subject class and registration number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C and D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

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

Instructions on how to fill in the Optical Mark Sheet

Shade the index number in a 5 digit format on the optical mark sheet:

2nd digit and the last 4 digits of the Registration Number.

Example:

Student	Examples of Registration No.	Shade:
	2105648	15648

This document consists of **15** printed pages and **1** blank page.

Suggestion solution for P1 (MCQ)

1	C	7	D	13	B	19	D	25	B
2	A	8	D	14	A	20	D	26	A
3	A	9	C	15	D	21	D	27	B
4	B	10	B	16	A	22	B	28	D
5	C	11	C	17	C	23	B	29	B
6	B	12	A	18	C	24	C	30	A

1 Technetium (Tc) is a second row transition element that does not occur naturally on Earth. One of its isotopes has 56 neutrons.

What is the nucleon number of this isotope?

- A 43 B 56 C 99 D 112

Ans: C

Refer to Periodic Table.

Tc has atomic number 43, i.e. proton number = 43
 nucleon number = proton + neutron = 43 + 56 = 99

2 Which row has the greater number of particles?

- A 1 mol of liquid sulfuric acid
 B 12000 cm³ of oxygen gas at s.t.p.
 C 32.5 g of zinc
 D 16 g of nitrogen gas

Ans: A

1 mol of liquid sulfuric acid has 6.02×10^{23} particles. There is no dissociation as the sulfuric acid is in liquid form.

12000 cm³ of oxygen gas at s.t.p has $\frac{12000}{22700} = 0.5286$ moles = 3.18×10^{23} particles

32.5g of Zinc has $\frac{32.5}{65.4} = 0.4969$ moles = 2.99×10^{23} particles

16 g of nitrogen gas has $\frac{16}{28} = 0.5714$ moles = 3.44×10^{23} particles

3 Which species will have the smallest deflection when passed through the same electric field?

- A ²³Na⁺ B ¹¹B³⁺ C ¹⁹F⁻ D ³²S²⁻

Ans: A

Angle of deflection, $\theta \propto \frac{\text{charge}}{\text{mass}}$

The species with the smallest charge to mass ratio will have the smallest deflection.

$$^{23}\text{Na}^+ : \frac{+1}{23}$$

$$^{11}\text{B}^{3+} : \frac{+3}{11}$$

$$^{19}\text{F}^- : \frac{-1}{19}$$

$$^{32}\text{S}^{2-} : \frac{-2}{32} = \frac{-1}{16}$$

4 0.0353 g of a sample of volatile organic compound was completely vaporized at 50 kPa and 300K. The vapour occupied a volume of 40 cm³. On complete combustion in excess oxygen, 80 cm³ of carbon dioxide and 80 cm³ of water vapour were formed. All gaseous volumes were measured under identical conditions.

What would be the molecular formula of the compound?

- A C₂H₂O B C₂H₄O C C₂H₆O D C₃H₈

Ans: B

Using $M_r = mRT/PV$; $M_r = 44.0$
 where $m = 0.0353$ g, $T = 300$ K, $p = 50 \times 10^3$ Pa, $V = 40 \times 10^{-6}$ m³,
 $R = 8.31$ J K⁻¹ mol⁻¹

From CO₂(g) evolved:

No. of moles of C = $80\text{cm}^3 / 40\text{cm}^3 = 2$ mol

Mass of C = $12.0 \times 2 = 24.0$ g

From H₂O(g) produced

No. of moles of H = $(80\text{cm}^3 / 40\text{cm}^3) \times 2 = 4$ mol

Mass of H = $1.0 \times 4 = 4.0$ g

Mass of oxygen = $44 - 24 - 4 = 16.0$ g

For A, $M_r = 42.0$ g

For B, $M_r = 44.0$ g (2 carbon, 4 hydrogen and 1 oxygen atom)

For C, $M_r = 46.0$ g

For D, $M_r = 44.0$ g

5 Which species has the most number of unpaired electrons?

- A Co²⁺ B N C Fe D S

Ans: C

	electronic configuration	unpaired electrons	box diagram										
Co ²⁺	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁷	3	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>↑↓</td> <td>↑↓</td> <td>↑</td> <td>↑</td> <td>↑</td> </tr> </table> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td colspan="5" style="text-align: center;">3d</td> </tr> </table>	↑↓	↑↓	↑	↑	↑	3d				
↑↓	↑↓	↑	↑	↑									
3d													
N	1s ² 2s ² 2p ³	3	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>↑</td> <td>↑</td> <td>↑</td> </tr> </table> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td colspan="3" style="text-align: center;">2p</td> </tr> </table>	↑	↑	↑	2p						
↑	↑	↑											
2p													
Fe	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁶ 4s ²	4	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>↑↓</td> <td>↑</td> <td>↑</td> <td>↑</td> <td>↑</td> </tr> </table> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td colspan="5" style="text-align: center;">3d</td> </tr> </table>	↑↓	↑	↑	↑	↑	3d				
↑↓	↑	↑	↑	↑									
3d													
S	1s ² 2s ² 2p ⁴	2	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>↑↓</td> <td>↑</td> <td>↑</td> </tr> </table> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td colspan="3" style="text-align: center;">2p</td> </tr> </table>	↑↓	↑	↑	2p						
↑↓	↑	↑											
2p													

6 Rubidium and bromine form ions that are isoelectronic.

- 1 Ionic radius of rubidium is smaller than its atomic radius.
- 2 Ionic radius of bromine is larger than its atomic radius.
- 3 Ionic radius of bromine is smaller than that of rubidium.

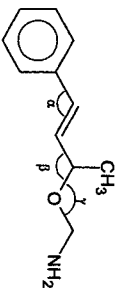
Which statements are correct?

- A 1, 2 and 3 B 1 and 2 only C 1 and 3 only D 2 and 3 only

Ans: B

Proton number	Ion	
Rb 37	Rb ⁺	For Rb vs Rb ⁺ , since the same nuclear charge is attracting less electrons for the ion, the outermost electrons are more tightly held in Rb ⁺
Br 35	Br ⁻	For Br vs Br ⁻ , since the same nuclear charge is attracting more electrons for the ion, the outermost electrons are less tightly held in Br ⁻
		Ionic radius is smaller. Option 1 is true.
		Ionic radius is larger. Option 2 is true.
		For Br ⁻ vs Rb ⁺ , there are less nuclear charge (less protons) attracting the same number of electrons in Br ⁻ than in Rb ⁺ , the outermost electrons are less tightly held by nucleus in Br ⁻ .
		Ionic radius of Br ⁻ is larger. Option 3 is not true.

7 Which row correctly shows the bond angles for α , β , γ in the molecule below?



	α	β	γ
A	109.5°	120°	109.5°
B	120°	109.5°	107°
C	120°	107°	105°
D	120°	109.5°	105°

Ans: D

- α : 3 Bond pairs (1 C=C, 1 C-C and 1 C-H) – Bond Angle of 120°
 β : 4 bond pairs (3 C-C and 1 C-H) – Bond Angle of 109.5°
 γ : 2 lone pairs & 2 bond pairs (2 C-O) – Bond Angle of 105°

8 In which pair is the melting point of the second species higher than that of the first species?

- A C and Si
 B K and Rb
 C NaCl and NaBr
 D SiCl₄ and SiO₂

Ans: D

C and Si are both giant covalent structure and atoms held by covalent bonds. C atoms have a smaller orbital size than Si and hence greater degree of orbital overlap leading to stronger covalent bonds in C than Si. More energy is needed to break the stronger covalent bonds in C than Si. Hence, C has a higher melting point than Si.

K and Rb are both metallic lattices. Both K and Rb contribute the same number of electrons to the sea of mobile electrons. K⁺ has a larger charge to size ratio than Rb⁺ due to having a smaller ionic radius. More energy is needed to break the stronger metallic bonds in K than in Rb. Hence, K has a higher melting point than Si.

NaCl and NaBr are both giant ionic lattices. The product of the charges are the same for both NaCl and NaBr, however, the interionic distance for NaCl is smaller than NaBr. Since $L.E \propto \frac{q_+ \times q_-}{r_+ + r_-}$, more energy is needed to break the stronger ionic bonds in NaCl than NaBr. Hence, NaCl has a higher melting point than NaBr.

SiCl₄ is simple molecular structure and SiO₂ is giant covalent lattice structure. More energy is needed to overcome the covalent bonds in SiO₂ than the weak r-d in SiCl₄. Hence, SiO₂ has a higher melting point than SiCl₄.

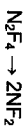
9 When liquid N₂F₄ is heated, it decomposes into a single product, B.

Which statements are correct?

- 1 N-F bonds are broken during this decomposition.
- 2 The enthalpy change when N₂F₄ decomposes into B is approximately +160 kJ mol⁻¹.
- 3 Molecules of B are non-linear.

- A 1, 2 and 3 B 1 and 2 only C 2 and 3 only D 1 only

Ans: C



From the equation, can see that only N-N bonds are broken. Hence statement 1 is incorrect. Based on Data Booklet, N-N bond is +160 kJ mol⁻¹, so statement 2 is correct because that is the only bond broken in the reaction. Statement 3 is correct because there are lone pair(s) on N of NF₂ molecule, so it has to be non-linear.

10 Three experiments were carried out involving acids and alkalis of the same concentration. The temperature changes were recorded as shown in the table below.

Volumes of acids and alkalis added together	$\Delta T / ^\circ\text{C}$
25.0 cm ³ of HCl(aq) + 25.0 cm ³ of NaOH(aq)	ΔT_1
50.0 cm ³ of HCl(aq) + 50.0 cm ³ of NaOH(aq)	ΔT_2
25.0 cm ³ of HCl(aq) + 25.0 cm ³ of NH ₃ (aq)	ΔT_3

Which row shows the correct relative magnitude of ΔT values?

- A** $\Delta T_2 > \Delta T_3 > T_1$ **B** $\Delta T_1 = \Delta T_2 > \Delta T_3$ **C** $\Delta T_2 = \Delta T_3 > \Delta T_1$ **D** $\Delta T_1 = \Delta T_2 = \Delta T_3$

Ans: **B**

Assuming the concentration of both acid and alkali are 1 mol dm⁻³.

- (i) 25.0 cm³ of HCl(aq) + 25.0 cm³ of NaOH(aq): 0.025 mol of H₂O produced, $m = 50.0$.
 (ii) 50.0 cm³ of HCl(aq) + 50.0 cm³ of NaOH(aq): 0.05 mol of H₂O produced, $m = 100.0$.
 (iii) 25.0 cm³ of HCl(aq) + 25.0 cm³ of NH₃(aq): 0.025 mol of H₂O produced, $m = 50.0$.

Given $\Delta T = \frac{\Delta H_{\text{rxn}}}{mc}$ and both c and ΔH_{rxn} of strong acid and strong alkali are constant,

$$\Delta T \propto \frac{n_{\text{H}_2\text{O}}}{m}$$

Hence, $\Delta T_1 = \Delta T_2$

Magnitude of ΔH_{rxn} of strong acid and weak alkali < ΔH_{rxn} of strong acid and strong alkali
 Hence, $\Delta T_1 = \Delta T_2 > \Delta T_3$

11 Some ΔH values are given below.

	enthalpy change of formation / kJ mol ⁻¹
Fe ₂ O ₃	- 824.2
CO	- 110.5
CO ₂	- 393.5

In the industrial production of iron, iron(III) oxide is reduced by carbon monoxide.

What is the enthalpy change of reaction for one mole of iron formed?

- A** - 24.8 kJ mol⁻¹
B + 24.8 kJ mol⁻¹
C + 541.2 kJ mol⁻¹
D + 541.2 kJ mol⁻¹

Ans: **A**



$$\begin{aligned} \Delta H_{\text{rxn}} &= \sum \Delta H_{\text{formation of products}} - \sum \Delta H_{\text{formation of reactants}} \\ &= 3(-393.5) - [-824.2 + 3(-110.5)] \\ &= -24.6 \text{ kJ mol}^{-1} \end{aligned}$$

Hence, enthalpy change of reaction for one mole of iron formed = $24.6 \div 2 = 12.3 \text{ kJ mol}^{-1}$

- 12 Nitrogen and hydrogen form ammonia in an exothermic reaction. The rate and yield of the reaction can be altered by changing the experimental conditions.

Which row correctly describes the effect of the changes in condition?

change in condition	equilibrium yield	effects	
		rate of forward reaction	rate of backward reaction
1 increasing temperature	decreases	increases	increases
2 increasing temperature	increases	decreases	increases
3 addition of catalyst	increases	increases	no effect
4 addition of catalyst	no effect	increases	increases

- A 1 and 4 only B 2 and 4 only C 2 and 3 only D 1 and 3 only

Ans: A (Option 1 and 4 are correct)

Change in condition	effects	
	equilibrium yield	Rates of forward and back reaction
increasing temperature	Eqm shifts to remove some heat, favouring backward endothermic reaction. Hence yield decreases	At higher temperature, K.E. of reactant particles increase. There is a greater proportion of particles with energy greater than activation energy for both forward and backward reactions. Hence both rate of both forward and backward reactions increase.
addition of catalyst	Increases rate of reaction, allowing eqm to be reached faster. No change in yield.	Lower activation energy for both forward and backward reactions. Both rate of both forward and backward reactions increase.

- 13 Four solutions, each of concentration 0.1 mol dm^{-3} , were tested with a pH meter. The results are shown.

solution	pH
$\text{CH}_3\text{CO}_2\text{H}$	4
HNO_3	1
CH_3NH_2	11
NaOH	14

Which statement is incorrect?

- A Conjugate base of $\text{CH}_3\text{CO}_2\text{H}$ is less stable than that of HNO_3 .
 B HNO_3 has a lower pH than $\text{CH}_3\text{CO}_2\text{H}$ because it is more soluble.
 C NaOH has a higher concentration of hydroxide ions in solution than CH_3NH_2 .
 D Mixing equal volume of CH_3NH_2 and HNO_3 form a solution with pH less than 7.

Ans: B

Option A: Correct
 HNO_3 and $\text{CH}_3\text{CO}_2\text{H}$ are of same concentration. Given that $\text{CH}_3\text{CO}_2\text{H}$ has pH 4, implies that there is less dissociation for $\text{CH}_3\text{CO}_2\text{H}$. i.e. Conjugate base of $\text{CH}_3\text{CO}_2\text{H}$ is less stable than that of HNO_3 .

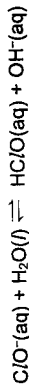
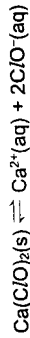
Option B: Incorrect
 HNO_3 has a lower pH than $\text{CH}_3\text{CO}_2\text{H}$ because HNO_3 dissociates fully while $\text{CH}_3\text{CO}_2\text{H}$ partially dissociates.

Option C: Correct
 NaOH has a higher concentration of hydroxide ions in solution than CH_3NH_2 , hence NaOH has a higher pH.

Option D: Correct
 Mixing equal volumes of CH_3NH_2 and HNO_3 gives salt $\text{CH}_3\text{NH}_3^+\text{NO}_3^-$ only.
 $\text{CH}_3\text{NH}_2 + \text{HNO}_3 \rightarrow \text{CH}_3\text{NH}_3^+\text{NO}_3^-$

$\text{CH}_3\text{NH}_3^+\text{NO}_3^-$ dissociates to give CH_3NH_3^+ and NO_3^- .
 CH_3NH_3^+ , conjugate acid of CH_3NH_2 , undergoes hydrolysis to give H_3O^+ , hence pH < 7.
 $\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+$

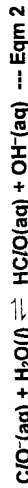
- 14 Solid calcium hypochlorite pellets, $\text{Ca}(\text{ClO})_2(\text{s})$, are added to swimming pools to form $\text{HC}(\text{O})(\text{aq})$ which kills disease-causing bacteria and algae.



What is the effect on the solubility of calcium hypochlorite and bacterial growth when pH increases?

	effect on solubility of calcium hypochlorite	effect on bacterial growth
A	decreases	increases
B	decreases	decreases
C	increases	increases
D	increases	decreases

Ans: A



When pH increases, $[\text{OH}^-]$ increases. Position of equilibrium in eqm 2 shifts left leading to an increase in $[\text{ClO}^-]$ which in turn causes the position of equilibrium in eqm 1 to shift left. Solubility of calcium hypochlorite decreases. $[\text{HC}(\text{O})]$ that kills bacteria also decreases and hence bacterial growth increases.

- 15 A mixture of two oxides of period 3 elements is added to water and the resultant solution has a pH value below 7.

What could be the constituents of the mixture?

- A Al_2O_3 and MgO
 B Na_2O and MgO
 C Na_2O and P_4O_{10}
 D ~~Soluble oxide~~

Ans: D

- A Al_2O_3 insoluble in water and MgO sparingly soluble in water: hence pH slightly > 7
 B Na_2O gives NaOH in water and MgO sparingly soluble in water: hence pH > 7
 $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$
 C Na_2O (gives NaOH in water) and P_4O_{10} (gives H_3PO_4 in water)
 $\text{H}_3\text{PO}_4 + \text{NaOH} \rightarrow \text{Na}_2\text{HPO}_4 + 3\text{H}_2\text{O}$
 PO_4^{3-} , conjugate base of H_3PO_4 , undergoes hydrolysis to give OH^- , hence pH > 7 .
 $\text{PO}_4^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{OH}^-$
 D SO_3 (gives H_2SO_4 in water) and P_4O_{10} (gives H_3PO_4 in water), hence pH < 7 .

- 16 Anhydrous magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, decomposes when heated, giving a white solid and a mixture of two gases, D and E. E is oxygen.

What is the ratio of $\frac{\text{mass of D released}}{\text{mass of E released}}$?

