NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY
9729/01

Paper 1 Multiple Choice

Thursday 19 September 2019
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, 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.
A Data Booklet is provided.

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:
	1805648	85648

This document consists of **12** printed pages.

1 When a sports medal with a total surface area of 150 cm^2 was evenly coated with silver by electrolysis, its mass increased by 0.216 g.

How many atoms of silver were deposited per cm^2 on the surface of the medal?

A 8.0×10^{18} **B** 1.8×10^{19} **C** 1.2×10^{21} **D** 4.1×10^{22}

2 Which species is deflected to the greatest extent in an electric field?

A e^- **B** H^+ **C** He^{2+} **D** F^-

3 In an experiment, 50.0 cm^3 of a 0.10 mol dm^{-3} solution of **M**$^{3+}$ salt reacted exactly with 25.0 cm^3 of 0.10 mol dm^{-3} aqueous sodium sulfite.

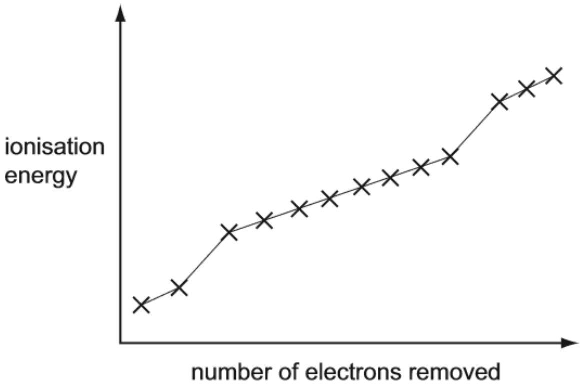
The half-equation for oxidation of sulfite ion is shown below.

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$

What is the final oxidation number of **M**?

A +1 **B** +2 **C** +4 **D** +5

4 The graph shows the first thirteen successive ionisation energies for element **E**.



What can be deduced about element **E** from the graph?

A It is in Period 3 of the Periodic Table.

B It is a d−block element.

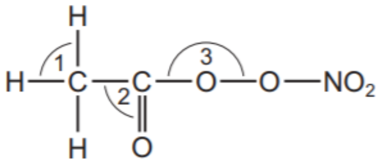
C It is in Group 2 of the Periodic Table.

D It is aluminium.

5 What is the order of increasing radii for the three species shown?

	smallest ⟶		largest
A	Ar	Ca^{2+}	K^+
B	Ar	K^+	Ca^{2+}
C	Ca^{2+}	K^+	Ar
D	K^+	Ar	Ca^{2+}

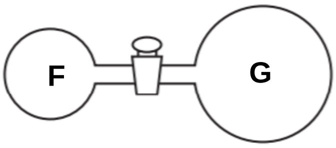
6 Organic nitrates in photochemical smog can cause breathing difficulties. The diagram shows an example of an organic nitrate molecule.



What is the order of increasing bond angles?

A 1 < 2 < 3 **B** 2 < 1 < 3 **C** 3 < 1 < 2 **D** 3 < 2 < 1

7 Two glass vessels **F** and **G** are connected by a closed valve.



F contains helium at 20 °C at a pressure of 1×10^5 Pa. **G** has been evacuated, and has three times the volume of **F**. In an experiment, the valve is opened and the temperature of the whole apparatus is raised to 100 °C.

What is the final pressure in the system?

A 3.18×10^4 Pa **B** 4.24×10^4 Pa **C** 1.25×10^5 Pa **D** 5.09×10^5 Pa

8 Carbon monoxide burns readily in oxygen to form carbon dioxide.

What can be deduced from this information?

1 The +4 oxidation state of carbon is more stable than the +2 state.

2 The standard enthalpy change of formation of carbon dioxide is less negative than that of carbon monoxide.

3 The value of the equilibrium constant for the following reaction is likely to be high.

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

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

9 Two reactions and their enthalpy changes are shown.

$$2C(s) + 2H_2(g) \longrightarrow C_2H_4(g) \qquad \Delta H^\ominus = +52.2 \text{ kJ mol}^{-1}$$

$$C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g) \qquad \Delta H^\ominus = -175.8 \text{ kJ mol}^{-1}$$

These data can be used to calculate the enthalpy change for the reaction shown.

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g) \qquad \Delta H^\ominus_1$$

What is the value of $\Delta H^\ominus_1$?

A –228.0 kJ mol^{-1} **B** –123.6 kJ mol^{-1} **C** +123.6 kJ mol^{-1} **D** +228.0 kJ mol^{-1}

10 Butanedioate ions can be dehydrogenated to form trans-butenedioate ions. The enzyme fumarase speeds up this reaction.

How does fumarase speed up this reaction?

A Fumarase increases the kinetic energy of the reactants.

B Fumarase increases the frequency of collisions between reactants.

C Fumarase lowers the activation energy of the dehydrogenation reaction.

D Fumarase is specific for this dehydrogenation reaction.

11 The reaction between ethanedioate ions and acidified manganate(VII) ions as shown below takes place very slowly in the cold but can be accelerated with heat or with addition of Mn^{2+} catalyst.

$$2MnO_4^- + 5C_2O_4^{2-} + 10H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

The reaction rate for the reaction can be measured by noting the time elapsed for the purple colour of the manganate(VII) ions to disappear.

The following results were obtained.