- A ~~0.174~~ B $\frac{1}{0.267}$ C $\frac{1}{0.348}$ D $\frac{1}{3.43}$

Ans: A

Thermal decomposition: $\text{Mg}(\text{NO}_3)_2(\text{s}) \rightarrow \text{MgO}(\text{s}) + 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

Mass of E = $\frac{1}{2}(32.0) = 16.0 \text{ g}$

Mass of D = 2 (46.0) = 92.0 g

$$\text{Ratio of } \frac{\text{mass of D released}}{\text{mass of E released}} = \frac{92}{16} = \frac{92/92}{16/92} = \frac{1}{16/92} = \frac{1}{0.174}$$

17 Addition of warm concentrated sulfuric acid, H_2SO_4 , to crystals of sodium halides gives the following observations.

compound	observation
NaF	evolution of a colourless gas which etches a damp glass rod
NaCl	evolution of a choking colourless gas which produces a white cloud in contact with ammonia vapour
NaBr	evolution of a brown vapour and of pungent fumes which turn potassium dichromate(VI) paper green
NaI	evolution of a purple vapour and a gas smelling of rotten eggs

Which statements are consistent with the observations?

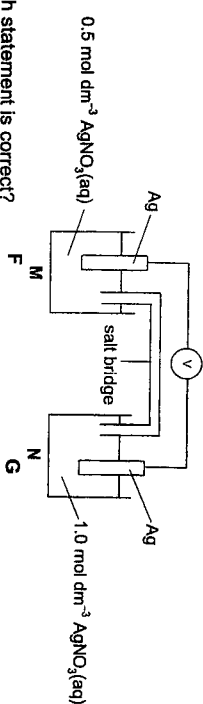
	hydrogen halide is produced in all four reactions	H_2SO_4 is acting as a reducing agent in all four reactions	SO_2 and H_2S are reduction products of H_2SO_4
A	true	false	true
B	true	true	false
C	false	false	true
D	false	true	false

Ans: C

compound	observation
NaF	evolution of a colourless gas (HF) which etches a damp glass rod
NaCl	evolution of a choking colourless gas (HCl) which produces a white cloud in contact with ammonia vapour
NaBr	evolution of a brown vapour (Br_2) and of pungent fumes (SO_2) which turn potassium dichromate(VI) paper green
NaI	evolution of a purple vapour (I_2) and a gas smelling of rotten eggs (H_2S)

hydrogen halide is produced in all four reactions	H_2SO_4 is acting as a reducing agent in all four reactions	SO_2 and H_2S are reduction products of H_2SO_4
Not true. HX produced for NaF and NaCl	Not true. For NaF and NaCl, HX gas is produced. Hence no change in oxidation state of F and Cl	True. SO_2 and H_2S are reduction products as seen for compounds NaBr and NaI.

18 The following electrochemical cell was set up and the E_{cell} value was found to be +0.018 V.



Which statement is correct?

- A Electrode potential of AgNO_3 / Ag electrode in half-cell F is found to be -0.782V .
- B The E_{cell} value becomes less positive when solid sodium chloride is added to half-cell F.
- C The E_{cell} value becomes 0.00V by adding concentrated ammonia gradually to AgNO_3 in half-cell G.
- D The change in the magnitude of the E_{cell} value is the same when same number of moles of iodide or bromide is added to half-cell G separately.

Ans: C

Option A: Incorrect

From Data Booklet:



$$E_{\text{cell}} = E^\circ(\text{Ag}^+/\text{Ag}) + E_{\text{ox}}(\text{Ag}/\text{Ag}^+)$$

$$0.018 = (+0.80) + E_{\text{ox}}(\text{Ag}/\text{Ag}^+)$$

$$E_{\text{ox}}(\text{Ag}/\text{Ag}^+) = -0.782\text{V}$$

$$E(\text{Ag}^+/\text{Ag}) = -E_{\text{ox}}(\text{Ag}/\text{Ag}^+) = +0.782\text{V}$$

Option B: Incorrect

Addition of NaCl decrease $[\text{Ag}^+]$ in half-cell F due to formation of AgCl. By LCP, eqm position of (2) shifts right to partially offset the decrease in $[\text{Ag}^+]$, favouring oxidation.

~~$E_{\text{ox}}(\text{Ag}/\text{Ag}^+)$ in half-cell F become more positive and E_{cell} value becomes more positive.~~

$$E_{\text{cell}} = E^\circ(\text{Ag}^+/\text{Ag}) + E_{\text{ox}}(\text{Ag}/\text{Ag}^+)$$

Option C: Correct

Gradual addition of concentration ammonia decreases $[\text{Ag}^+]$ in half-cell G due to formation of $[\text{Ag}(\text{NH}_3)_2]^+$. By LCP, eqm position of (1) shifts left to partially offset the decrease in $[\text{Ag}^+]$. $E(\text{Ag}^+/\text{Ag})$ for half-cell G become less positive until $E(\text{Ag}^+/\text{Ag}) = +0.782\text{V}$, and E_{cell} becomes 0.00V .

Option D: Incorrect

Addition of iodide and bromide decrease $[\text{Ag}^+]$ in half-cell G due to formation of AgI and AgBr. By LCP, eqm position of (1) shifts left to partially offset the decrease in $[\text{Ag}^+]$. $E(\text{Ag}^+/\text{Ag})$ for half-cell G become less positive and E_{cell} decreases. However, K_{sp} of AgI is lower than that of AgBr, this resulted $[\text{Ag}^+]$ to decrease differently, hence the change in the magnitude of E_{cell} value will also be different.

19 Which statement about the anodising of aluminium using dilute sulfuric acid is correct?

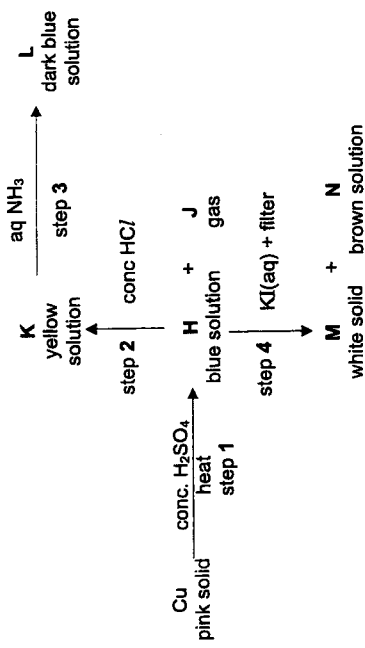
- A Water is reduced at the cathode.
- B Oxygen is produced at the cathode.
- C The Al object to be anodised is the negative electrode.
- D The mass of the anode increases.

Ans: D

The aluminium object to be anodised is the anode that is connected to the positive terminal of the battery. The aluminium object is the positive electrode.

During anodisation, H^+ is reduced at the cathode to produce H_2 while H_2O is oxidised at the anode to produce O_2 which increase the thickness of the Al_2O_3 layer on the surface of the aluminium object. Hence mass of anode increased.

20 Consider the following reaction scheme.



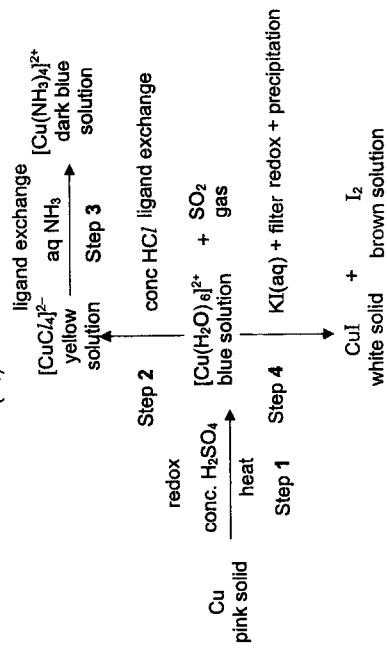
Which statement is correct?

- A $[\text{Cu}(\text{OH})_4]^{2-}$ is the dark blue complex in L.
- B Infinite dilution of solution K gives a pale yellow solution.
- C Cation in compounds K and M has the same oxidation state.

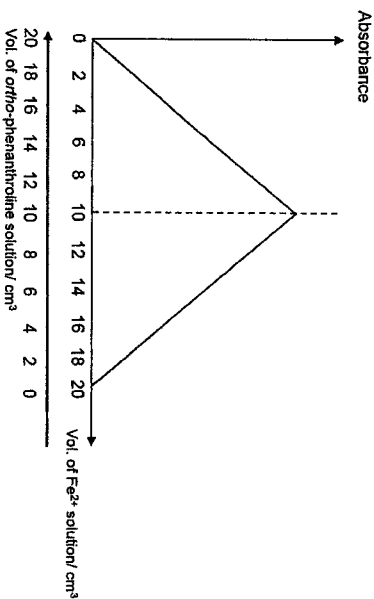
~~D Step involves both redox and precipitation reactions.~~

Ans: D

- step 1: $\text{Cu(s)} + 2\text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{CuSO}_4(\text{aq}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ (redox reaction)
- step 2: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \rightleftharpoons [\text{CuCl}_4]^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$ (ligand exchange)
- step 3: $[\text{CuCl}_4]^{2-}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq})$ (ligand exchange)
- step 4: $2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^-(\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{I}_2(\text{aq})$ (redox + precipitation)



- 21 Fe^{2+} ion forms a red octahedral complex with *ortho*-phenanthroline molecules. Various samples containing different volumes of 1×10^{-5} mol dm $^{-3}$ Fe^{2+} and 3×10^{-5} mol dm $^{-3}$ *ortho*-phenanthroline were prepared. The following graph was obtained when the colour intensity of the samples was measured using a colorimeter.



Which statement about the complex ion is correct?

- A The complex ion absorbs red light.
 B The overall charge of the complex ion is -4 .
 C The co-ordination number of the Fe^{2+} ion is 3.
 D *Ortho*-phenanthroline is a bidentate ligand.

Ans: D

Mole ratio of Fe^{2+} and *ortho*-phenanthroline is $1:3$ (1×10^{-7} mol : 3×10^{-7} mol)

1 mole of Fe^{2+} combined with 3 mole of *ortho*-phenanthroline to form complex ion. Since there are 3 ligands and the coordination no. of Fe^{2+} is 6 as it forms octahedral complex, *ortho*-phenanthroline is a bidentate ligand.

Ortho-phenanthroline molecule has no charge, hence, the overall charge of the complex ion has the same charge as Fe^{2+} .

The colour observed is the complementary colour of the wavelength of light absorbed. Since the colour of complex ion is red, the wavelength of light absorbed is not red light.

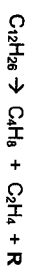
- 22 One molecule of dodecane, $\text{C}_{12}\text{H}_{26}$, is cracked to produce three products, **R**, **S** and **T**. **R** is a straight chain alkane. **S** and **T** are straight chain alkenes with different M_r values. Which statements about **R**, **S** and **T** are correct?

- 1 If **S** and **T** are but-1-ene and ethene respectively, **R** will be hexane.
 2 If **R** is butane, only one, either **S** or **T**, exhibits cis-trans isomerism.
 3 **R** could be octane.

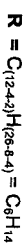
- A 1, 2 and 3 B 1 and 2 only C 2 and 3 only D 1 only

Ans: B

- 1 If **S** and **T** are but-1-ene and ethene respectively, **R** will be hexane. **True**.



S **T**



- 2 If **R** is butane, only one, either **S** or **T**, exhibits cis-trans isomerism. **True**.



R

S + **R** = 8 carbons + 16 hydrogens

Given that **S** and **T** are straight chain alkenes with different M_r values, **S** and **T** cannot be C_4H_8 .

S and **T** is C_2H_4 (no cis-trans) + C_6H_{12} (cis-trans) or C_3H_6 (no cis-trans) + C_5H_{10} (cis-trans).

- 3 **R** could be octane. **NOT True**.

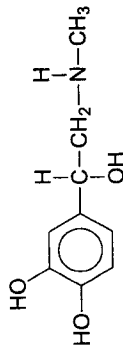


R

If **R** is octane, **S** + **T** = 4 carbons + 8 hydrogens

Given that **S** and **T** are straight chain alkenes with different M_r values, hence **R** cannot be octane.

23 Adrenalin is a stimulant produced in the adrenal glands. It has the following structure.



Which statement about adrenalin is correct?

- A One mole of adrenalin can only react with one mole of ethanoyl chloride.
- B One mole of adrenalin reacts with two moles of hydrogen chloride.
- C It gives effervescence with potassium carbonate.
- D It reacts with ethanoic acid to form amide.

Ans: B

Option A:

Lone pair electrons on O atom of OH group and N atom of amine group in Adrenalin could undergo nucleophilic acyl substitution reaction with ethanoyl chloride. With three OH groups and one amine group, one mole of adrenalin could react with four moles of ethanoyl chloride.

Option B:

HC/ undergo nucleophilic substitution with secondary alcohol of Adrenalin (but not phenol due to C-O bond of phenol has double bond character which is very difficult to break) to form halogen compound. HC/ undergoes acid base reaction with amine group in adrenalin to form salt. Hence, one mole of adrenalin could react with two moles of hydrogen chloride.

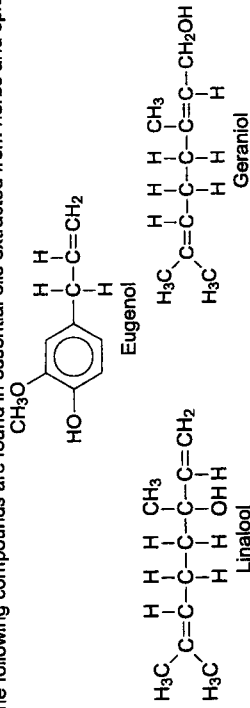
Option C:

Carboxylic acid, a stronger acid than phenol, can react with carbonate, but phenol does not react with carbonate. No effervescence is observed with potassium carbonate.

Option D:

Amide is only formed from the reaction between acyl chloride and amine. Amine undergoes acid base reaction with carboxylic acid to form a salt.

24 The following compounds are found in essential oils extracted from herbs and spices.

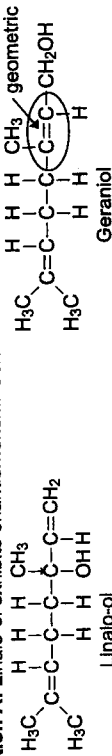


Which statement is Incorrect?

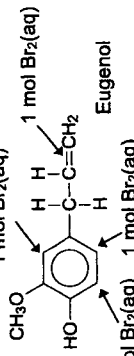
- A Both Linalool and Geraniol exhibit stereoisomerism.
- B One mole of Eugenol reacts with at least two moles of Br₂ in the absence of light.
- C ~~Linalool gives yellow precipitate with 2,4-dinitrophenylhydrazine.~~
- D Geraniol decolorises cold acidified KMnO₄.

Ans: D

Option A: Linalool exhibits enantiomerism. Geraniol exhibits cis-trans isomerism.

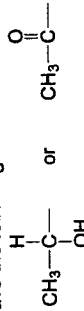


Option B: Eugenol can undergo both electrophilic substitution and electrophilic addition with Br₂(aq)



Note: Like -OH, -OCH₃ is a 2, 4 directing and strong activating group. Hence, Br₂ could undergo electrophilic substitution at 2, 4 position w.r.t -OCH₃. Therefore, a total of 4 moles of Br₂ can react per mole of Eugenol (Electrophilic substitution with 3 moles of Br₂ and electrophilic addition with 1 mole of Br₂.)

Option C: Linalool does not have the following structure and hence it will not give yellow ppt with iodoform test.



Option D: Each C=C bond in Geraniol undergoes mild oxidative to form diol in cold acidified KMnO₄. KMnO₄ decolourises as it is reduced to Mn²⁺ in acidic medium.

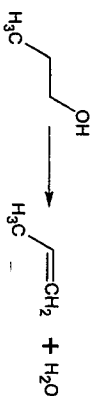
25 Which reactions of propan-1-ol produce water as a by-product?

- 1 passing propan-1-ol vapour over hot Al_2O_3
- 2 mixing propan-1-ol with warm ethanoic acid and a few drops of concentrated H_2SO_4
- 3 warming propan-1-ol with HCN

A 1, 2 and 3 B 1 and 2 only C 2 and 3 only D 1 only
 Ans: B

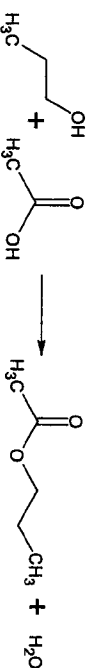
Option 1

Passing propan-1-ol vapour over hot Al_2O_3 causes it dehydration to form a C=C, giving H_2O as the by-product.



Option 2

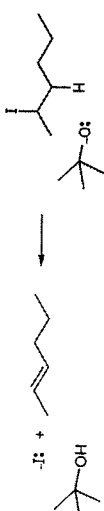
Mixing propan-1-ol with warm ethanoic acid and a few drops of concentrated H_2SO_4 results in esterification, producing H_2O as the by-product.



Option 3

Warming propan-1-ol with HCN would not result in any reaction and HCN does not dissociate readily to give CN^- to react with the alcohol group. Neither does the alcohol group undergo nucleophilic substitution under the given conditions.

26 Hex-2-ene can be made by the reaction shown.



Which statement about this reaction is correct?

- A $(\text{CH}_3)_3\text{CO}^-$ is behaving as a Lewis base.
- B $(\text{CH}_3)_3\text{CO}^-$ is behaving as an oxidising agent.
- C The C-I bond breaks via homolytic fission.
- D This is a nucleophilic substitution reaction.

Ans: A

Option A (Correct)

$(\text{CH}_3)_3\text{CO}^-$ has a lone pair of electrons which is used to remove a H^+ from the starting reactant.

Option B (Incorrect)

There is no change in the oxidation state of any of the atoms.

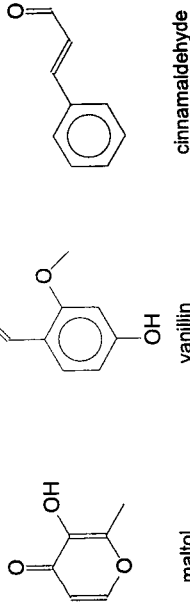
Option C (Incorrect)

The C-I bond breaks via heterolytic fission to give an I^- .