Expt	Volume / cm^3				Time / s
	$C_2O_4^{2-}$(aq)	MnO_4^-(aq)	Mn^{2+}(aq)	water	
1	20	30	5	25	30
2	20	30	10	20	15
3	20	15	10	35	15
4	20	20	20	20	10

Which conclusions can be drawn about the reaction?

1 The reaction is first order with respect to Mn^{2+} (aq).

2 MnO_4^- is involved in the rate-determining step.

3 The unit of rate constant is $mol^{-1}\,dm^3\,s^{-1}$.

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

12 In which reactions does NH_3 behaves as a Lewis base?

1 $2NH_3 \longrightarrow NH_2^- + NH_4^+$

2 $HSO_4^- + NH_3 \longrightarrow SO_4^{2-} + NH_4^+$

3 $Ag^+ + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+$

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

13 The numerical values of the solubility products of three metal sulfides are tabulated below.

compound	numerical value of solubility product
CuS	8.5×10^{-45}
Ag_2S	1.6×10^{-49}
Bi_2S_3	1.1×10^{-73}

What is the order of increasing molar solubility of the three metal sulfides in water?

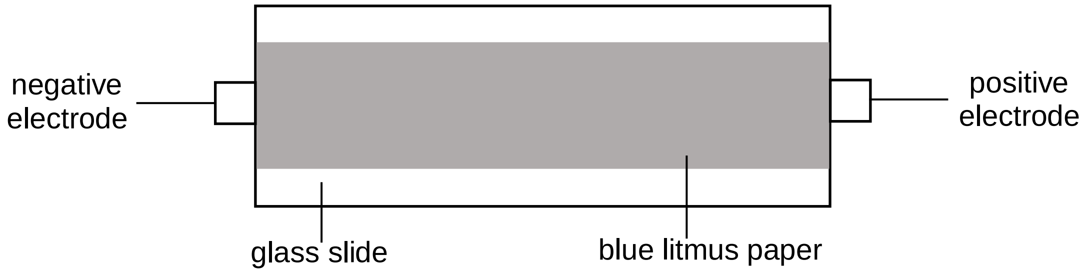
A $Bi_2S_3 < Ag_2S < CuS$

B $CuS < Ag_2S < Bi_2S_3$

C $Ag_2S < Bi_2S_3 < CuS$

D $CuS < Bi_2S_3 < Ag_2S$

14 A piece of blue litmus paper was soaked in concentrated NaC*l* solution and supported on a glass slides. The paper was connected to a direct current supply as shown in the diagram below.



What are the observations near the negative electrode and the positive electrode after the current had flown for some time?

	negative electrode	**positive electrode**
A	blue	red
B	red	blue
C	blue	bleached
D	bleached	blue

15 Which statement does **not** describe the chemical properties of Period 3 compounds?

A SiO_2 is formed from the hydrolysis of $SiCl_4$.

B Al_2O_3 is soluble in both acid and base.

C Equimolar of Na_2O and SO_3 can be mixed in water to give a pH neutral solution.

D The acidity of Period 3 chlorides in water decreases from $NaCl$ to PCl_5.

16 A 5.00 g sample of an anhydrous Group 2 metal nitrate loses 3.29 g in mass when heated strongly. What is the identity of the metal?

A magnesium **B** calcium **C** strontium **D** barium

17 Transition lenses are made of photochromic glass.

Photochromic glass darkens when exposed to bright light

Reaction 1 $Ag^+ + Cl^- \rightleftharpoons Ag + Cl$

Photochromic glass becomes more transparent again when the light is less bright.

Reaction 2 $Cu^+ + Cl \longrightarrow Cu^{2+} + Cl^-$

Reaction 3 $Cu^{2+} + Ag \longrightarrow Cu^+ + Ag^+$

Which statement about these reactions is correct?

A Ag^+ ion are oxidised.

B Cu^+ ion act as catalyst.

C Cu^+ ion act as an oxidising agent.

D The depth of colour of the photochromic glass is related to the concentration of Cl.

18 Which environmental problem is **not** made worse by the release of oxides of nitrogen from car engines?

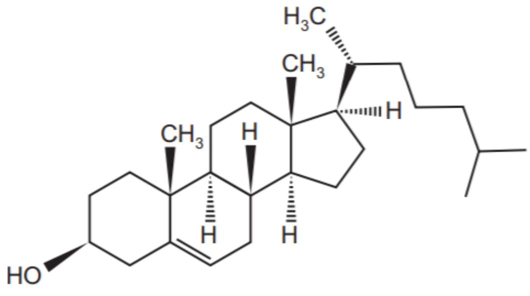
A acidification of lakes

B corrosion of buildings

C photochemical smog

D soil pollution

19 The diagram shows the structure of the naturally-occurring molecule cholesterol.



cholesterol

Which statements about cholesterol are correct?

1 The molecule contains a secondary alcohol group.

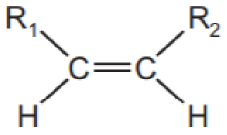
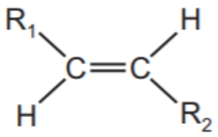
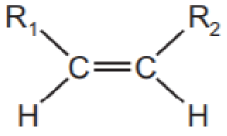
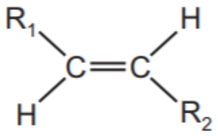
2 The molecule have two π bonds.