Option D (Incorrect)

This is an elimination reaction in which a H^+ and I^- is eliminated to give the hex-2-ene.

27 Maltol, vanillin and cinnamaldehyde are some naturally occurring flavouring agents.



Which pair of reagents would enable the three compounds to be distinguished from one another?

	reagent 1	reagent 2
A	2,4-dinitrophenylhydrazine	hot acidified $K_2Cr_2O_7$
B	$[Ag(NH_3)_2]^+$ solution	neutral aqueous $FeCl_3$
C	Fehling's solution	hot acidified $KMnO_4$
D	anhydrous $SOCl_2$	aqueous Br_2

Ans: **B**

Option A: (Incorrect)

The aldehyde group in both vanillin and cinnamaldehyde and ketone group for maltol give orange ppt with 2,4-DNPH. The aldehyde group in both vanillin and cinnamaldehyde can be oxidised and turns orange $K_2Cr_2O_7$ to green. Thus these compounds are unable to be distinguished apart.

Option B: (Correct)

The aldehyde group in both vanillin and cinnamaldehyde formed silver mirror with Tollen's reagent ($[Ag(NH_3)_2]^+$ solution), but maltol has no aldehyde. The phenol group in vanillin give violet complex with neutral aqueous $FeCl_3$. Thus, three compounds could be distinguished apart.

Option C: (Incorrect)

Only cinnamaldehyde formed brick-red ppt with Fehling's solution (aliphatic aldehyde). In the presence of hot acidified $KMnO_4$, maltol undergoes oxidative cleavage of C=C bond, while the aldehyde group of vanillin is oxidised to form carboxylic acid. Both maltol and vanillin decolourise purple $KMnO_4$. Thus these two compounds are unable to be distinguished apart.

Option D: (Incorrect)

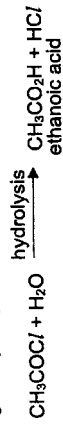
$SOCl_2$ has no reaction with maltol and vanillin despite both having a hydroxyl group. C-OH bond in both maltol and vanillin has a partial double bond character due to resonance and hence OH group cannot be substituted by Cl. Aqueous Br_2 decolourised in all three compounds due to presence of C=C or phenol group in each compound. Only vanillin formed white ppt. Thus, two out of three compounds could not be distinguished apart.

28 The following compounds were treated with hot acidified $KMnO_4$ (aq). Which compound gives an organic product that is **different** from the other three?

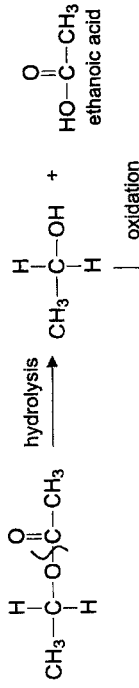
- A** $CH_3COC/$
- B** $CH_3CH_2OCOCCH_3$
- C** $CH_3CH=CHOH$
- D**

Ans: **D**

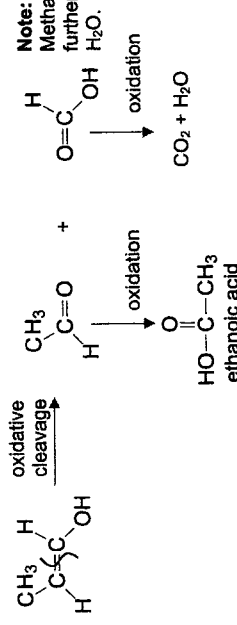
Option A: $CH_3COC/$ undergoes hydrolysis to form ethanoic acid (**organic product**).



Option B: Ester undergoes hydrolysis followed by oxidation of primary alcohol to form ethanoic acid.

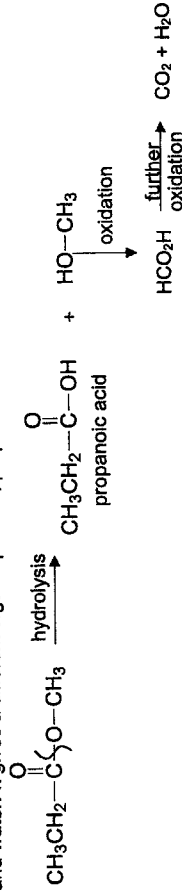


Option C: C=C bond undergoes oxidative cleavage followed by oxidation to form ethanoic acid, carbon dioxide and water.

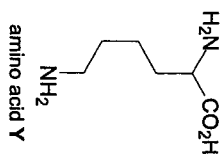


Note: Methanoic acid, HCO_2H , can be further oxidised to form CO_2 and H_2O .

Option D: Ester undergoes hydrolysis followed by oxidation to form propanoic acid, carbon dioxide and water. It gives a different organic product, propanoic acid.



29 Amino acid Y has three pK_a values given below:

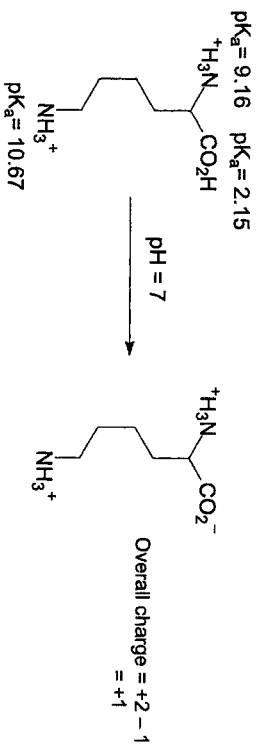


pK_a	α -carboxyl group	α -amino group	side chain
	2.15	9.16	10.67

What is the net charge of the predominant species of amino acid Y at pH 7?

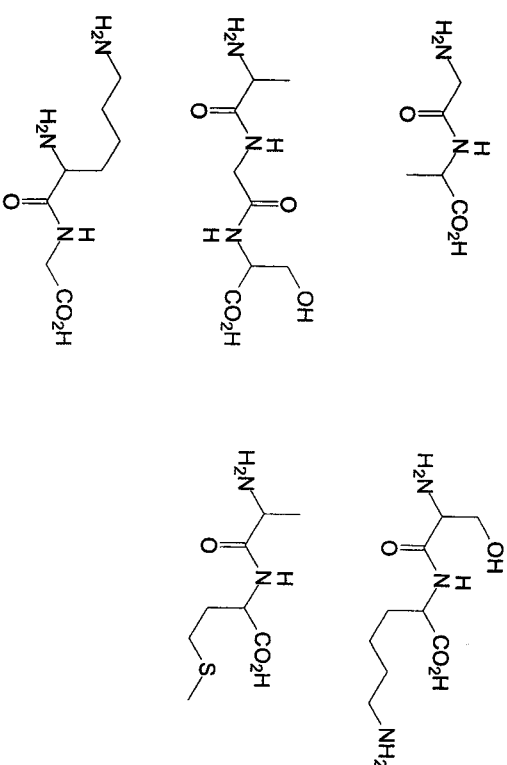
- A +2 B +1 C 0 D -1

Ans: B



Note:
 $pH > pK_a$, the acid group is deprotonated due to higher pH (more alkaline).
 $pH < pK_a$, the acid group is protonated due to lower pH (more acidic)

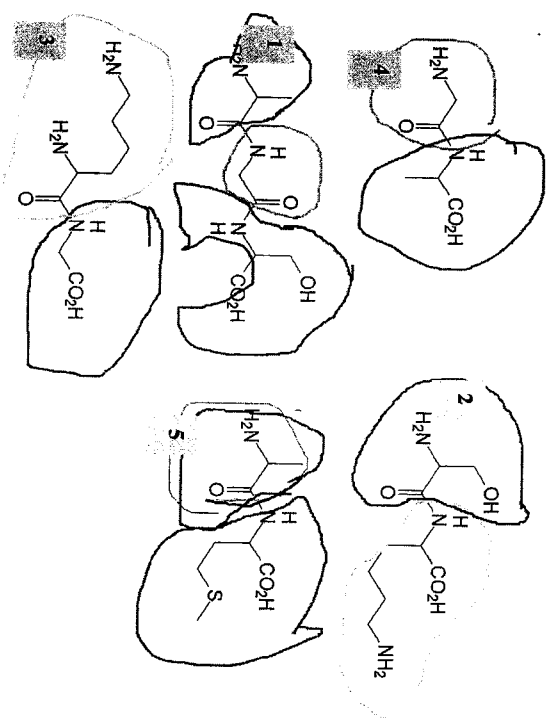
30 Heptapeptide X contains seven amino acid residues. When X is partially hydrolysed, the following dipeptide and tripeptide fragments are produced.

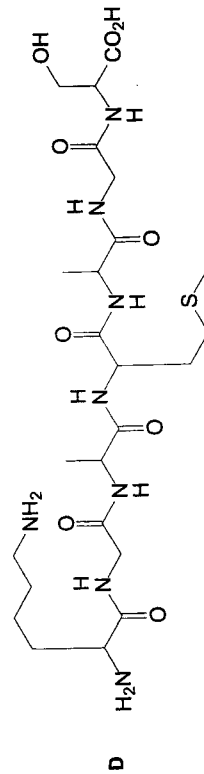
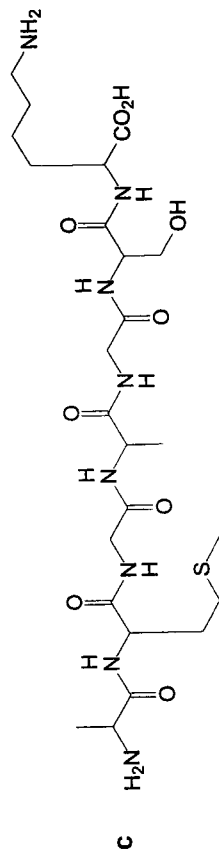
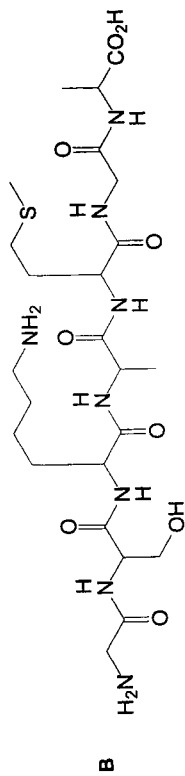
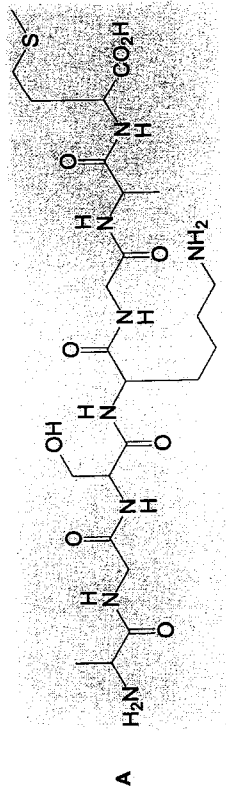


Which of the four heptapeptides on page 15 is the formula of X?

Ans: A

Identify the different amino acid residue by recognising the different R group attached to the alpha-carbon of the amino acid in the dipeptide and tripeptide fragments. Match the amino acid residue in the fragments to obtain the structure of the heptapeptide.

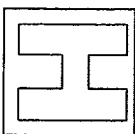




Suggestion solution for P1 (MCQ)

1	C	7	D	13	B	19	D	25	B
2	A	8	D	14	A	20	D	26	A
3	A	9	C	15	D	21	D	27	B
4	B	10	B	16	A	22	B	28	D
5	C	11	C	17	C	23	B	29	B
6	B	12	A	18	C	24	C	30	A

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2



CANDIDATE
NAME

SUBJECT
CLASS

REGISTRATION
NUMBER

CHEMISTRY

Paper 2 Structured Questions

9729/02
29 August 2022
2 hours

Candidates answer on Question Paper.

Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use paper clips, highlighters, glue or correction fluid.
Answers all questions.

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

	Marks	Weightings
Paper 1	/30	15%
Paper 2	/75	30%
Paper 3	/80	35%
Paper 4	/55	20%

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

Answer all the questions in the spaces provided.

- 1 (a) Chemists have recently established that four molecules of water are required for the dissociation of a single molecule of HCl (reported in Science, 2009).

Given that 1.00 dm³ of water contains 55.6 mol of H₂O, calculate the number of molecules of hydrogen chloride, HCl, that should therefore dissociate in 1.00 dm³ of water.

$$\begin{aligned} \text{No. of molecules of HCl} &= \frac{1}{4} \times 55.6 \times 6.02 \times 10^{23} = 8.3678 \times 10^{24} \\ &= 8.37 \times 10^{24} \quad [1] \end{aligned}$$

- (b) Commercial concentrated hydrochloric acid, HCl, fumes strongly on exposure to moist air and thus is known as 'fuming hydrochloric acid'.

1.00 cm³ of fuming hydrochloric acid was transferred with a graduated pipette to a 100 cm³ volumetric flask. The volume was made up to 100 cm³ with deionised water and the solution was labelled F. 10.0 cm³ of solution F was neutralised by 24.75 cm³ of 0.0500 mol dm⁻³ of aqueous sodium hydroxide.

Calculate the concentration of HCl in the fuming hydrochloric acid in mol dm⁻³.

[2]

$$\text{Amount of NaOH} = 0.02475 \times 0.0500 = 0.0012375 \text{ mol} \quad [1]$$

$$\text{Amount of HCl in volumetric flask} = 10 \times 0.0012375 = 0.012375 \text{ mol}$$

$$[\text{HCl}] = 0.012375 / 0.00100 = 12.4 \text{ mol dm}^{-3} \quad [1]$$

Must scale up, no ECF

- (c) (i) The halide ions, X⁻ (where X = Cl, Br, I), show clear trends in their physical and chemical properties.

State and explain the relative thermal stabilities of the hydrogen halides, HX.

[2]

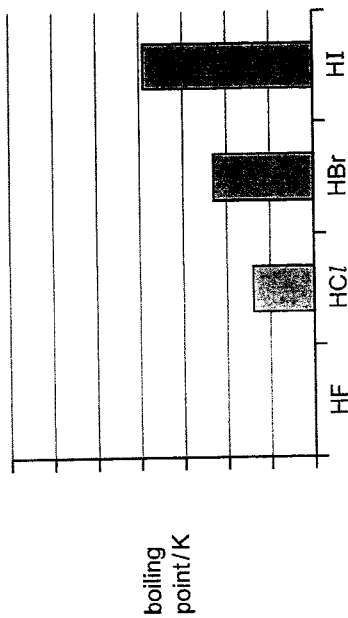
Thermal stability decreases from HCl to HI. [1]

H-X Bond energy decreases [½] OR Less effective overlapping between the orbitals of H atom and Halogen atom as size of halogen atom increases [½]

hence less energy to break the H-X decreases. [½]

Overall Percentage	
Grade	

The bar chart below shows the boiling points of HCl, HBr and HI. The boiling point of HF is not shown.



(ii) Explain why HI has a higher boiling point than HCl and HBr.

.....

HI, HCl and HBr has **instantaneous dipole-induced dipole attraction** between molecules. HI has the **largest electron cloud size/most number of electrons** [$\frac{1}{2}$], hence largest energy is required to overcome the **greater instantaneous dipole-induced dipole attraction** than in that HCl and HBr. [$\frac{1}{2}$]

(iii) Complete the bar chart above to show the boiling point of HF. Explain your answer.

.....

HF has the highest boiling point shown on graph [1]

More energy is required to overcome the **stronger hydrogen bonding between HF molecules**[1] than the instantaneous dipole-induced dipole attraction (and permanent dipoles) in HCl, HBr, HI

(d) Indium and aluminium are elements in Group 13 of the Periodic Table. Indium has very similar chemical properties to aluminium.

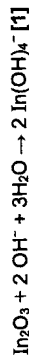
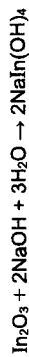
- Indium reacts vigorously with hydrochloric acid to form a colourless gas and a soluble salt.
- Indium oxide, In_2O_3 , is amphoteric. In_2O_3 is a white solid which dissolves in excess aqueous NaOH.
- Gaseous indium bromide, In_2Br_6 , contains coordinate bonds.

(i) Identify the formula of the salt formed when indium reacts with hydrochloric acid.

..... [1]
 InCl_3 [1]

(ii) Construct an equation for the reaction of In_2O_3 with excess aqueous NaOH.

..... [1]

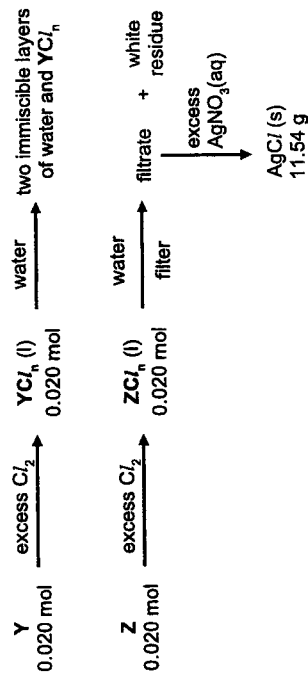


(iii) Draw a diagram that clearly shows the types of bonds in a molecule of In_2Br_6 (g). [1]



Must show dative bond from Br to In or label as dative [1]

(e) In the periodic table, element Y is above element Z in the same group. Elements Y and Z are subjected to a series of reactions shown in the flowchart below.



- (i) Calculate the value of
- n
- in
- ZCl_n
- .

Amount of $AgCl = 11.54 + 143.4 = 0.0805 \text{ mol}$
 ratio $Z:Cl$ is $1:4$
 $n = 4$ [1]

[1]

- (ii) Suggest the identities of elements Y and Z and explain why
- YCl_n
- and
- ZCl_n
- react differently with water.

.....

 [2]

Y: Carbon [$\frac{1}{2}$] and Z: Silicon [$\frac{1}{2}$]

Si in $SiCl_4$ has empty energetically accessible d orbitals / vacant orbitals in the valence shell [$\frac{1}{2}$] to accept the lone pair from water and hence can undergo hydrolysis while C in CCl_4 does not have. [$\frac{1}{2}$]

[2]

- (iii) Write a balanced equation for the reaction of
- ZCl_n
- with water.

..... [1]

 $ZCl_4 + 4 H_2O \rightarrow Z(OH)_4 + 4 HCl$ or
 $SiCl_4 + 4 H_2O \rightarrow Si(OH)_4 + 4 HCl$ or
 $SiCl_4 + 4 H_2O \rightarrow SiO_2 \cdot 2H_2O + 4 HCl$
 $SiCl_4 + 2 H_2O \rightarrow SiO_2 + 4 HCl$ [1]

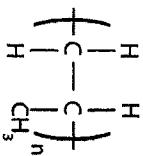
[Total:15]

2

- (a) Oil spills are hazardous as they affect the marine ecosystem, and the marine life-forms existence gets threatened. It becomes increasingly important to employ various clean up methods for tackling the menace that oil spills pose to the marine ecosystem.

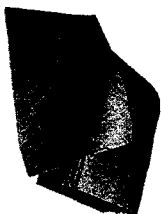
- (i) Oil consists mainly of hydrocarbons. Sheets of sorbents, usually made of materials like polypropylene, can be used to absorb oil.

The structure of polypropylene is given below.



Structure of polypropylene

Sorbent sheets



Suggest how sorbents are able to absorb and effectively remove oil from water.

.....

 [2]

The sorbents have large M_r with large electron cloud size/ non-polar [$\frac{1}{2}$] and can form strong [$\frac{1}{2}$] instantaneous dipole – induced dipole interactions [$\frac{1}{2}$] between the oil and material of the sorbent and hence allowing oil to be removed. The sorbents do not form favourable interactions/ weaker d/d [$\frac{1}{2}$] with water and hence do not absorb water.

Must state "strong" or to the effect

- (ii) Another method for removing the oil spill that is floating on the sea surface is to ignite and burn it off. One of the major components of oil is decane,
- $C_{10}H_{22}$
- . Such burning of oil will cause an increase in temperature of the sea.

A simulation was done with the following scenario: 500 g of decane floating over 200 dm^3 of water was burnt off.Given that the enthalpy change of combustion of decane is $-300.9 \text{ kJ mol}^{-1}$, determine the rise in temperature of the body of water. M_r of decane ($C_{10}H_{22}$) = $10 \times 12 + 22 = 142$ Amount of decane burnt = $(500) \div 142 = 3.521 \text{ mol}$ [1]Amount of heat released = $3.521 \times 300.9 \times 1000 = 1.059 \times 10^6 \text{ J}$ [1] $q = mc\Delta T$ $\Delta T = 1.059 \times 10^6 \div (200 \times 1000 \times 4.18) = 1.27 \text{ K}$ (3.s.f) [1]

- (iii) The actual temperature rise differs from the calculated value in (a) (ii). Suggest a reason for the discrepancy.

..... [3]

Decane does not undergo complete combustion.

Incomplete transfer of heat energy.

Fuel is burning on the surface of the water/ heat transfer to air and not water. heat loss to air.

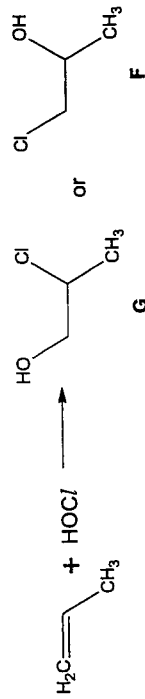
OR Sea water heat capacity differs from that water.

OR Some of the heat energy is used to evaporate the water.

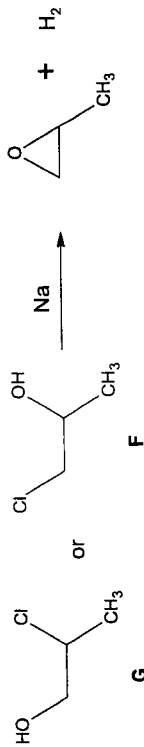
[1]

- (b) Propene is the second most important starting material in the petrochemical industry. It is involved in a two-step synthesis to make a class of compounds known as epoxides.

Step 1: Propene is reacted with HOCl to give two possible products, **G** or **F**.



Step 2: The mixture of **G** and **F** is treated with Na to give the epoxide.



- (i) State the type of isomerism between **G** and **F**.
 Structural/ constitutional/ positional isomerism[1].....

- (ii) Determine the type of reaction that occurs in **each step**.

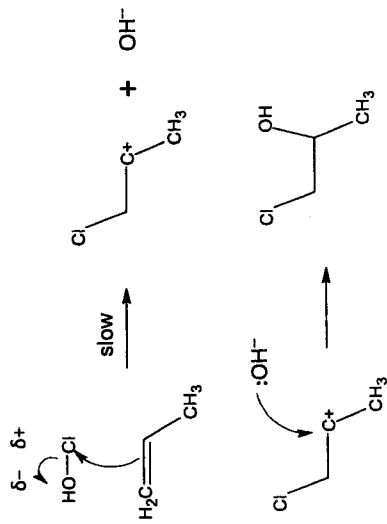
Step 1: (electrophilic addition) [1]

Step 2: (nucleophilic substitution) [1]

[2]

- (iii) Outline the mechanism for formation of **F** in step 1. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[2]



General marking

- (iv) Hence explain why **F** is the major product in the first step.

.....

F is formed via a secondary carbocation that has more electron-donating alkyl groups [$\frac{1}{2}$] to disperse the positive charge/electron deficiency [$\frac{1}{2}$] in the carbocation, making the carbocation more stable [$\frac{1}{2}$] than that of **G**, hence forming in greater quantity [$\frac{1}{2}$], leading to **F** as the major product.

[2]

- (v) Suggest the importance of Na in the formation of epoxide.

.....
 To deprotonate the OH [$\frac{1}{2}$], and generate a stronger nucleophile [$\frac{1}{2}$], for the intramolecular nucleophilic substitution.

[1]

- (c) Allyl chloride, $\text{C}_2\text{H}_5\text{CH}=\text{CH}_2$, is produced by the chlorination of propene at high temperatures



- (i) At lower temperatures, the main product is 1,2-dichloropropane.

Explain why the formation of allyl chloride, C_3H_5Cl , occurs at high temperatures.

At high temperature, there is sufficient energy for the Cl_2 molecule to undergo homolytic fission / break $Cl-Cl$ bond to form free radicals.

[1]

Must recognise to form radicals/ free radical substitution

(ii) $C_3H_5CH=CH_2$ contains a $C=C$ bond. Draw labelled diagrams to show how orbitals overlap to form

- a σ (sigma) bond
- sp^2-sp^2 orbital labelled

- a π (pi) bond.
- p-p orbital labelled

Must show hybridised orbital vs p orbital
No need to label head-on vs sideways overlap → show in diagram

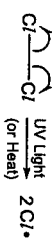
[2]

(iii) Describe the mechanism for the formation of $C_3H_5CH=CH_2$ in equation 1.

[3]

Free radical substitution [1]

Initiation:



Propagation:



Termination:



Minus $\frac{1}{2}$

Header

Half headed arrow

...

(iv) Other than $C_3H_5CH=CH_2$, two other mono-substituted chloropropenes can also

be formed by the same mechanism in (c) (iii).

Complete Table 2.1 with

- the structures of the two other chloropropenes
- the expected ratio in which the three chloropropenes will be formed

chloropropene	$C_3H_5CH=CH_2$	$CH_3CCl=CH_2$ [1/2]	$CH_3CH=CHCl$ [1/2]
Ratio [1]	3	1	2

Table 2.1

[2]

[Total:22]

3 Vanadium is a transition metal that form stable coloured ions of various oxidation states in aqueous solutions. Some of the ions of vanadium and their corresponding colours are shown in the table below.

formula of vanadium ion	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
colour of aqueous solution	yellow	blue	green	violet

(a) Explain why vanadium can form ions of variable oxidation states.

Due to the *close similarity in energies* of the **3d and 4s orbitals** [1], both 3d and 4s electrons can be removed from vanadium to form **stable ions** of different oxidation states:.....

[1]

(b) Data about calcium and vanadium are given below.

	calcium	vanadium
relative atomic mass	40.1	50.9
electronic configuration	$[Ar]4s^2$	$[Ar]3d^34s^2$
atomic radius (metallic) /nm	0.197	0.122
density / g cm ⁻³	1.54	6.07

Using the data provided, explain why the density of vanadium is significantly greater than that of calcium. (No calculations are required.)

- V has stronger metallic bonds as both 3d and 4s electrons could contribute to the sea of delocalised electrons [$\frac{1}{2}$].

- Smaller atomic radii [$\frac{1}{2}$].

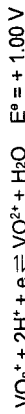
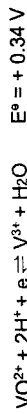
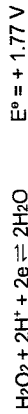
- With more atoms of higher relative atomic mass [$\frac{1}{2}$] in a more closely packed metallic lattice or packed per unit volume [$\frac{1}{2}$].

vanadium has significant higher density than calcium.

[2]

- (c) Predict, by calculating E°_{cell} values, the reaction(s) that occur in each experiment. State the observation(s) that would be made in each experiment.

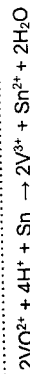
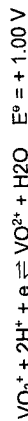
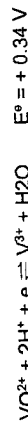
- (i) Experiment A:
Excess acidified hydrogen peroxide is added to an aqueous solution containing VO^{2+} ion.



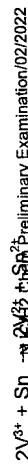
Blue yellow

Observation: blue to yellow [1] OR blue to green to yellow. [2]

- (ii) Experiment B:
Excess tin is added to an acidic aqueous solution containing VO^{2+} ion.

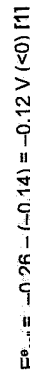


blue green



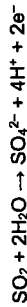
green violet

[Turn over



[3]

- (d) The vanadium-containing ion in 50 cm^3 of a $0.800 \text{ mol dm}^{-3}$ solution of ammonium metavanadate, NH_4VO_3 , reacts with 506 cm^3 of sulfur dioxide gas measured at 20.0°C and 98.0 kPa . In the reaction, sulfur dioxide is oxidised according to the equation given below.



- (i) Calculate the final oxidation state of the vanadium ion in the solution.

- (ii) Hence write a balanced equation for the reaction between VO_3^- and SO_2 .

$$pV = nRT$$

$$n\text{SO}_2 = \frac{pV}{RT} = \frac{(98 \times 10^3 \times 506 \times 10^{-6})}{8.31 \times (20 + 273)} = 0.02 \text{ mol}$$

$$n\text{VO}_3^- = 50 \times \frac{0.800}{1000} = 0.04 \text{ mol}$$

no. of electron transferred in the reaction = $0.02 \times 2 = 0.04 \text{ mol}$

no. of electron gained per mole of $\text{VO}_3^- = \frac{0.04}{0.04} = 1$

The oxidation state of V in $\text{VO}_3^- = +5$

Final oxidation state of the vanadium ion in the solution = $5 - 1 = +4$ [1]



- (e) Vanadium(V) oxide, V_2O_5 , is obtained by the action of heat on ammonium metavanadate, NH_4VO_3 . V_2O_5 is an orange-coloured solid that catalyses the Contact process:



- (i) State the type of catalysis involved.

Heterogeneous catalyst [1]

- (ii) Explain briefly how V_2O_5 catalyses the Contact process. [1]

Adsorption. [$\frac{1}{2}$]

The gaseous reactant molecules are adsorbed onto V_2O_5 surface with the formation of weak interaction/bonds [$\frac{1}{2}$]

Reaction

Surface concentration of the reactant molecules increases; the reaction proceeds through the adsorbed state and existing and in the reactant molecules. The activation energy is lowered [$\frac{1}{2}$]

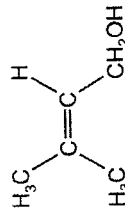
Using relevant data from the *Data Booklet*, describe and explain which compounds, manganese(II) carbonate, MnCO_3 , or magnesium carbonate, MgCO_3 , is more suited for use as the cathode electrode in supercapacitors.

Ionic radius: $\text{Mn}^{2+} = 0.083\text{nm}$ and $\text{Mg}^{2+} = 0.065\text{nm}$ [1]
 Both Mn^{2+} and Mg^{2+} has the same charge of +2, but Mn^{2+} has smaller ionic radius than that of Mg^{2+} . Hence Mn^{2+} has lower charge/ionic size ratio with lower polarising power [1/2]. More energy is needed to break less polarized C-O bond [1/2] of carbonate anion in MnCO_3 , therefore MnCO_3 is more suited with higher thermal stability [1].

[3]
 [Total: 11]

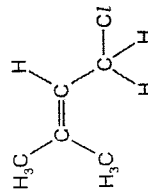
- 5 Prenol is a naturally occurring organic molecule found in many fruits. It contains both an alkene and an alcohol functional group.

Prenol



- (a) State the reagents and conditions to convert **G** to prenol.

G



[1]

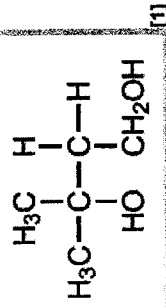
NaOH/KOH(aq) , heat [1]

- (b) Prenol reacts with steam to form a mixture of three isomers, **J**, **K** and **L**, with molecular formula $\text{C}_5\text{H}_{12}\text{O}_2$.

- (i) When **J** is heated with excess acidified potassium manganate(VII), it forms an organic product which does not react with 2,4-dinitrophenylhydrazine.

Suggest a structure of **J**.

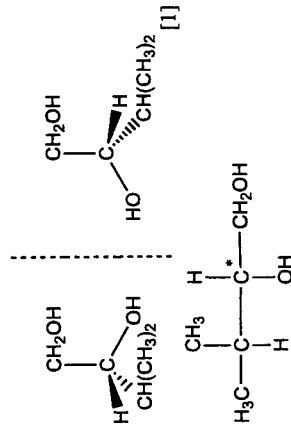
[1]



- K** and **L** are stereoisomers. **K** and **L** both react when heated with excess acidified potassium manganate(VII) to form **M**, $\text{C}_5\text{H}_8\text{O}_3$. **M** forms an orange precipitate on reaction with 2,4-dinitrophenylhydrazine.

- (ii) Name the type of stereoisomerism shown by **K** and **L**, and draw structures to illustrate the stereoisomerism.

Optical/enantiomerism [1].....[2]

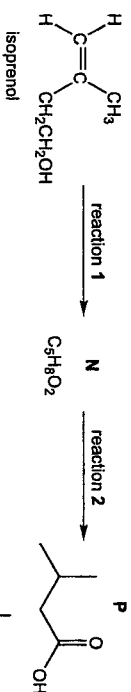


- (iii) Give the balanced equation to represent the reaction of **K**, $\text{C}_5\text{H}_{12}\text{O}_2$, with acidified potassium manganate(VII) to form **M**, $\text{C}_5\text{H}_8\text{O}_3$.

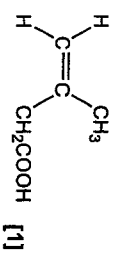
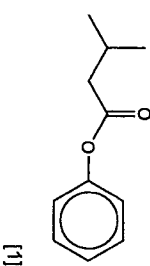
Use [O] to represent an atom of oxygen provided by the oxidising agent.

$\text{C}_5\text{H}_{12}\text{O}_2 + 3[\text{O}] \rightarrow \text{C}_5\text{H}_8\text{O}_3 + 2\text{H}_2\text{O}$ [1].....[1]

- (c) Isoprenol is a structural isomer of prenol. The series of reactions shows how isoprenol can be used to form **Q**, a sweet-smelling liquid.



(i) Suggest the structure of N. [1]



(ii) Suggest the reagents and conditions for reactions 1 and 2. [1]

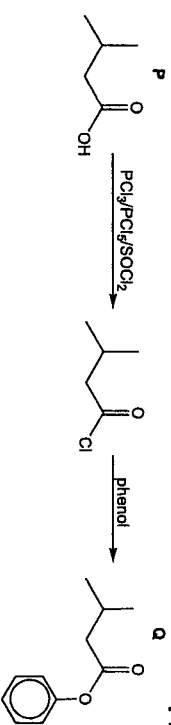
reaction 1:

reaction 2: [2]

Step 1: $\text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4(\text{aq})$, heat with reflux [1]
(Cannot be KMnO_4 , otherwise will cleave C=C bond)

Step 2: H_2, Ni , high temperature/ H_2, Pt [1]
(Cannot be $\text{LiAlH}_4, \text{NaBH}_4$, cos non-polar C=C bond)

(iii) Suggest the step(s) to convert P to Q, showing the structure(s) of any intermediate(s) formed. [3]



Intermediate [1]

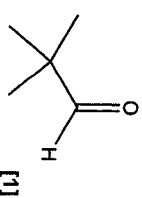
Step 1: $\text{PCl}_5/\text{PCl}_5/\text{SOCl}_2$, anhydrous [1] or zero

Step 2: Phenol [½], $\text{NaOH}(\text{aq})$ [½]

(iv) Compound S, a structural isomer of isoprenol, gives a brick-red precipitate when treated with alkaline solution of copper(II) tartrate. S gives only one

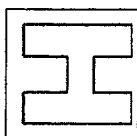
mono-chlorinated product when reacted with chlorine gas under ultraviolet light.

Suggest the structure of S. [1]



[Total: 14]

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2



CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

Paper 3 Free Response

9729/03
13 September 2022
2 hours

Candidates answer on Question Paper.

Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams or graphs.

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

Section A

Answer all questions.

Section B
Answer one question.

A Data Booklet is provided.

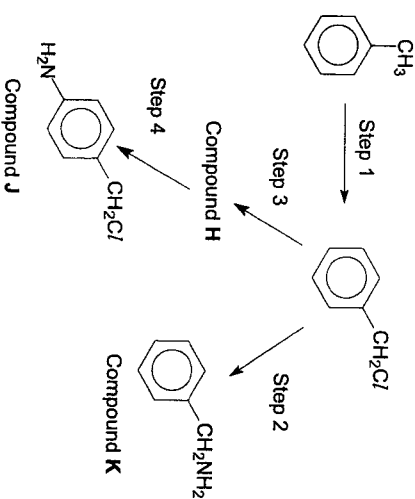
The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use	
Section A	
1	/18
2	/19
3	/23
Section B	
4	/20
5	/20
Paper 3 Total	/80

This document consists of **28** printed pages.