3 All carbon atoms in the four rings lie in the same plane.

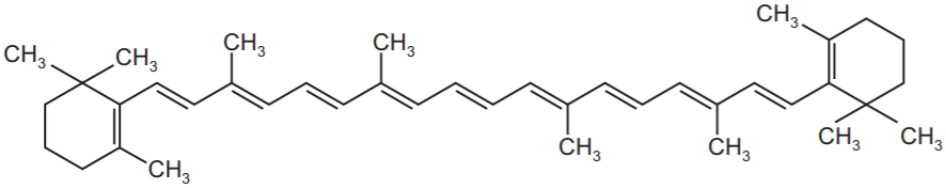
A 1, 2 and 3 **B** 1 and 2 **C** 1 and 3 **D** 1 only

20 The presence of 11−cis retinal, $C_{20}H_{28}O$, in cells in the eye is important for vision. The structure of retinal includes an aldehyde group, a cyclohexene ring and a long aliphatic side chain, in which a carbon-carbon double bond exists between carbons numbered 11 and 12.

Which pair of statements about 11−cis retinal could be correct?

	total number of C=C double bonds	arrangement around adjacent carbons C11 and C12
A	5	
B	5	
C	6	
D	6	

21 β-carotene is responsible for the orange colour of carrots.



β-carotene

β-carotene is oxidised by hot, concentrated, acidified $KMnO_4$. When an individual molecule of β-carotene is oxidised in this way, many product molecules are formed.

How many of these product molecules contain ketone functional group?

A 4 **B** 6 **C** 8 **D** 11

22 Under identical conditions, even though it proceeds by the same mechanism, reaction 1 is faster than reaction 2.

reaction 1 $CH_3CHBrCH_3 + NaCN \longrightarrow CH_3CH(CN)CH_3 + NaBr$
reaction 2 $CH_3CHBrCH_3 + NaI \longrightarrow CH_3CHICH_3 + NaBr$

What factor will explain this result?

A The C−I bond is a stronger bond than the C−Br bond.

B The C−N bond is a stronger bond than the C−I bond.

C The cyanide ion is a stronger nucleophile than the iodide ion.

D The cyanide ion is a weaker nucleophile than the iodide ion.

23 Butanedioic acid occurs in amber, algae, lichens, sugar cane and beets. It may be synthesised in two steps from 1,2−dibromoethane.

$$BrCH_2CH_2Br \xrightarrow[\text{step 1}]{} \mathbf{K} \xrightarrow[\text{step 2}]{} HO_2CCH_2CH_2CO_2H$$

Which reagents could be used for this synthesis?

	step **1**	step **2**
A	HCN(g)	HC*l*(aq)
B	HCO_2Na(aq)	HC*l*(aq)
C	ethanolic KCN	H_2SO_4(aq)
D	NaOH(aq)	acidified $K_2Cr_2O_7$

24 Many, but not all, organic reactions need to be heated before reaction occurs.

Which reaction occurs at a good rate at room temperature (20 °C)?

A $CH_3OH + PCl_5 \longrightarrow CH_3Cl + POCl_3 + HCl$

B $CH_3CH_2Br + KCN \longrightarrow CH_3CH_2CN + KBr$

C $CH_3CH_2OH \longrightarrow C_2H_4 + H_2O$

D $CH_3CH_2CN + 2H_2O \longrightarrow CH_3CH_2CO_2H + NH_3$

25 2.76 g of ethanol were mixed with an excess of aqueous acidified potassium manganate(VII). The reaction mixture was then boiled under reflux for one hour. The organic product was then collected by distillation. The yield of product was 75.0%.

What mass of product was collected?

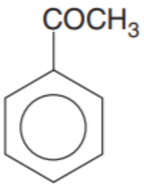
A 1.98 g **B** 2.07 g **C** 2.70 g **D** 4.80 g

26 A compound **N** has all of the following properties:

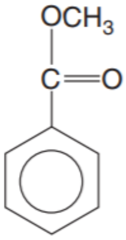
- it is neutral;
- it gives an orange precipitate with 2,4−dinitrophenylhydrazine;
- it evolves white fumes of HCl when treated with PCl_5 in the cold.

Which molecule is compound **N**?

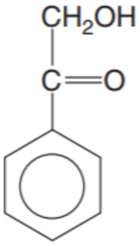
A



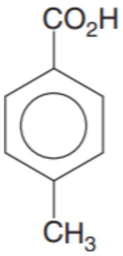
B



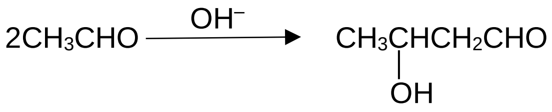
C



D

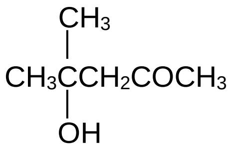


27 In the presence of dilute alkali, some aldehydes and ketones undergo the 'aldol reaction' where they dimerise to form a hydroxycarbonyl compound (an aldol). For example, ethanal reacts as shown to form 3–hydroxybutanal.



$$2CH_3CHO \xrightarrow{OH^-} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CHO$$

Which carbonyl compound will undergo the aldol reaction to produce the aldol shown below?



$$CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}CH_2COCH_3$$

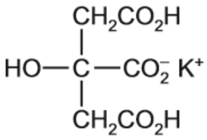
A CH_3COCH_3

B CH_3CH_2CHO

C $(CH_3)_2CHCHO$

D $CH_3CH_2COCH_3$

28 Monopotassium citrate is used as an emulsifying agent in powdered milk. It may be represented by the formula shown.



$$HO-\overset{\displaystyle CH_2CO_2H}{\overset{|}{\underset{\displaystyle CH_2CO_2H}{\underset{|}{C}}}}-CO_2^-\,K^+$$

Which statements about monopotassium citrate are correct?

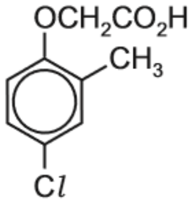
1 It can exist as a pair of enantiomers.

2 It can act as a dibasic acid.

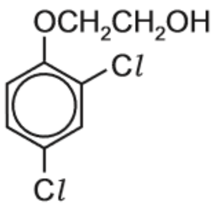
3 It can form esters with both carboxylic acids and alcohols.

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

29 **L** and **M** are two widely-used selective weed killers.



L



M

Which reagent will distinguish **L** from **M**?

A acidified $AgNO_3(aq)$

B acidified $KMnO_4(aq)$

C $Na(s)$

D $Na_2CO_3(aq)$

30 Which pair of compounds is formed when the ester $CH_3OCOC_2H_5$ is boiled with aqueous sodium hydroxide?

A CH_3OH + $C_2H_5CO_2H$

B CH_3ONa + $C_2H_5CO_2Na$

C CH_3OH + $C_2H_5CO_2Na$

D CH_3CO_2Na + C_2H_5OH

Answer Keys to 2019 SH2 H2 Chemistry Prelim MCQ

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

1 Amount of Ag deposited = $\frac{0.216}{107.9}$ = 0.002002 mol

Amount of Ag per cm^2 = $\frac{0.002002}{150}$ = 0.00001335 mol per cm^2

No of Ag atom per cm^2 = 0.00001335 × 6.02 × 10^{23} = 8.034 × 10^{18} atom per cm^2

Ans: **A**

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

Mass of electron is approximately $\frac{1}{2000}$ the mass of a proton, hence electron has the largest angle of deflection.

Ans: **A**

3 Amount of SO_3^{2-} = $\frac{25.0}{1000}$ × 0.10 = 0.0025 mol
Amount of electron transferred = 0.0025 × 2 = 0.005 mol
Amount of M^{3+} reacted = $\frac{50.0}{1000}$ × 0.10 = 0.005 mol
Mol ratio M^{3+} : e^- = 1 : 1

During **reduction**, 1 mol of M^{3+} gains 1 mol of e^-.
Oxidation state of M^{3+} **decreases by 1 unit** from **+3** to **+2**.

Ans: **B**

4 The sharp rise between 2nd and 3rd I.E. shows that there are 2 valence electron in the outermost shell. Hence it is in Group 2.

The next inner quantum shell contains 8 electrons, for d-block element, the next inner quantum shell should contain 3s, 3p and 3d electrons, which would be more than 8.

It cannot be a Period 3 Group 2 element as Mg only has 12 electrons.

Ans: **C**

5 The species are isoelectronic (same number of electrons) with same shielding effect.
Nuclear charge increases from Ar < K^+ < Ca^{2+}
Hence nuclear attraction towards valence electrons increases from Ar < K^+ < Ca^{2+}.

Ca^{2+} would have the smaller radius while Ar has the largest radius.

Ans: **C**

6 Bond angle 1 is 109.5° (4b.p. 0l.p. → tetrahedral)

Bond angle 2 is 120° (3b.p. 0l.p. → trigonal planar)

Bond angle 3 is 104.5° (2b.p. 2l.p. → bent)

Ans: **C**

7 $p_1V_1 = nRT_1$
$p_2V_2 = nRT_2$

$$\frac{p_1V_1}{p_2V_2} = \frac{T_1}{T_2}$$

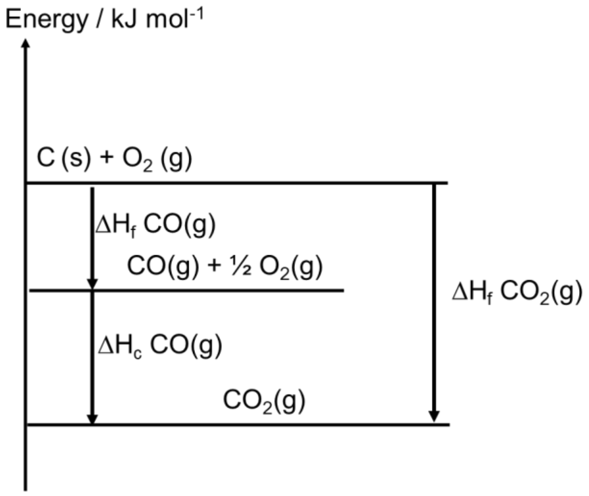
$$\frac{(1\times10^5)\times V_1}{p_2\times4V_1} = \frac{(20+273)}{(100+273)}$$

p_2 = 31830 Pa

Ans: **A**

8 $CO(g) + ½ O_2(g) \rightarrow CO_2(g)$

Combustion is an exothermic process, this means that energy level of CO_2 is lower than CO. Hence option 1 is correct.

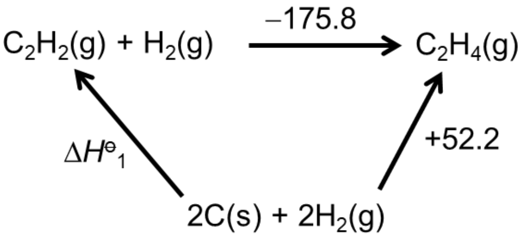


Option 2 is wrong. ΔH_f $CO_2(g)$ should be more negative than that of CO(g).