- Section A**
Answer all the questions in this section.
- 1 (a) Amines can be synthesised from methylbenzene, shown by the following steps.



- (i) Suggest the structure for compounds H. [1]
- (ii) Suggest reagents and conditions for steps 1, 2, 3 and 4 in Fig. 1.1. [4]
- (iii) Suggest why the yield for step 2 is not high. [1]
- The K_b values of three bases, at 25°C, are shown in table 1.2.

Table 1.2	
base	$K_b/\text{mol dm}^{-3}$
ammonia	1.8×10^{-5}
compound K	4.5×10^{-4}
compound J	7.4×10^{-10}

- (iv) Explain the relative magnitudes of the K_b values in table 1.2. [2]

(i) 1 or 0

(ii) Step 1: UV light, limited $\text{C}/_2$. 1 or 0

Step 2: ethanolic NH_3 , heat in sealed tube.

Step 3: conc H_2SO_4 , Conc HNO_3 , 60°C (- CH_2Cl has negligible effect on benzene) -accept T lower than 60°C.

Step 4: conc HCl , Sn, heat followed by NaOH(aq) or (step 1 then 2)

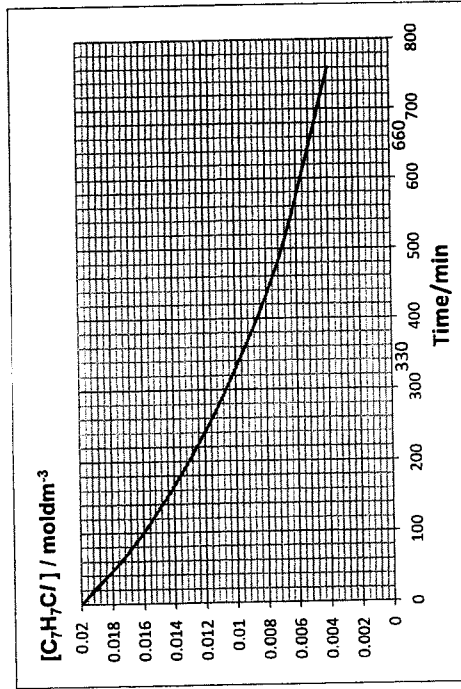
1 or 0 for each step

(iii) The primary amine produced, due to the electron donating alkyl group $\frac{1}{2}$, is a stronger nucleophile than NH_3 , $\frac{1}{2}$ hence can compete/further react with NH_3 for $\text{C}_7\text{H}_7\text{Cl}$ to form a secondary amine instead of the compound **K**. ($\frac{1}{2}$ for stating polysubstitution)

(iv) Smaller K_b value means a weaker base. Lone pair on **N** in **J** is less available $\frac{1}{2}$ compared to that of **K** to accept H^+ as the electron density at **N** is reduced $\frac{1}{2}$ via resonance with the adjacent benzene $\frac{1}{2}$ (lone pair on **N** is delocalised into the benzene ring) while the electron density at **N** in **K** is increased by the electron donating effect of the alkyl group $\frac{1}{2}$.

(b) The rate of reaction for step 2 in Fig. 1.1 can be followed by measuring the change in concentration of $\text{C}_7\text{H}_7\text{Cl}$ with time. The reaction was carried out with the other reactant in large excess.

Fig. 1.2 shows the concentration of $\text{C}_7\text{H}_7\text{Cl}$ monitored against time for step 2.



Showing all your working and drawing clearly any construction lines, use Fig. 1.2 to determine:

(i) The order with respect to $\text{C}_7\text{H}_7\text{Cl}$. Explain your reasoning. [2]

(ii) The initial rate, in $\text{mol dm}^{-3} \text{min}^{-1}$ [1]

Given that the half-life magnitude of $\text{C}_7\text{H}_7\text{Cl}$ is not affected by the change in concentration of the other reactant.

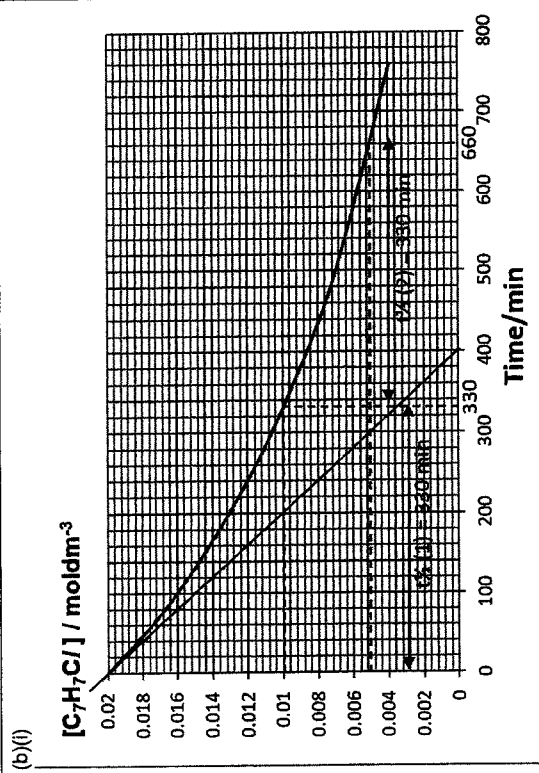
(iii) Write the rate equation for step 2 in Fig. 1.1, and calculate a value for the rate constant, stating its units. [2]

(iv) Hence, outline a mechanism for step 2 in Fig. 1.1 to form all the products. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

(v) Explain why step 2 proceeds via the mechanism you describe in b(iv). [1]

(vi) Suggest and explain the difference in reactivity when 4-bromomethylbenzene undergoes the same reaction. [1]

[Total : 18]



1m for showing how the half-life is obtained.

Since half-life of $\text{C}_7\text{H}_7\text{Cl}$ is constant at 330 min, it is 1st order wrt to $\text{C}_7\text{H}_7\text{Cl}$. 1m

(ii) Initial rate = $-\left(\frac{\text{gradient at } t=0}{400}\right) = 5 \times 10^{-5} \text{ moldm}^{-3} \text{ s}^{-1}$ 1m

(iii) ~~Rate = 1m~~

Two methods:

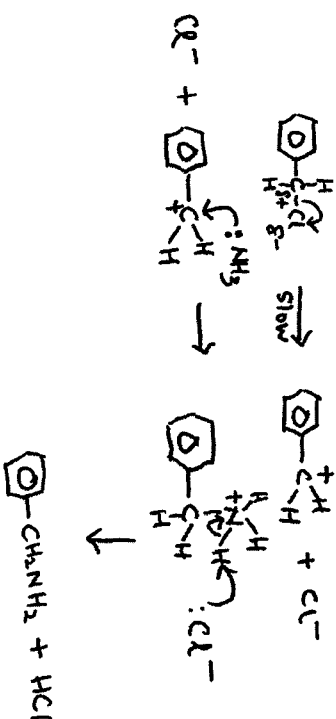
Making use of the initial rate calculated in (ii)

$$k = 5 \times 10^{-5} \div 0.02 = 2.5 \times 10^{-3} \text{ s}^{-1}$$

Making use of the half-life magnitude:

$$k = \frac{\ln 2}{t_{1/2}} = 2.1 \times 10^{-3} \text{ s}^{-1} \frac{1}{2} \text{ m each for answer and units}$$

- (iv) Nucleophilic substitution (S_N1)



Accept show formation of HCl in separate step.
 Draw S_N2 based on S_N1 rate equation on (iii) – 1m for name of mechanism
 Draw S_N2 based on S_N2 rate equation in part (iii) – full credit

1m for name of mechanism
 ½ for slow
 1 m for curly arrows and charges
 1m for balanced equations

- (v) Explain why step 2 proceeds via the mechanism you describe in b(iv). [1]
 The carbocation intermediate can be resonance stabilised i.e. the positive charge of the cation can be dispersed via resonance with the adjacent benzene ring. 1m
 Or
 The bulky benzene ring poses steric hindrance to the incoming nucleophile if it occurs via S_N2 or one step mechanism. 1m
 Cannot accept s_N2 explanation
- (vi) C-Br in 4-bromomethylbenzene is resistant to substitution [½], as it has double bond character due to the continuous p orbital overlap [½] involving Br and benzene ring.

- 2 Hydrogen cyanide, HCN, is extremely toxic and with sufficient concentrations it leads to rapid death. During the Second World War, a form of hydrogen cyanide known as Zyklon B was used in the Nazi gas chambers.

- (a) (i) Draw a dot-and-cross diagram to illustrate the bonding in HCN. [1]
 HCN can be oxidised to cyanogen, C_2N_2 .



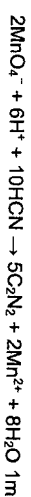
- (ii) Suggest a suitable oxidant to oxidise HCN to C_2N_2 in acidic solution, using the Data Booklet.
 Write an equation for the reaction and calculate the E°_{cell} . [2]

2(a)(i)



(ii) KMnO_4 in acidic medium

$$E^\circ_{\text{cell}} = +1.52 - (+0.37) = +1.15 \text{ V} > 0 \text{ (reaction is spontaneous)} \quad 1\text{m}$$



Note: Can use any oxidizing agent with $E^\circ > +0.37\text{V}$

- (b) The synthesis of HCN was developed in the early 1900s. The most commonly used procedure is the *Andrussow* process. A less common method is the *BMA* process.
- Andrussow* process:
 $\text{CH}_4(g) + \text{NH}_3(g) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{HCN}(g) + 3 \text{H}_2\text{O}(l) \quad \Delta H = -506 \text{ kJ mol}^{-1}$
BMA process:
 $\text{CH}_4(g) + \text{NH}_3(g) \rightarrow \text{HCN}(g) + 3 \text{H}_2(g)$
- (i) Using information from the *Data Booklet*, calculate the enthalpy change of reaction for the *BMA* process given above [2]
- (ii) By considering the spontaneity of reaction, suggest why the *Andrussow* process is the preferred procedure at low temperature. [2]

(b) (i) $\Delta H = 4 \times 410 + 3 \times 390 - [410 + 890 + 3 \times 436]$
 $= +202 \text{ kJ mol}^{-1}$ 1m for final answer, 1 m for working
 (correct number and type of bonds identified- 1m)

(ii) *Andrussov* process has a negative ΔS since there is decrease in number of gas particles, which causes a decrease in number of ways to arrange the particles in space. 1m
 $\Delta G = \Delta H - T\Delta S$, at low temperature, $\Delta H > |T\Delta S|$, it is more likely to have $\Delta G < 0$ at low temperature.

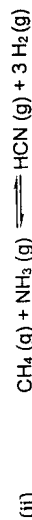
(c) The BMA process is a reversible reaction at 500°C. Starting with equal amount of CH_4 and NH_3 , the reaction is allowed to reach equilibrium at 500°C under a constant pressure of 1 atm.

- (i) Write an expression for the K_p of BMA process stating its units. [1]
- (ii) Given that the partial pressure of H_2 is 0.3 atm, calculate the value of K_p at 500°C. [2]
- (iii) Discuss the effect of increase in total pressure on
- the proportion of HCN ,
 - K_p value
 - rate of reaction

(i)

$$K_p = \frac{P_{\text{HCN}}^3 P_{\text{H}_2}}{P_{\text{CH}_4} P_{\text{NH}_3}} \quad \text{units: atm}^2$$

1/2 each for expression and units (0 if wrong expression)



At equilibrium, $P_{\text{H}_2} = 3 \times P_{\text{HCN}}$
 $\therefore P_{\text{HCN}} = 0.1 \text{ atm}$

Since the reaction is carried out at a constant pressure of 1 atm,

$$P_{\text{CH}_4} + P_{\text{NH}_3} + P_{\text{CH}_4} + P_{\text{NH}_3} = 1 \text{ atm}$$

since partial pressure of the gaseous products ($P_{\text{HCN}} + P_{\text{H}_2}$) = 0.4 atm

$$P_{\text{CH}_4} + P_{\text{NH}_3} = 0.6 \text{ atm}$$

1m for partial pressures

$$\text{Hence } P_{\text{CH}_4} = 0.3 \text{ atm} = P_{\text{NH}_3}$$

$$K_p = \frac{0.1(0.3)^3}{(0.3)(0.3)} = 0.03 \quad 1 \text{ m (ecf)}$$

(iii)

Increase in pressure will shift the equilibrium to the reactant side as it has smaller number of gas particles $\frac{1}{2}$, this is to partially offset increase in total pressure. Hence proportion of HCN is reduced $\frac{1}{2}$.

Changes in pressure has no effect on K_p value $\frac{1}{2}$ as K_p values are affected by changes in T only $\frac{1}{2}$.

Increase in total pressure increases the concentration of the gaseous particles, increase in collision frequency increases the frequency of effective collision $\frac{1}{2}$, hence rate is expected to increase $\frac{1}{2}$.

(d) $\text{HCN}(\text{aq})$ has $\text{p}K_a = 4.79$ at 25 °C.

(i) Calculate the concentration of CN^- ion at pH 4, when the concentration of $\text{HCN}(\text{aq})$ is 0.06 mol dm^{-3} . [1]

Zinc cyanide, $\text{Zn}(\text{CN})_2$, is sparingly soluble in water.
 The numerical value of K_{sp} is 8.0×10^{-12} at 25°C.

(ii) Write an expression for the K_{sp} of $\text{Zn}(\text{CN})_2$ stating its units. [1]

(iii) By considering your answer to (d)(i), determine the minimum concentration of Zn^{2+} required to cause precipitation of $\text{Zn}(\text{CN})_2$ at pH 4. [2]

(iv) Describe and explain how the solubility of $\text{Zn}(\text{CN})_2$ is affected:

- by adding $\text{HCl}(\text{aq})$
- by adding concentrated $\text{ZnCl}_2(\text{aq})$

(i) $10^{-4.79} = \frac{10^{-4}[\text{CN}^-]}{0.06}$ [2]

$$[\text{CN}^-] = 9.73 \times 10^{-3} \text{ mol dm}^{-3} \quad 1 \text{ m}$$

(ii) $K_{sp} = [\text{Zn}^{2+}][\text{CN}^-]^2 \text{ mol}^3 \text{ dm}^{-9} \quad \frac{1}{2}$ each with correct expression.

(iii) For precipitation to occur, ionic product $> K_{sp}$

$$[\text{Zn}^{2+}](9.73 \times 10^{-3})^2 > 8.0 \times 10^{-12} \text{ 1m}$$

$$[\text{Zn}^{2+}] = 8.45 \times 10^{-8} \text{ mol dm}^{-3} \quad 1 \text{ m (ecf)}$$

(iv) Addition of strong acid will suppress the dissociation of weak acid HCN , causing the concentration of CN^- to reduce $\frac{1}{2}$ hence more $\text{Zn}(\text{CN})_2$ solid dissolves $\frac{1}{2}$ to partially offset the reduction in $[\text{CN}^-]$ solubility of $\text{Zn}(\text{CN})_2$ increases $\frac{1}{2}$.

Addition of $\text{ZnCl}_2(\text{aq})$ causes the concentration of Zn^{2+} to increase $\frac{1}{2}$, hence the precipitation $\frac{1}{2}$ process is favoured in order to partially offset the increase in $[\text{Zn}^{2+}]$ hence solubility of $\text{Zn}(\text{CN})_2$ decreases $\frac{1}{2}$.

- 3 (a) GABA, a naturally occurring neurotransmitter, has the condensed formula of $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$. It can be synthesised from 2-bromoethanal, CH_2BrCHO , shown by the following steps.

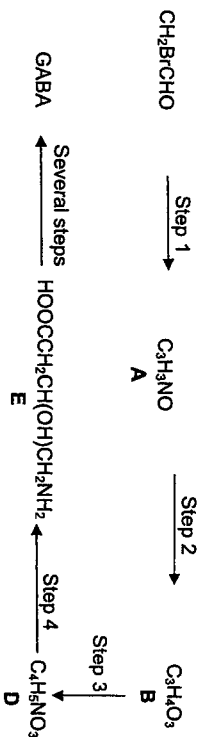
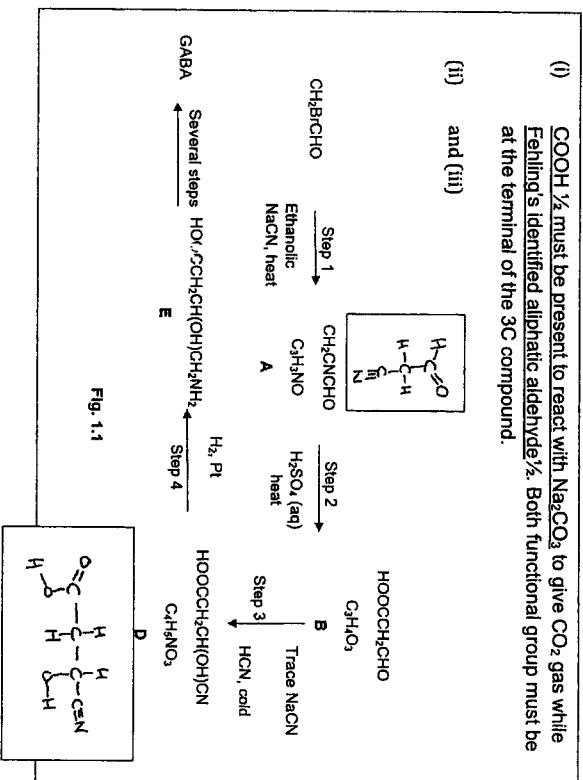


Fig. 3.1

Compound **B** gives effervescence with $\text{Na}_2\text{CO}_3(\text{aq})$ and it gives a brick red precipitate with warm Fehling's solution.