Since the combustion spontaneous (burns readily), the K_c for the equilibrium would be a very large value.

Ans: **C**

9



$\Delta H^\ominus_1 = 52.2 + 175.8 = +228$ kJ mol^{-1}

Ans: **D**

10 Option A is wrong. Increase in temperature would increase the kinetic energy.

Option B is wrong. Catalyst increases the frequency of **effective** collision.

Option D is a correct statement but does not explain “how” fumarase speed up the reaction.

Option C is correct. Fumarase is an enzyme that provides alternative reaction pathway with lower activation energy.

Ans: **C**

11 Rate of reaction = $\frac{change\ in\ vol\ of\ MnO_4{}^-}{time\ taken}$

Expt	Volume / cm^3				Time / s	rate
	$C_2O_4{}^{2-}$(aq)	$MnO_4{}^-$(aq)	Mn^{2+}(aq)	water		
1	20	30	5	25	30	1
2	20	30	10	20	15	2
3	20	15	10	35	15	1
4	20	20	20	20	10	2

Comparing expt 1 & 2, [$C_2O_4{}^{2-}$] and [$MnO_4{}^-$] is kept constant but when [Mn^{2+}] × 2, rate × 2. Hence it is first order w.r.t. Mn^{2+}. Option 1 is correct.

Comparing expt 2 & 3, [$C_2O_4{}^{2-}$] and [Mn^{2+}] is kept constant but when [$MnO_4{}^-$] ÷ 2, rate ÷ 2. Hence it is first order w.r.t. $MnO_4{}^-$.

We cannot determine the order of reaction w.r.t. $C_2O_4{}^{2-}$.

Rate = k[Mn^{2+}] [$MnO_4{}^-$] [$C_2O_4{}^{2-}$]^x

The slow step would involve one Mn^{2+} and one $MnO_4{}^-$ ion and **maybe** $C_2O_4{}^{2-}$ ion. Option 2 is correct.

We cannot deduce the order of reaction w.r.t. $C_2O_4{}^{2-}$ and hence we cannot conclude the units of the rate constant.

Ans: **B**

12 Lewis base is an electron pair donor.

In reaction 1 and 2, NH_3 donates electron pair to H^+.

In reaction 3, NH_3 donates electron pair to Ag^+.

Ans: **D**

13 $CuS (s) \rightleftharpoons Cu^{2+} (aq) + S^{2-} (aq)$

s s

$K_{sp} = s^2$

$s = \sqrt{(8.5 \times 10^{-45})}$

$= 9.22 \times 10^{-23}$ mol dm^{-3}

$Ag_2S (s) \rightleftharpoons 2Ag^{+} (aq) + S^{2-} (aq)$

2s s

$K_{sp} = (2s)^2(s)$

$4s^3 = 1.6 \times 10^{-49}$

$s = 3.42 \times 10^{-17}$ mol dm^{-3}

$Bi_2S_3 (s) \rightleftharpoons 2Bi^{3+} (aq) + 3S^{2-} (aq)$

2s 3s

$K_{sp} = (2s)^2(3s)^3$

$108s^5 = 1.1 \times 10^{-73}$

$s = 1.00 \times 10^{-15}$ mol dm^{-3}

Ans: **B**

14 At cathode (−ve electrode):

Species present: Na^+ and H_2O

[R] $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Blue litmus remains blue

At anode (+ve electrode):

Species present: Cl^- (concentrated) and H_2O

Note: Concentrated Cl^- will be oxidized in preference over H_2O.

[O] $2Cl^- \rightarrow Cl_2 + 2e^-$

Chlorine bleaches the litmus paper.

Ans: **C**

15 Statement A is correct. $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

Statement B is correct. Al_2O_3 is amphoteric oxide that can react with both acid and base to give soluble products.

Statement C is correct.

$Na_2O + H_2O \rightarrow 2NaOH$

$SO_3 + H_2O \rightarrow H_2SO_4$

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

Statement D is wrong. Acidity of Period 3 chlorides in water **increase** from $NaCl$ to PCl_5. pH of the resultant solution decreases from pH 7 to pH 1.

Ans: **D**

16 $M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + \frac{1}{2} O_2(g)$

Mass loss is due to NO_2 and O_2.
We can assume 3.29 g of $N_2O_5(g)$ is loss.

$M(NO_3)_2(s) \rightarrow MO(s) + N_2O_5(g)$
Amount of $N_2O_5 = \frac{3.29}{14.0\times2+16.0\times5}$ = 0.03046 mol

Amount of $M(NO_3)_2$ = 0.03046 mol

M_r of $M(NO_3)_2 = \frac{5.00}{0.03046}$ = 164.1

A_r of M = 164.1 – 2×(14.0+16.0×3) = 40.1
M is calcium.

Ans: **B**

17 Statement A is wrong. Ag^+ is reduced.

Statement B is correct. Cu^+ is used up in reaction 2 and regenerated in reaction 3.

Statement C is wrong. Cu^+ acts as a reducing agent in reaction 2.

Statement D is wrong. The depth of colour should be related to concentration of Ag(s).

Ans: **B**

18 Oxides of nitrogen can contribute to

- formation of smog through reaction with other air pollutants. PAN is a major component of smog which is harmful to plants and humans.