- (i) Suggest what these observations indicate about the functional groups in **B**. [1]
- (ii) Give the structures of compounds **A** and **D**. [2]
- (iii) Suggest reagents and conditions for steps 1, 2, 3 and 4 in Fig. 3.1. [4]
- (iv) Suggest why the yield for step 3 is very low. [1]
- (v) The conversion of **B** to **D** involves a nucleophilic addition. Suggest why only 50% of compound **D** can be used in drug synthesis. [2]



NJC/H2 Chem Preliminary Examination/03/2022

[Turn over

(iv) Presence of the COOH group suppresses the dissociation of HCN , reducing the concentration of :CN^- ion drastically; the reactive intermediate is protonated by the COOH group instead, so there is no more :CN^- ion present to react with the carbonyl carbon [1].

(v) :CN^- reacts with the trigonal planar carbonyl carbon with equal probability from above and below the plane, 1m
This gives rise to a racemic mixture ½ (optical isomers in 1:1 ratio).
Biological system can only work with one of the optical isomer (enantiomer) / msu be stereospecific. ½

- (b) Compound **E** undergoes intramolecular condensation reaction under suitable conditions. Isomer **F** is produced instead of isomer **G**.

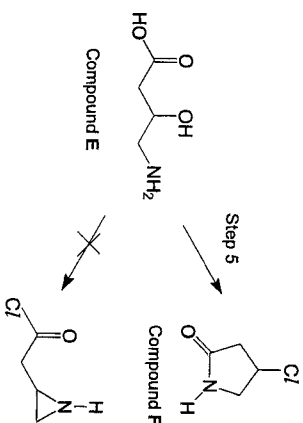


Fig. 3.2

- (i) Suggest the reagent and condition for step 5 in Fig. 3.2. [1]
- (ii) Give two reasons why isomer **F** is preferentially formed. [2]
- (iii) Explain why compound **F** is neutral. [2]

- (i) SOCl_2 , anhydrous / PCl_5 , anhydrous 1 or 0
- (ii)

Carboxyl C in acyl chloride is more partial positive/more electron deficient than C in C-Cl hence more likely to be substituted by N. 1

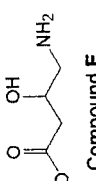
Compound G has a 3 membered ring ½, this is significantly less stable than the 5 membered ring in compound F as the bond angle in 3 membered ring is 60° which is far less than the optimum bond ½ angle of 109.5, predicted by VSEPR

NJC/H2 Chem Preliminary Examination/03/2022

- (iii) Lone pair of N is delocalised extensively $\frac{1}{2}$ into the carboxyl carbon due to the highly electronegative O $\frac{1}{2}$ electron density at N is significantly reduced due to resonance with carboxyl carbon with highly electronegative O
The lone pair $\frac{1}{2}$ is no longer available to receive a proton $\frac{1}{2}$, hence it is neutral.

- (c) Table 3.3 shows the pK_a values of different functional groups present in compound **E** and GABA.

Table 3.3

	pK_{a1} of carboxyl group	pK_{a2} of amino group
HOOCCH ₂ CH ₂ CH ₂ NH ₂ GABA	2.45	9.10
 Compound E	2.05	9.80

- (i) Suggest a reason why pK_{a1} value of compound **E** is of lower value than pK_{a1} of GABA. [1]
- (ii) Calculate the initial pH of 25.0 cm³ of 0.050 mol dm⁻³ of compound **E**. [1]
- (iii) Calculate the volumes of 0.10 mol dm⁻³ of NaOH required to form a buffer mixture with compound **E** at pH 2.05 and 9.80 respectively. [2]
- (iv) Sketch the pH-volume added curve you would expect when compound **E** is titrated against 0.10 mol dm⁻³ of NaOH. Include the volume and pH values given or calculated in (c)(ii) and (c)(iii) as well as the volumes required for each equivalence point.
You may assume that the graph tends towards pH 13 upon addition of excess NaOH. [2]
- (v) The working range for thymolphthalein is 9.3 to 10.5, comment on whether thymolphthalein is a suitable indicator for identifying the first endpoint. [1]
- (vi) Write two equations to describe how the buffer mixture at pH 9.80 from (c)(iii) can act as buffer when small amount of H⁺ or OH⁻ is added. [1]
- [Total: 23]

- (i) The additional OH group exerts electron withdrawing effect $\frac{1}{2}$ which further disperses the negative charge on the carboxylate ion $\frac{1}{2}$, making the conjugate base of **E** more stable than that from GABA, hence **E** undergoes greater acid dissociation with a smaller pK_{a1} value.

$$10^{-2.05} = \frac{[H^+]^2}{0.05}$$

$$[H^+] = 0.01257 \text{ mol dm}^{-3}$$

$$pH = 1.9 \text{ 1m}$$

- (ii) At pH 2.05 and 9.80, the conjugate acid base pair of pK_{a1} and pK_{a2} are equal in concentration.

This occurs when the COOH group is half neutralised.

$$\text{Amt of OH}^- \text{ required} = \text{amt of } -\text{COOH}$$

$$= \frac{1}{2} \times 0.025 \times 0.05$$

$$= 6.25 \times 10^{-4}$$

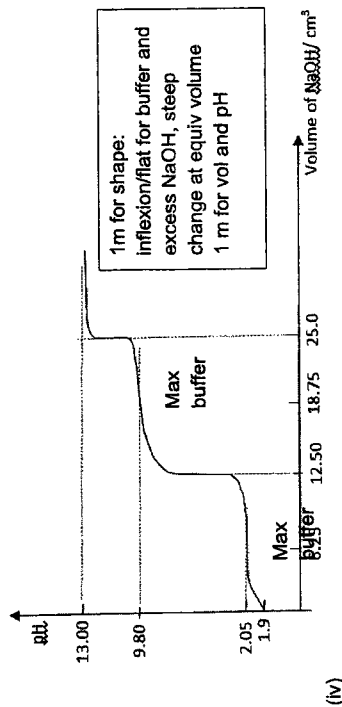
$$\text{Vol of NaOH required} = 6.25 \times 10^{-4} + 0.1 \times 1000$$

$$= 6.25 \text{ cm}^3 \text{ 1m}$$

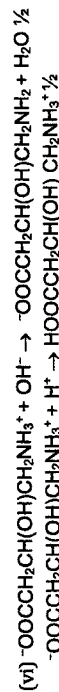
Vol of NaOH required for complete neutralisation of $-\text{COOH} = 12.50 \text{ cm}^3$

Another 6.25 cm³ more to neutralise half of $-\text{NH}_3^+$

So volume of NaOH required to form buffer at pH = 9.80 is 18.75 cm³. 1m

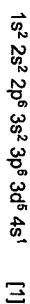


- (v) Thymolphthalein is not a suitable indicator $\frac{1}{2}$ for the first equivalence point as its working range is beyond the steep change in pH. $\frac{1}{2}$



Answer one question from this section.

- 4 (a) State the electronic configuration of chromium. [1]

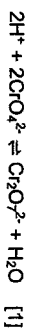


- (b) Chromium(VI) ions commonly exist as oxo-anions such as CrO_4^{2-} , which is yellow in color and $\text{Cr}_2\text{O}_7^{2-}$, which is orange.

- (i) Explain why chromium(VI) ions exist as oxo-anions instead of $[\text{Cr}(\text{H}_2\text{O})_6]^{6+}$. [1]

- (ii) Write the equation for the conversion of CrO_4^{2-} to $\text{Cr}_2\text{O}_7^{2-}$ in acidic medium. Predict the observation when NaOH is added to this solution at equilibrium. [2]

Cr^{6+} has high charge/size [$\frac{1}{2}$] and thus undergoes hydrolysis [$\frac{1}{2}$] in water to form a $\text{Cr}_2\text{O}_7^{2-}$ / is able to polarise the electron cloud of oxygen [$\frac{1}{2}$] to form an oxo-anion.



OH^- will react with H^+ hence the $[\text{H}^+]$ will decrease, POE will shift LHS [$\frac{1}{2}$] to partially offset the decrease, resulting in yellow color of CrO_4^{2-} observed. [$\frac{1}{2}$]

- (c) E is a hydrated salt containing 13.0 % of Cr, 27.0 % of H_2O and 60.0 % of Br by mass. When 0.400 g of E is dissolved in water, an octahedral complex cation is formed. When treated with aqueous silver nitrate, this solution immediately gives 0.188 g of cream precipitate.

- (i) Calculate the mole ratio of Cr: H_2O : Br in the hydrated salt E. [1]

- (ii) Identify the cream precipitate and hence, determine the formula of the complex cation formed when E is dissolved in water. [2]

- (iii) Draw the structure of the complex cation present in E, showing clearly how the ligands are arranged around chromium cation. Indicate the overall charge of this complex ion. [1]

Cr(i)	Cr	H_2O	Br
% by mass	13.0	27.0	60
No. of moles	0.25	1.5	0.75
Mole ratio	1	6	3 [1]
Formula	$\text{Cr}(\text{H}_2\text{O})_6(\text{Br})_3$		

Cr(ii) Cream precipitate: AgBr [1]

No. of moles of AgBr = $0.188 / (108 + 79.9) = 0.00100$ mol

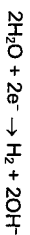
No. of moles of E = $0.400 / (52.0 + 6(18.0) + 3(79.9)) = 0.00100$ mol

No. of moles of Br^- anion : No of moles of E

1 : 1

- (d)

When a current of 1.0 A was passed through aqueous potassium maleate ($\text{KO}_2\text{CCH}=\text{CHCO}_2\text{K}$) for 15 minutes, it was found that 110 cm^3 H_2 measured at r.t.p. was collected at the cathode. The following reaction took place.



Ethyne, C_2H_2 , and CO_2 gas were produced at the anode. In order to determine the stoichiometry of the anode reaction, the volume of the gases collected at the anode was measured. The anode gas was first passed through aqueous NaOH before being collected in a gas syringe. The following data was collected:

- mass of bottle containing NaOH before experiment = 10.501 g
- mass of bottle containing NaOH after experiment = 10.904 g
- initial reading on syringe = 10.0 cm^3
- final reading on syringe = 120.0 cm^3

- (i) Using the data obtained from the cathode and the Data Booklet, calculate a value for Faraday constant. [2]

- (ii) Calculate the volume of CO_2 produced at the anode, assuming r.t.p. conditions. [2]

- (iii) Hence, state the volume of ethyne gas and suggest an ionic equation for the reaction that occurred at the anode. [2]

$$(i) Q = It = n_e F$$

$$Q = 1.0 \times 15 \times 60 = 900 \text{ C [1]}$$

$$n(\text{H}_2) = 110 / 24000 = 0.00458 \text{ mol}$$

$$n(\text{e}^-) = 2 n(\text{H}_2) = 0.00917 \text{ mol}$$

$$F = 900 / (0.00917) = 98100 \text{ (3sf) [1]}$$

.....

.....

.....

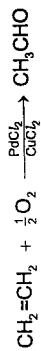
.....

.....

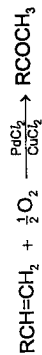
.....

.....

- (e) Ethanal used to be manufactured from ethyne. These days, ethene is being used as the reactant instead. Widely known as the Wacker-Tsuji Oxidation, ethene and oxygen are bubbled together through an aqueous solution containing CuCl_2 and PdCl_2 catalysts:



The Wacker-Tsuji Oxidation is also useful for the synthesis of ketone:

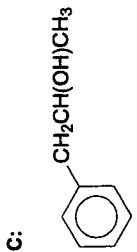
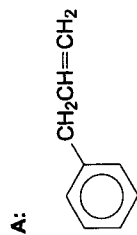
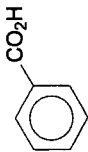


Compound **A**, C_8H_{10} , is used as a reactant in the Wacker-Tsuji oxidation reaction to give compound **B**, $\text{C}_8\text{H}_{10}\text{O}$. **B** gives a yellow precipitate when warmed with aqueous alkaline I_2 . When **B** is reacted with LiAlH_4 in dry ether, compound **C** is formed. **A**, **B** and **C** all react with hot acidified KMnO_4 to give compound **D**, $\text{C}_7\text{H}_6\text{O}_2$.

Suggest the structures of Compound **A** to **D** and explain the reactions described. [6]

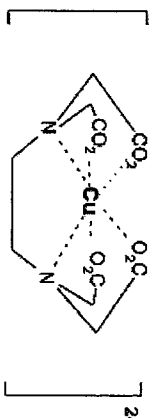
Clues	Deductions
Compound A has molecular formula C_8H_{10}	A contains benzene A has degree of unsaturation = 5
Since A undergo Wacker-Tsuji oxidation B gives a yellow precipitate when warmed with aqueous alkaline I_2 .	It must contain a terminal alkene B is the product of Wacker-Tsuji oxidation and is a carbonyl compound. B must be a methyl carbonyl.
B is reacted with LiAlH_4 in dry ether	B undergo reduction
A , B and C all react with hot acidified KMnO_4	A , B , C all undergo side chain oxidation to give the same product A , B , C all have only 1 alkyl side chain.

D must be the product of side chain oxidation:

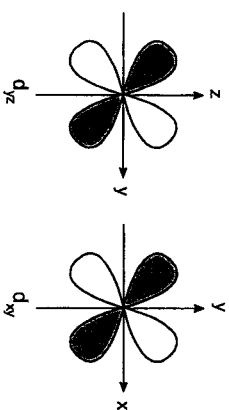


- 5 (a) Copper and its compounds have a wide variety of uses. Copper-EDTA complexes are commonly used in cosmetics and it gives the blue colour in many shampoos.

The structure of the copper-EDTA complex is given below.



- (i) State the electronic configuration of the copper ion in the copper-EDTA complex. [1]
- (ii) Two of the d orbitals are given below. Sketch the shapes of the other three d orbitals present in copper, labelling your orbitals clearly. [3]



- [2]
- (iii) Explain why the copper-EDTA complex is blue. [3]

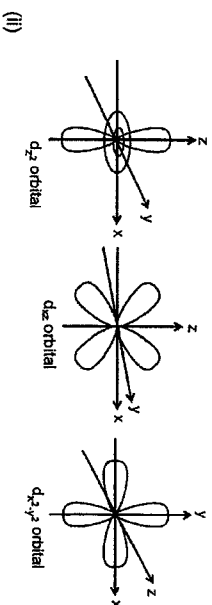
(i) Let oxidation number of Cu be x.

Since each carboxylate is a -1 charge

$X + (-4) = -2$

$X = +2$

$\text{Cu}^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$



3/3 (including label for orbitals and appropriate axis) - [2]

2/3 - [1] 1/3 - [½] without 3d axis-0/1/1

(iii) In the presence of EDTA ligands, the degenerate d-orbitals of the Cu^{2+} ion are split into two different energy levels with a small energy gap, ΔE . [1]
Electrons in the lower energy d-orbitals can absorb light of a certain wavelength with energy corresponding to the energy gap, ΔE , and be promoted to the higher energy d-orbitals. [1] (d-d transition).

The light not absorbed would be reflected and the colour of the complex is the complementary of the wavelength absorbed! [1], giving rise to a colour observed

- (iv) Cobalt and copper are both common transition elements.

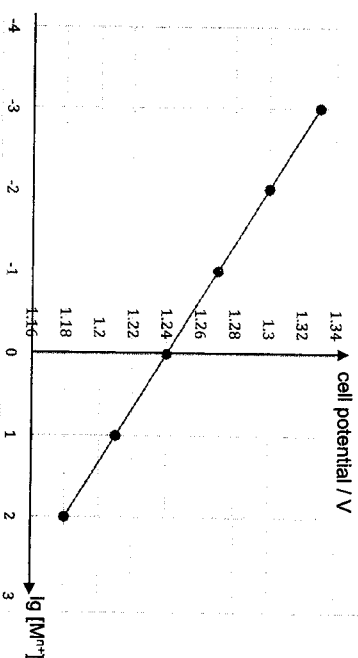
Comment on the similarity of the atomic radii between cobalt and copper. [1]

Nuclear charge increases from Co to Cu while shielding effect also increases [½] as electrons are added to the inner 3d subshell. As such, nuclear attraction remains relatively constant [½] and their atomic radii are similar.

- (b) An experiment was set up to investigate how the cell potential of a cell containing a metal, M, in contact with an aqueous solution of its ions, $\text{M}^{n+}(\text{aq})$, changed as $\text{M}^{n+}(\text{aq})$ was diluted.
As a standard Hydrogen Electrode was not available, a half-cell consisting of Cl^- , ClO^- in alkaline medium under standard conditions was used to connect to the half-cell with M in contact with $\text{M}^{n+}(\text{aq})$.

- (i) Draw a fully labelled diagram of the electrochemical cell set-up as described above, in order to measure the changes in cell potential. [3]

- (ii) The cell potential was measured for various concentrations of $\text{M}^{n+}(\text{aq})$ and the results of cell potential against $\log [\text{M}^{n+}]$ obtained are plotted in the graph as shown below.



Given that the cell potential of a cell, E_{cell} , is related to the standard electrode potential, E°_{cell} , by the equation:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.06 \lg[M^{n+}]}{n}$$

use your graph to determine

- (i) the charge, n , of the M^{n+} ions [2]
 (ii) the E°_{cell}
- (iii) Given that the standard electrode potential for Cl^- , ClO^- in alkaline conditions is $+0.80 \text{ V}$.

Calculate the standard electrode potential of the metal, M , and suggest its identity. [2]

metal M electrode

Pt electrode

1 mol dm⁻³ of each Cl^- , OH^- 25°C

$M^{n+}(\text{aq})$ ions

each electrode within half cell [½]
 each correct label of species and concentration [½]
 salt bridge [½]
 voltmeter [½]
 if battery use instead – max 1m

(ii) Gradient = -0.0300
 $-0.06 / n = -0.0300$
 $n = 2$ [1]
 $\log_{10} 1 = 0$
 y-intercept = 1.24 V [1] or uses equation to calculate
 (iii) $1.24 = E(\text{ClO}^-/\text{Cl}^-) + E_{\text{ox}}(M/M^{2+})$
 $= +0.80 + E_{\text{ox}}(M/M^{2+})$
 $(E_{\text{ox}}(M/M^{2+}) = +0.44 \text{ V}$ [½])
 $E(M^{2+}/M) = -0.44 \text{ V}$ [1]
 $M = \text{Fe}$ [1]

- (c) In the presence of HClO_4 , alcohols react with nitriles to form N -alkylamides. This is known as the *Ritter reaction*, as shown in Fig. 5.1.