  Hydrocarbons + O_2 + NO_2 + light → peroxyacetyl nitrate (PAN)

- formation of ozone at lower atmosphere. **High concentration of ozone at lower atmosphere causes respiratory problems.**

  $NO_2 \rightarrow NO + O$
  $O + O_2 \rightarrow O_3$

- NO_2 **acts as a catalyst for the oxidation** of SO_2 to SO_3, $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$

  $NO_2 + SO_2 \rightarrow SO_3 + NO$
  $NO + \frac{1}{2} O_2 \rightarrow NO_2$ (regenerated)
  SO_3 dissolves in rainwater to cause acid rain (H_2SO_4).

Ans: **D**

19 Option 1 is correct. The molecule contains a secondary alcohol group.

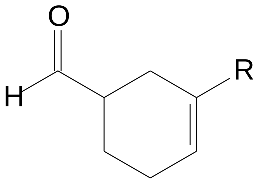
Option 2 is wrong. The C=C bond consists of one σ and one π bond.

Option 3 is wrong. Most of the C atoms are sp^3 hybridized with tetrahedral geometry. This shows that the C atoms are not in the same plane.

Ans: **D**

20 The C=C bond between C11 and C12 is in a cis arrangement.

Considering the following structure with aldehyde and cyclohexene ring,



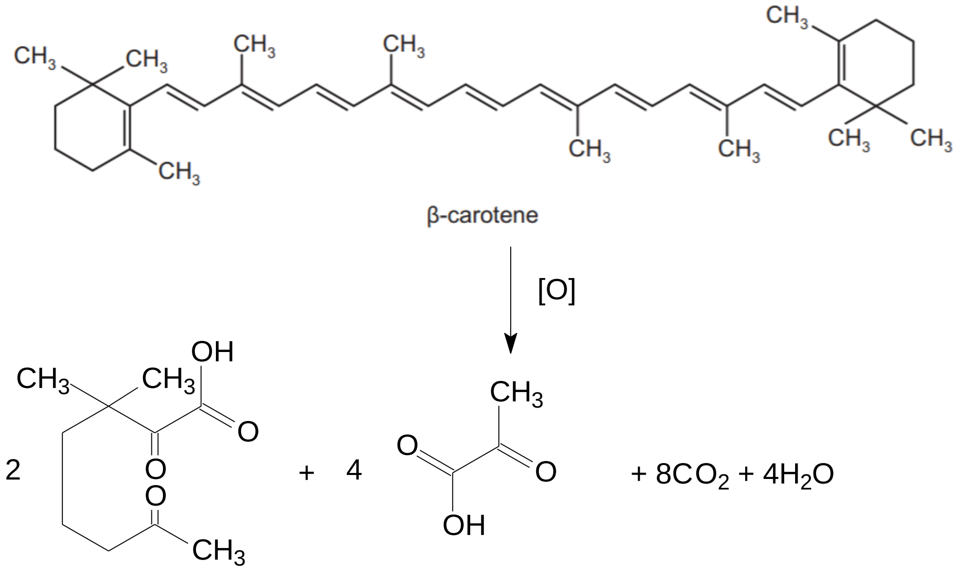
The long aliphatic side chain has a formula of $C_{13}H_{19}$.

When drawing out, there will need to have 4 C=C in the long aliphatic side chain.

Total number of C=C in the molecule = 5

Ans: **A**

21

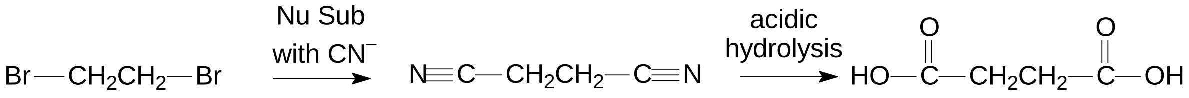


Ans: **B**

22 The example shows that CN^- can undergo nucleophilic substitution with C−Br at a faster rate than I^-. Option C is the best explanation.

Ans: **C**

23



$Br{-}CH_2CH_2{-}Br \xrightarrow[\text{with } CN^-]{\text{Nu Sub}} N{\equiv}C{-}CH_2CH_2{-}C{\equiv}N \xrightarrow{\text{acidic hydrolysis}} HO{-}\overset{\overset{O}{\|}}{C}{-}CH_2CH_2{-}\overset{\overset{O}{\|}}{C}{-}OH$

Ans: **C**

24 Reaction A can occur at room temperature.

Reaction B requires heating with ethanolic KCN for nucleophilic substitution.

Reaction C requires heating with concentrated H_2SO_4 for elimination.

Reaction D requires heating for hydrolysis.

Ans: **A**

25 Ethanol, C_2H_5OH (M_r = 46.0), reacts with hot acidified $KMnO_4$ to gives ethanoic acid, CH_3COOH (M_r = 60.0).

Amount of ethanol = $\frac{2.76}{46.0}$ = 0.06 mol
Theoretical yield of ethanoic acid = 0.06 × 60.0 = 3.6 g
Mass of 75% yield of ethanoic acid = 0.75 × 3.6 = 2.7 g

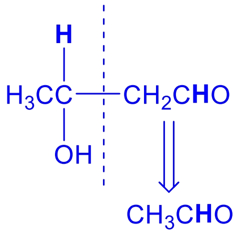
Ans: **C**

26 Compound N

- does not contain carboxylic acid/phenol/amine
- contains a carbonyl group that undergoes condensation reaction with 2,4−DNPH
- contains an alcohol or carboxylic acid group that undergoes substitution with PCl_5

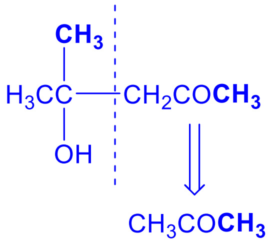
Ans: **C**

27 From the question, the following pattern is observed:



$$H_3CC(H)(OH)-CH_2CHO \Downarrow CH_3CHO$$

Replacing the bold –H with –CH_3 and working backwards,



$$H_3CC(CH_3)(OH)-CH_2COCH_3 \Downarrow CH_3COCH_3$$

Ans: **A**

28 Statement 1 is wrong. There is no chiral carbon in the compound.

Statement 2 is correct. There are two carboxylic functional group.