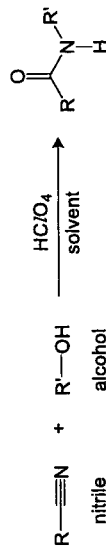


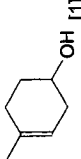
Fig. 5.1

Compounds **A** and **B** react in the presence of HClO_4 to give compound **C** via the Ritter reaction.

Compound **A** has the molecular formula $\text{C}_4\text{H}_{10}\text{O}$. When heated under reflux with acidified $\text{K}_2\text{Cr}_2\text{O}_7$, it gives a product that gives a yellow precipitate when warmed with aqueous alkaline iodine.

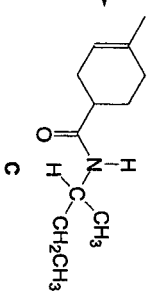
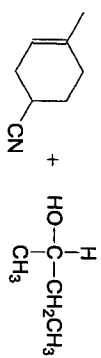
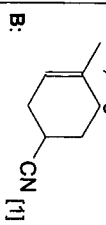
Compound **D** is a 6-membered ring molecule and has the molecular formula $\text{C}_7\text{H}_{12}\text{O}$. When heated with acidified KMnO_4 , it forms $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_2\text{CO}_2\text{H}$. **D** reacts with PCl_5 followed by hot ethanolic KCN to give **B**.

Suggest the structures of compounds **A** to **D** and explain the reactions described. [6]

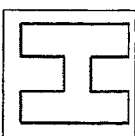
Clue	Deductions
A has the molecular formula $\text{C}_4\text{H}_{10}\text{O}$ and undergo the Ritter reaction.	A must be an alcohol.
A react with hot acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to give a product gives a yellow precipitate when warmed with aqueous alkaline iodine	A undergo oxidation to give alcohol A must be secondary alcohol. A : $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ [1]
D has the molecular formula $\text{C}_7\text{H}_{12}\text{O}$.	D has 6-membered ring structure.
D undergo oxidation to give $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_2\text{CO}_2\text{H}$	Increase of 4 O upon oxidation. D must be a ring structure with ketone Making use of the formula of the product of D 's oxidation: D must be  [1]

D reacts with gaseous HCl followed by hot ethanolic KCN to give **B**

B is formed from **D** undergoing two nucleophilic sub: 1) to give a RX and then 2) to give RCN. [1]



From pattern given in question, C is deduced. [1]



NATIONAL JUNIOR COLLEGE
SH2 Year-End Practical Examination
Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

9729/04

Paper 4 Practical

16 August 2022

Candidates answer on the Question paper

2 hours 30 minutes

Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your identification number and name.

Give details of the practical shift and laboratory where appropriate, in the boxes provided. Write in 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. You may lose marks if you do not show your working or if you do not use appropriate units. Qualitative Analysis Notes are printed on pages 22 and 23.

At the end of the examination, fasten all your work securely together. The number of marks is given in brackets [] at the end of each question or part question.

This document consists of 23 printed pages including this cover page.

Shift
Laboratory

For Examiner's use	
1	/ 9
2	/ 21
3	/ 17
4	/ 8
Total	/ 55

Answer all the questions in the spaces provided.

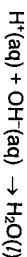
1 Determination of the enthalpy change of a reaction, ΔH_r

FA 1 is 1.00 mol dm⁻³ sodium hydrogen carbonate, NaHCO₃ (to be used for Q3 as well)

FA 2 is 2.00 mol dm⁻³ sodium hydroxide, NaOH

FA 3 is 2.00 mol dm⁻³ sulfuric acid, H₂SO₄

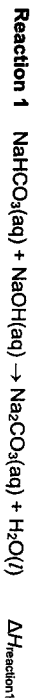
An acid-base neutralisation reaction involves reacting the two solutions, to produce water molecules. The equation for this neutralisation reaction is given below.



You will follow the instructions to perform two experiments, **Experiment A** and **Experiment B**. Record your results in **Tables 1.1** and **1.2**.

Experiment A

Reaction between **FA 1**, NaHCO₃, and **FA 2**, NaOH.



The molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction 1}}$, is the enthalpy change when 1.00 mol of NaHCO₃ reacts completely with NaOH.

- Using a 50 cm³ measuring cylinder, transfer 30.0 cm³ of **FA 1** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm³ glass beaker. Place the lid on the cup.
- Stir and measure the temperature of this **FA 1**, T_{FA1} .
- Using another 50 cm³ measuring cylinder, measure 20.0 cm³ of **FA 2**.
- Stir and measure the temperature of this **FA 2**, T_{FA2} .
- Add **FA 2** from the measuring cylinder to the **FA 1** in the Styrofoam cup. Immediately replace the lid.
- Using the thermometer, stir the mixture continuously until a maximum temperature is reached. Read and record this temperature T_{max} .
- Calculate the weighted average initial temperature, T_{average} , of **FA 1** and **FA 2** using the formula given below:

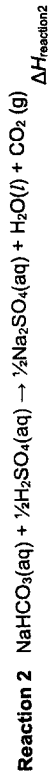
$$T_{\text{average}} = \frac{(V_{\text{FA1}} \times T_{\text{FA1}}) + (V_{\text{FA2}} \times T_{\text{FA2}})}{(V_{\text{FA1}} + V_{\text{FA2}})}$$

Experiment A	
T_{FA1} /°C	
T_{FA2} /°C	
T_{average} /°C	
T_{max} /°C	
ΔT_{max} /°C	

Table 1.1

Experiment B

Reaction between **FA 1**, NaHCO_3 , and **FA 3**, H_2SO_4 .



The molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction 2}}$, is the enthalpy change when 1.00 mol of NaHCO_3 reacts completely with H_2SO_4 .

- Using a measuring cylinder, transfer 30.0 cm^3 of **FA 1** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker. Place the lid on the cup.
- Stir and measure the temperature of this **FA 1**, T_{FA1} .
- Using another measuring cylinder, measure 20.0 cm^3 of **FA 3**.
- Stir and measure the temperature of this **FA 3**, T_{FA3} .
- Add slowly, the **FA 3** from the measuring cylinder to the **FA 1** in the Styrofoam cup. Immediately replace the lid.
- Using the thermometer, stir the mixture continuously until a minimum temperature is reached. Read and record this temperature T_{min} .
- Calculate the weighted average initial temperature, T_{average} , of **FA 1** and **FA 3** using the formula given below:

$$T_{\text{average}} = \frac{(V_{\text{FA1}} \times T_{\text{FA1}}) + (V_{\text{FA3}} \times T_{\text{FA3}})}{(V_{\text{FA1}} + V_{\text{FA3}})}$$

	Experiment B
T_{FA1} / °C	
T_{FA3} / °C	
T_{average} / °C	
T_{min} / °C	
ΔT_{max} / °C	

Table 1.2

[2]

For both Tables 1.1 & 1.2:
 1m - All temperature readings are recorded to the nearest 0.1 °C.
 1m - $\Delta T_{\text{max/min}}$ must be correctly calculated (with sign -ve) i.e. T_{max} - average initial temperature.

(a) For the purpose of calculations, you should assume that the mixture has a density of 1.00 g cm^{-3} and specific heat capacity, c , of 4.18 $\text{J g}^{-1} \text{K}^{-1}$.

- (i) Use your results from Table 1.1 to calculate a value for the molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction1}}$.

$$q = (20.0 + 30.0)(1.00) \times 4.18 \times \Delta T_{\text{max}} \quad 1\text{m}$$

$$n(\text{NaHCO}_3) = 1.00 \times 30.0/1000 = 0.03 \text{ mol}$$

$$\Delta H_{\text{reaction1}} = -q / n(\text{NaHCO}_3) \quad (\text{this reaction is exothermic}) \quad 1\text{m (with unit)}$$

$$\Delta H_{\text{reaction1}} = \dots\dots\dots [2]$$

- (ii) Use your results from Table 1.2 to calculate a value for the molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction2}}$.

$$q = (20.0 + 30.0)(1.00) \times 4.18 \times \Delta T_{\text{min}} \quad 1\text{m}$$

$$n(\text{NaHCO}_3) = 1.00 \times 30.0/1000 = 0.03 \text{ mol}$$

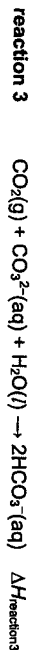
$$\Delta H_{\text{reaction1}} = +q / n(\text{NaHCO}_3) \quad (\text{this reaction is endothermic}) \quad 1\text{m (do not penalise if no units if already penalised in part 1)}$$

$$\Delta H_{\text{reaction2}} = \dots\dots\dots [2]$$

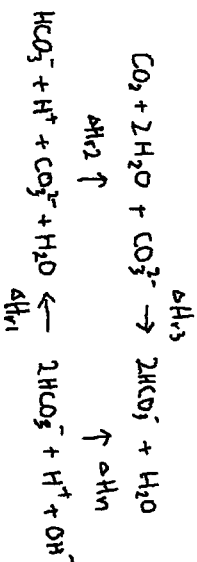
(b) Ionic equations for neutralisation, reaction 1, and reaction 2 are shown below.

$\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(l)$	$\Delta H_{\text{rxn}} = -57.1 \text{ kJ mol}^{-1}$
$\text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(l)$	$\Delta H_{\text{reaction 1}}$
$\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(\text{g})$	$\Delta H_{\text{reaction 2}}$

Carbon dioxide reacts with solutions of carbonate ions according to the following equation.



Using your calculated answers in (a), together with the given value of enthalpy change of neutralisation, ΔH_{rxn} , construct an energy cycle to determine a value for the enthalpy change for this reaction, $\Delta H_{\text{reaction 3}}$.



$$\Delta H_{\text{reaction 3}} = (-\Delta H_{\text{rxn}}(\text{iii})) + (-\Delta H_{\text{rxn}}(\text{i})) + (-57.1)$$

1m – cycle

1m – substitute values correctly in eqn

1m – final ans

$$\Delta H_{\text{reaction 3}} = \dots\dots\dots [3]$$

[Total: 9]

2 Qualitative analysis of some organic and inorganic compounds

You are provided with liquids FA 4, FA 5, FA 6, FA 7, and FA 8.

You are to perform the tests described in Tables 2.1 and 2.3 and record your observations.

At each stage of any test, you are to record details of the following:

- colour changes seen
- the formation of any precipitate and its solubility in an excess of the reagent added
- the formation of any gas and its identification by a suitable test
- if there is no observable change, write **no observable change**

You should indicate clearly at which stage in a test a change occurs, recording your observations alongside the relevant tests.

In all tests, the reagents should be added gradually until no further change is observed unless you are instructed otherwise. If any solution is warmed, a boiling tube must be used. Rinse and reuse test-tubes where possible.

No additional or confirmatory tests for ions present should be attempted.

(a) FA 4, FA 5, FA 6 and FA 7 are organic compounds with the molecular formula shown.

- FA 4: $\text{C}_6\text{H}_{10}\text{O}$
- FA 5: $\text{C}_8\text{H}_{16}\text{O}$
- FA 6: $\text{C}_8\text{H}_{16}\text{O}$
- FA 7: $\text{C}_8\text{H}_{16}\text{O}_2$

You will perform some of the tests described in Table 2.1.

Using the observations in Table 2.1 and the given molecular formula, you will then deduce the identities of FA 4, FA 5, FA 6 and FA 7.

Perform the tests given in Table 2.1. Some of the observations have been completed for you. There is no need to carry out those tests. Record your observations in Table 2.1.

Safety: Organic compounds are flammable. Transfer your organic waste into the waste bottle for disposal after the end of the assessment.

Test	Procedure	Observations with FA 4, C ₂ H ₆ O Propanal	Observations with FA 5, C ₃ H ₈ O Propanone	Observations with FA 6, C ₃ H ₈ O Propan-2-ol	Observations with FA 7, C ₃ H ₇ O ₂ Propanoic acid
1.	[Z-4-DNPH] To 1 cm depth of unknown liquid, add 1 cm depth of 2,4-dinitrophenylhydrazine solution.	Orange precipitate observed	Orange precipitate observed	No observable change	No observable change
2.	To 1 cm depth of unknown liquid, add aqueous sodium carbonate. Test for and identify any gas evolved.	No observable change	No observable change	No observable change	No observable change
3.	[Iodoform Test] To 1 cm depth of unknown liquid, add 8 drops of aqueous sodium hydroxide followed by iodine solution dropwise, until a permanent orange/red colour is present. Warm the mixture in a beaker of hot water for two minutes.	No observable change	Yellow precipitate observed	Yellow precipitate observed	No observable change

4.	[Tollens' reagent] To 1 cm depth of aqueous silver nitrate, slowly add 1 cm depth of aqueous sodium hydroxide. Add aqueous ammonia slowly, with shaking, until the precipitate formed dissolves. You may use a clean glass rod to stir the mixture and help dissolve the precipitate. Add 1 cm depth of unknown liquid to this mixture, shake the tube and let it stand.	Yellow precipitate observed	No observable change	No observable change	No observable change
----	-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	-----------------------------	----------------------	----------------------	----------------------

Table 2.1

¼ m for each correct observation

(b) Complete Table 2.2 with the identities of FA 4, FA 5, FA 6, and FA 7.

Give evidence from the observations in Table 2.1 to support your conclusions.

Compound	Evidence
FA 4 Propanal	Positive Tollen's test suggest it is an aldehyde. Hence, propanal.
FA 5 Propanone	Positive 2,4 DNP test and negative Tollen's suggests it's a ketone. Positive triodomethane test suggests it's a methyl ketone. Hence, propanone.
FA 6 Propan-2-ol	Positive triiodomethane test but negative 2,4 DNP test suggests it's a methyl alcohol. Hence propan-2-ol. Allow propanol if all negative observation.
FA 7 Propanoic acid	Effervescence with Na_2CO_3 suggests it's a carboxylic acid. Hence propanoic acid.

Table 2.2

1m for each correct compound + required evidence in red

[4]

FA 8 is a mixture of two salts and contains two cations.

You will perform a series of test-tube reactions and use the observations to help you identify the two cations.

(c)	Test	Observation
1.	Test the FA 8 solution using Universal indicator paper.	<ul style="list-style-type: none"> Universal indicator paper turns orange pH 3 – 4
2.	Prepare about 2 cm ³ of dilute sulfuric acid in a clean test tube.	<ul style="list-style-type: none"> White ppt formed accept if grey/grey-green then green ppt insoluble in excess NaOH (turning brown in contact with air)
3.	Place about 2 cm ³ of FA 8 into another clean test-tube. Carefully add aqueous sodium hydroxide, dropwise with shaking, until no further change is seen.	<ul style="list-style-type: none"> green residue turns brown in contact with air/ brown residue obtained colourless/pale yellow filtrate White ppt observed
3.	Swift and filter the mixture, collecting the filtrate in the test tube containing dilute sulfuric acid.	<ul style="list-style-type: none"> Observe the residue and filtrate until no further change is seen.
3.	To 1cm ³ of FA 8, carefully add aqueous potassium manganate, dropwise with shaking, until no further change is seen.	<ul style="list-style-type: none"> Purple KMnO_4 decolourises Colourless solution turns yellow Orange/ Brown (eventually purple)

Table 2.3

½ m for each point

[5]

(d) (i) Identify the cations in FA 8.

Cation 1: Fe^{3+}

Cation 2: Al^{3+}

[2]

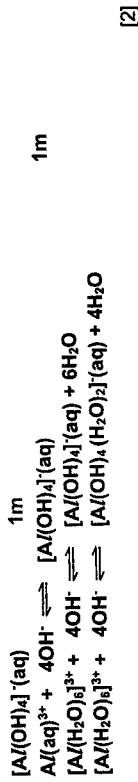
(ii) With the aid of an equation, explain the observation for Test 1 in Table 2.3.



From test 1, colour of Universal indicator paper is orange which shows that the solution is acidic (pH = 3). Al^{3+} has high charge over size ratio, polarises and weakens the O-H bond of H_2O , causing one of the six H_2O to undergo hydrolysis to give $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ and H_3O^+ , resulting in an acidic solution.
(Give 1m if hydrolysis explained correctly even if cation is absent or wrong)

[2]

(iii) Identify the metal-containing complex formed when excess sodium hydroxide is added to FA 8. Write equations to illustrate the formation of this complex.



(iv) FA 8 contains either the sulfate ion or a halide anion.

Describe two tests, using only the bench reagents provided, which will allow you to identify the anion present.

In each case, state how you will decide if the test result is positive.

[You DO NOT need to carry out these tests.]

Test 1: Add AgNO₃ 1m
 No ppt – SO₄²⁻
 Ppt – halide

Test 2: Add NH₃(aq) to determine solubility of ppt formed in test 1 1m
 White ppt, soluble – Cl⁻
 Cream ppt, partially soluble – Br⁻
 Yellow ppt, insoluble – I⁻

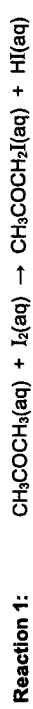
..... [2]
 [Total: 21]

3 To determine the order of reaction with respect to the concentration of iodine in the iodination of propanone reaction

- FA 12 is 1.00 mol dm⁻³ propanone, CH₃COCH₃
- FA 13 is 1.00 mol dm⁻³ sulfuric acid, H₂SO₄
- FA 14 is an aqueous solution of iodine, I₂
- FA 15 is 0.0150 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃
- FA 1 is 1.00 mol dm⁻³ sodium hydrogen carbonate, NaHCO₃ (same solution used in Q1)

You are also provided with a starch indicator.