Statement 3 is correct. Tertiary alcohol group can react with carboxylic acid to form ester. Carboxylic acid groups can react with alcohol to form ester.

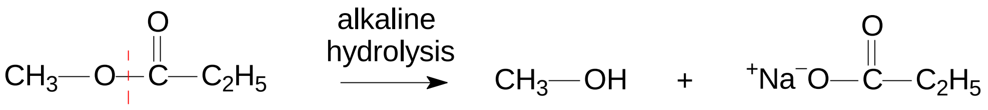
Ans: **C**

29

	L	**M**
Acidified $AgNO_3$(aq)	No ppt	No ppt
Acidified $KMnO_4$(aq)	Purple $KMnO_4$ turns colourless	Purple $KMnO_4$ turns colourless
Na(s)	Effervescence of H_2(g)	Effervescence of H_2(g)
Na_2CO_3(aq)	Effervescence of CO_2(g)	No effervescence of CO_2(g)

Ans: **D**

30



$$CH_3-O-\overset{\overset{O}{\|}}{C}-C_2H_5 \xrightarrow{\text{alkaline hydrolysis}} CH_3-OH + {}^{+}Na\,{}^{-}O-\overset{\overset{O}{\|}}{C}-C_2H_5$$

Ans: **C**

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

Monday 16 September 2019
2 hours

Candidates answer on the 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.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

For Examiner's Use	
1	/17
2	/9
3	/17
4	/18
5	/14
P2 Total	/75

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

Overall Percentage	
Grade	

This document consists of **20** printed pages.

[Turn over

1 **(a)** Brass is a mixture of copper and zinc. When a piece of brass is placed in dilute hydrochloric acid, only one of the metals present dissolves.

Explain the observation and write an equation for the reaction that occurs.

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………………………………………………………………………………………………[3]

(b) Copper and zinc are the two electrodes in a *Daniell* cell. The cell is set up as shown in Fig 1.1.

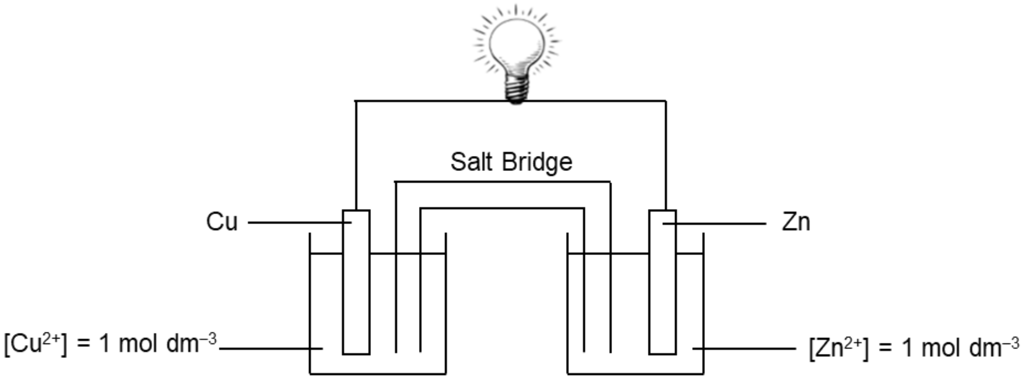

Fig 1.1

(i) Indicate the direction of electron flow **on Fig 1.1**. [1]

(ii) Write the equation for the reaction taking place and calculate $\Delta G^\ominus$ for the reaction.

………………………………………………………………………………………

[3]

(iii) Discuss the effect of the following changes on the cell potential of the above cell.

(I) adding excess amount of aqueous ammonia into the Zn^{2+}/Zn half-cell

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

……………………………………………………………………………………………… [2]

(II) using a smaller copper electrode

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

……………………………………………………………………………………………… [2]

(iv) How many hours will it take for this galvanic cell to plate 15.0 g of metallic copper from 1 mol dm^{-3} solutions of $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ using a current of 5.0 A?

[2]

(v) The Nernst equation is an equation that relates the cell potential, E_{cell}, of an electrochemical reaction to the standard cell potential, $E^{\ominus}_{cell}$. It can be simplified and written as

Nernst equation : $E_{cell} = E^{\ominus}_{cell} - \frac{RT}{zF}\ln Q$

where *R* is the ideal gas constant *T* is temperature in Kelvin

z is the number of electron transferred *F* is Faraday's constant

Q is $\frac{[Zn^{2+}]}{[Cu^{2+}]}$ for the *Daniell* cell

Using the above equation, calculate Q for the overall redox reaction of the *Daniell* cell when it reaches equilibrium at 25 °C.