The iodination of propanone, to form iodopropanone, proceeds as shown in the equation below.

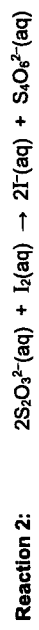


This reaction is first order with respect to both CH₃COCH₃ and H⁺ ions.

You are to investigate the order of reaction with respect to I₂.

A reaction mixture containing FA 12, FA 13, and FA 14 is first prepared. At different chosen times, aliquots (fixed volumes) of this reaction mixture is removed and quenched using excess FA 1.

It is necessary that you titrate each aliquot against FA15 before transferring the next aliquot. I₂ and S₂O₃²⁻ react as shown in Reaction 2.



The required order of reaction can be obtained by the graphical analysis of your results.

The first aliquot should be removed approximately 4 minutes after the reagents were mixed. You will then remove four further aliquots, at time intervals of your choice, up to a maximum time of 30 minutes.

In an appropriate format in the space provided on page 14, prepare a table in which to record for each aliquot

- the time of transfer, *t*, in minutes and seconds,
- the decimal time, *t*_d, in minutes, to 0.1 min, for example, if *t* = 4 min 33 s then *t*_d = 4 min + 33/60 = 4.6 min,
- the burette readings and the volume of FA 15 added.

Safety: Propanone is flammable. Transfer your titrated solutions into the waste bottle for later disposal.

Keep the conical flask (reaction mixture) stoppered except when removing aliquots.

Experiment

NOTE READ THE FULL PROCEDURE BEFORE STARTING YOUR EXPERIMENT

- Label each of the boiling tubes 1 to 5.
- Add approximately 10 cm³ of FA 1 to each of these boiling tubes.
- Fill a burette with FA 15

Preparing the reaction mixture

- Using a 50 cm³ measuring cylinder, transfer 25.0 cm³ of FA 12 into the 100 cm³ beaker.
- Using the same 50 cm³ measuring cylinder, transfer 25.0 cm³ of FA 13 into the same 100 cm³ beaker.
- Using another 50 cm³ measuring cylinder, transfer 50.0 cm³ of FA 14 into the 250 cm³ conical flask, labelled reaction mixture.
- Pour the contents of the 100 cm³ beaker into this 250 cm³ conical flask. Start the stopwatch, insert the stopper and swirl the mixture thoroughly. Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You must not stop the stopwatch until you have collected all of your aliquots.

Removing aliquots of reaction mixture and titration

- At approximately 4 minutes, using a 10.0 cm³ pipette, remove a 10.0 cm³ aliquot of the reaction mixture.
- Immediately transfer this aliquot into the boiling tube labelled 1 and swirl the mixture. Read and record the transfer time in minutes and seconds, to the nearest second, when half of the reaction mixture has emptied from the pipette. Replace the stopper in the flask.
- Pour all the contents of boiling tube 1 into a clean 250 cm³ conical flask. Wash out the boiling tube and add the washings to the conical flask.
- Titrate the iodine in this solution with FA 15. Add about 1 cm³ of starch indicator when the colour of the solution turns pale yellow. The solution will turn blue-black. The end-point is reached when the dark blue-black colour just disappears. Record your results.
- Empty the contents of this conical flask into the waste bottle. Wash this conical flask thoroughly with water.
- At approximately 8 minutes, repeat points 8 to 12. Transfer this aliquot into the boiling tube labelled 2.
- Repeat point 8 to 12 for the remaining boiling tubes at about four-minute intervals.

(a) Results

Actual time	t/min	Initial burette reading/cm ³	Final burette reading/cm ³	Volume of FA 15 used/cm ³
4 min 6s	4.1	0.00	15.90	15.90
8 min 3s	8.1	15.90	30.30	14.40
12 min 3s	12.1	0.00	12.90	12.90
15 min 56s	15.9	12.90	24.40	11.50
19 min 59s	20.0	24.40	34.50	10.10

[1]: Tabulates initial and final burette readings, volume of FA 15 added, chosen time, actual time and decimal time with correct headers and units

[4]

[1]: record all volumes to 0.05 cm³, actual time in min and s, correct calculation of t to 1 dp

[1]: Data collected within 30 min

[1]: correct conversion of t to t_d

- (b) (i) On Fig 3.1, plot a graph of volume of sodium thiosulfate, FA 15, on the y-axis, against decimal time, t_d , on the x-axis. Start the x-axis at $t_d = 0$. You should choose a scale which will allow you to extrapolate your graph back to $t_d = 0$.
 Draw the most appropriate best-fit line taking into account all of your plotted points.

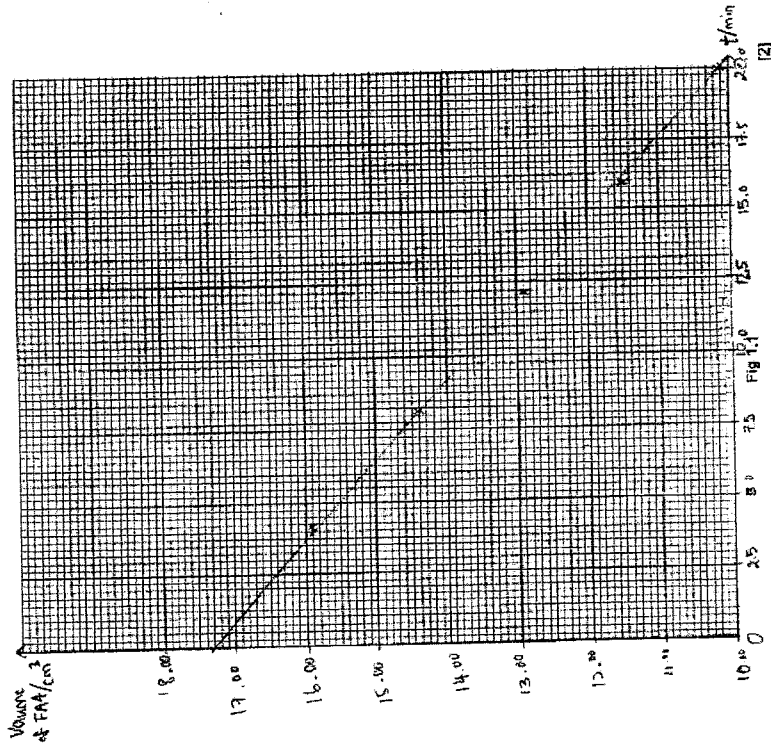


Fig 3.1

[3]

[1]: Both axes are correctly labelled + Scale must be chosen so that plotted points occupy at least half the graph grid in both x and y directions (taking into consideration the extrapolation) + no odd scale

[1]: One plotted point is within $\pm \frac{1}{2}$ small square

[1]: Drawing best fit straight line – Data points must reflect a str line

- (ii) Deduce the order of reaction with respect to the I_2 in reaction 1. Explain your answer.

Order of reaction is zero with respect to I_2
 Graph is a straight line with constant gradient / rate of reaction is independent of $[I_2]$ / $[I_2]$ decreases linearly with time / $[I_2]$ does not affect rate / $[I_2]$ decreases at a constant rate.
 1 or 0 [1]

- (c) (i) Write the rate equation for the iodination of propanone.

Rate = $k [CH_3COCH_3][H^+]$ 1m with ecf [1]

- (ii) Calculate the gradient of the line you have drawn in Fig 3.1, showing clearly how you did this.

Gradient = $\frac{y_2 - y_1}{x_2 - x_1} = \frac{9 - 14.8}{18.75} = -0.309 \text{ cm}^3 \text{ min}^{-1} \text{ (3 s.f.)}$ 1m
 Show construction lines on graph + coordinates on the graph or in the working

gradient = $\text{cm}^3 \text{ min}^{-1}$ [1]

- (iii) Use your answer from (c)(ii) to determine the rate of change of amount of $S_2O_3^{2-}$ ions required in mol min^{-1} .

rate of change = (c)(ii) $\times 0.01/1000$
 $= 0.309 \times 0.01/1000$
 $= 3.09 \times 10^{-6}$
 $= 3.09 \times 10^{-6} \text{ mol min}^{-1} \text{ (3 s.f.)}$ 1m

rate of change of amount of $S_2O_3^{2-}$ ions required = mol min^{-1} [1]

- (iv) Hence, deduce the rate of disappearance of I_2 in mol min^{-1} .

$I_2 \rightleftharpoons 2S_2O_3^{2-}$
 rate of disappearance of $I_2 = \frac{1}{2} \times$ (c)(iii)
 $= \frac{1}{2} \times 3.09 \times 10^{-6}$
 $= 1.545 \times 10^{-6}$
 $= 1.55 \times 10^{-6} \text{ mol min}^{-1} \text{ (3 s.f.)}$ 1m

rate of disappearance of $I_2 =$ mol min^{-1} [1]

- (v) Use your answer from (c)(iv) to calculate the rate of change of $[I_2]$ in the reaction mixture.

$$\begin{aligned} \text{rate of change of } [I_2] &= (c)(iv) \div 10/1000 \\ &= 1.545 \times 10^{-4} \div 10/1000 \\ &\approx 1.55 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1} \text{ (3 s.f. with units)} \end{aligned} \quad 1m$$

rate of change of $[I_2]$ in the reaction mixture = mol $\text{dm}^{-3} \text{ min}^{-1}$ [1]

- (vi) Hence, calculate the value of the rate constant for this reaction, giving its units.

$$\begin{aligned} (c)(v) &= k[CH_3COCH_3][H^+] \\ 1.545 \times 10^{-4} &= k [CH_3COCH_3][H^+] \\ 1.545 \times 10^{-4} &= k(1.00 \times 1/2)(1.00 \times 2 \times 1/2) \\ k &= 1.24 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1} \text{ (3 s.f. with units)} \end{aligned} \quad 1m \text{ for ans } 1m \text{ for units}$$

rate constant = [2]

- (d) Step 7 requires you to mix each aliquot immediately with an excess of sodium hydrogen carbonate solution, FA 1. Suggest a clear explanation for this requirement.

It is added to react with acid catalyst $\frac{1}{2}$ m so that the reaction will stop $\frac{1}{2}$ m / It is to quench the reaction by reacting with the acid catalyst. [1]

- (e) Explain why the concentration of iodine in FA 14 used is very much lower than the concentrations of propanone in FA 12 and of H^+ ions in FA 13.

The low concentration of iodine means that very little propanone and acid are reacted away from the reaction mixture and hence the concentration of propanone and acid remain effectively constant. Hence, the order of reaction with respect to iodine can be determined because any change in the rate is due to the change in concentration of iodine. 1m [1]

[Total: 17]

4 Planning – Extension to Q3

You are to plan a series of experiments to verify that the order with respect to propanone in the iodination of propanone is 1.



This investigation can be carried out by monitoring the time taken for the colour of a limited amount of iodine to be discharged when reacting with varying concentrations of propanone.

You may assume that it takes approximately 1 minute for the iodine colour to be discharged when a mixture of 20 cm^3 of 2.00 mol dm^{-3} of propanone, CH_3COCH_3 and 10 cm^3 of 1.00 mol dm^{-3} sulfuric acid, H_2SO_4 is reacted with 10 cm^3 of 1.00 mol dm^{-3} iodine, I_2 and 1 cm^3 of starch.

You may assume that you are provided with:

- Only 60 cm^3 of 2.00 mol dm^{-3} propanone, CH_3COCH_3
- 1.00 mol dm^{-3} sulfuric acid, H_2SO_4
- 1.00 mol dm^{-3} solution of iodine, I_2
- 100 cm^3 volumetric flasks
- starch indicator
- stopwatch
- the equipment normally found in a school or college laboratory.

To obtain 1.00 mol dm^{-3} propanone:

- 1) Using a burette, transfer 50 cm^3 of 2.00 mol dm^{-3} propanone to a 100 cm^3 volumetric flask.
- 2) Top up to the mark with deionised water.
- 3) Shake to ensure homogeneous solution.

Repeat steps 1 to 3 with 1.00 mol dm^{-3} propanone to obtain 0.50 mol dm^{-3} propanone.
Repeat steps 1 to 3 with 0.50 mol dm^{-3} propanone to obtain 0.25 mol dm^{-3} propanone.
Repeat steps 1 to 3 with 0.25 mol dm^{-3} propanone to obtain 0.125 mol dm^{-3} propanone.

[1] Serial dilution concept

[1] Correct dilution procedure
- top up to mark
- shake to ensure homogenous
- apparatus

[2]

(b) Plan a procedure to collect sufficient data to allow a graph to be plotted to determine the order of reaction with respect to propanone.

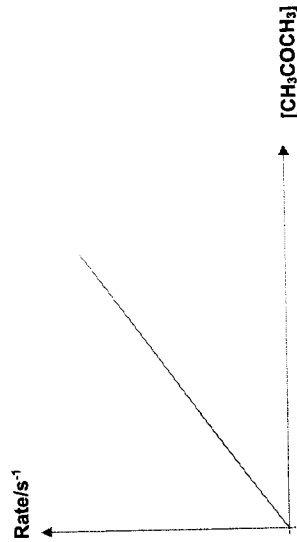
You are to use the 1.00 mol dm^{-3} , 0.50 mol dm^{-3} , 0.25 mol dm^{-3} and $0.125 \text{ mol dm}^{-3}$ propanone solutions you have prepared in (a) in your procedure.

In your plan you should include brief details of:

- the apparatus you would use,
- the quantity you would use,
- the procedure you would follow,
- a table detailing the data you would collect,
- how you would verify that the order with respect to propanone is 1.

- Using a 50 cm^3 measuring cylinder, add 20.0 cm^3 of 1.00 mol dm^{-3} of propanone to a 250 cm^3 conical flask.
- Using a 10 cm^3 measuring cylinder, add 10.0 cm^3 of 1.00 mol dm^{-3} sulfuric acid, H_2SO_4 , into the flask.
- Using another 50 cm^3 measuring cylinder, measure out 20.0 cm^3 of 1.00 mol dm^{-3} iodine, I_2 , and add 1 cm^3 of starch into the measuring cylinder.
- Add the contents of the measuring cylinder in step 3 into the flask and start the stopwatch when half the volume is added.
- Swirl the flask once.
- Stop the stopwatch when the blue-black colour is discharged. Record the time taken.
- Repeat the experiment with propanone of concentrations 0.50 mol dm^{-3} and 0.25 mol dm^{-3} .

Expt	$[\text{CH}_3\text{COCH}_3]$	Time/s	Rate/ s^{-1}
1 (given)	2.00		
2	1.00		
3	0.50		
4	0.25		



Since it is 1st order with respect to propanone, a straight line graph passing through the origin will be obtained.

[2]

Marking

- [1] – Sound general flow
- [1] – specifying apparatus – burette not necessary
- [1] – correct volumes to be used
- [1] – suggesting appropriate graph to be plot and interpretation

[4]

(c) A student suggested that preparing individual solutions of propanone of varying concentrations for use in this analysis is very time consuming and not necessary.

Suggest how the above procedure can be modified to investigate the order with respect to propanone by just using 2.00 mol dm^{-3} propanone.

You may find it helpful to use of a table to illustrate your answer.

Change the concentration of propanone by adding varying volumes of 2.00 mol dm^{-3} propanone and topping up the solution with water to ensure total volume is constant.

Expt	Vol of $2.00 \text{ mol dm}^{-3} \text{ CH}_3\text{COCH}_3$ added/ cm^3	Volume of H_2O added / cm^3	Total Volume of reaction mixture/ cm^3	Time/s	Rate/ s^{-1}
1	20	0			
2	15	5			

Graph plot will be Rate vs Vol of CH_3COCH_3 .

[1] – Using water to vary concentration by keeping total volume constant

[1] – Suggestion of volume of propanone replacing concentration in graph plotting.

.....

[Total: 8]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	NH ₃ (aq)
aluminium, Al ³⁺ (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH ₄ ⁺ (aq)	ammonia produced on heating	-
barium, Ba ²⁺ (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca ²⁺ (aq)	white ppt. with high [Ca ²⁺ (aq)]	no ppt.
chromium(III), Cr ³⁺ (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu ²⁺ (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe ²⁺ (aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe ³⁺ (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg ²⁺ (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn ²⁺ (aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn ²⁺ (aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anions	reaction
carbonate, CO ₃ ²⁻	CO ₂ liberated by dilute acids
chloride, Cl ⁻ (aq)	gives white ppt. with Ag ⁺ (aq) (soluble in NH ₃ (aq))
bromide, Br ⁻ (aq)	gives pale cream ppt. with Ag ⁺ (aq) (partially soluble in NH ₃ (aq))
iodide, I ⁻ (aq)	gives yellow ppt. with Ag ⁺ (aq) (insoluble in NH ₃ (aq))
nitrate, NO ₃ ⁻ (aq)	NH ₃ liberated on heating with OH ⁻ (aq) and Al foil
nitrite, NO ₂ ⁻ (aq)	NH ₃ liberated on heating with OH ⁻ (aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO ₂ in air)
sulfate, SO ₄ ²⁻ (aq)	gives white ppt. with Ba ²⁺ (aq) (insoluble in excess dilute strong acids)
sulfite, SO ₃ ²⁻ (aq)	SO ₂ liberated by dilute acids; gives white ppt. with Ba ²⁺ (aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	test and test result
ammonia, NH ₃	turns damp red litmus paper blue
carbon dioxide, CO ₂	gives white ppt. with limewater (ppt. dissolves with excess CO ₂)
chlorine, Cl ₂	bleaches damp litmus paper
hydrogen, H ₂	"pops" with a lighted splint
oxygen, O ₂	relights a glowing splint
sulfur dioxide, SO ₂	turns aqueous potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl ₂	greenish yellow gas	pale yellow	pale yellow
bromine, Br ₂	reddish brown gas / liquid	orange	orange-red
iodine, I ₂	black solid / purple gas	brown	purple