[2]

(vi) In another set-up conducted at 25 °C, the concentration of Cu^{2+} ions and Zn^{2+} ions have been adjusted to 0.125 mol dm^{-3} and 0.002 mol dm^{-3} respectively.

Using the Nernst equation, calculate the e.m.f. of this cell.

[2]

[Total: 17]

Question 2 starts on the next page

2 Saccharin is an artificial sweeting agent used in some soft drinks and produced in various ways. Fig 2.1 shows the original route by *Remsen and Fahlberg*, starting with methylbenzene undergoing electrophilic substitution reaction using chlorosulfonic acid, C*l*SO$_3$H. This is also known as aromatic sulfonation process.

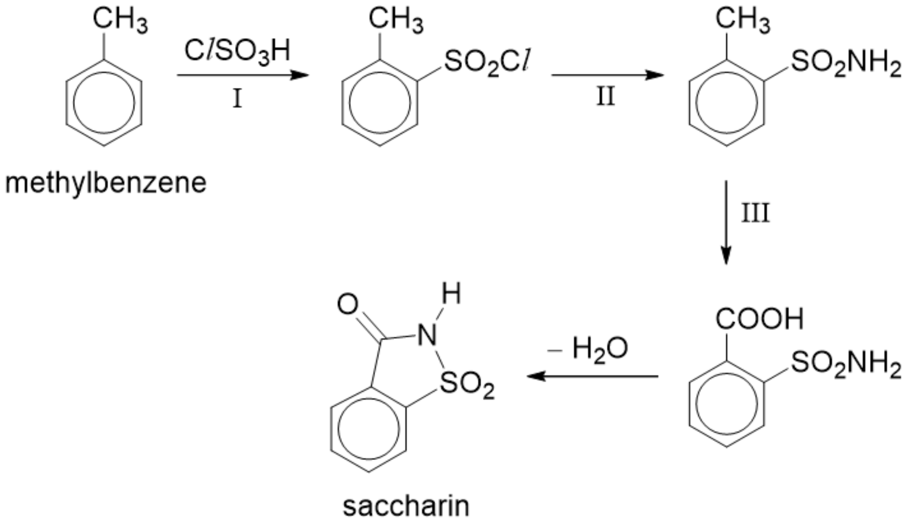

Fig 2.1

(a) Draw a dot-and-cross diagram of chlorosulfonic acid, C*l*SO$_3$H and hence state the bond angle for C*l*−S−O.

C*l*−S−O bond angle : …………….. [2]

(b) **(i)** Reaction I of the aromatic sulfonation process involves the formation of an electrophile. Identify the electrophile.

Electrophile : ………………….. [1]

(ii) Hence, describe the mechanism for reaction I of the reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

[2]

(iii) State the types of reaction that occur during reactions II and III.

reaction II : ……………………………………

reaction III : …………………………………... [2]

(iv) Suggest reagents and conditions for reactions II and III.

reaction II : ………………………………………………..

reaction III : ……………………………………................... [2]

[Total : 9]

3 Perchlorate (ClO_4^-) compounds are used as oxidisers in some fireworks to aid the combustion reaction. These perchlorates can contaminate bodies of water near fireworks displays. Elevated concentrations of perchlorate in water can affect wildlife and it may also affect human health if it contaminates drinking water.

(a) One common perchlorate present in fireworks is ammonium perchlorate, NH_4ClO_4. Given that the solubility of ammonium perchlorate is 30.6 g per 100 cm^3, express its solubility in mol dm^{-3} and hence, calculate the solubility product, K_{sp}, for NH_4ClO_4.

[2]

(b) A group of NJC students conducted a study to determine the perchlorate content of the water in the Singapore River before and after the fireworks display in the National Day Parade Rehearsal.

They followed the methodology described below one week before the rehearsal:

- Collect a 100.0 cm^3 sample of the river water and acidify it with 10 cm^3 of 1 mol dm^{-3} sulfuric acid.
- The resulting solution is added to an excess of 50 cm^3 of 5×10^{-5} mol dm^{-3} iron(II) sulfate solution. The mixture is then made up to 250 cm^3. This is solution **X**.
- A 25.0 cm^3 sample of solution **X** is pipetted into a conical flask.

The 25.0 cm^3 solution is titrated against 1×10^{-6} mol dm^{-3} potassium manganate(VII) to determine the amount of remaining iron(II) ions in the sample.

(i) Write the half equation for the conversion of perchlorate ions to chlorine in the acidic medium and hence the overall equation for the reaction between perchlorate and iron(II) ions.

Half equation : ……………………………………………………………………………

Overall equation : ……………………………………………..…………………………

[2]

(ii) Describe how you would recognise the endpoint of the titration.

……………………………………………………………………………………………. [1]

(iii) The 25.0 cm^3 sample of solution **X** required 30.00 cm^3 of potassium manganate(VII) for complete reaction.

Calculate the concentration of perchlorate ions in the river water.

[3]

(iv) Given that the perchlorate concentration in the Singapore River increased by 20% in the 24 hours after the fireworks display for the National Day Parade rehearsal, calculate the concentration of perchlorate ions in the river 24 hours after the fireworks display.

If you did not manage to work out an answer for **(b)(iii)**, you may assume the concentration of perchlorate ions in the river water is 2.5×10^{-6} mol dm^{-3}.

[1]

(v) Table 3.1 shows the health effects on fishes due to varying concentration of perchlorate ion in the river.

types of fish	abnormalities in skeletal growth	increased angiogenesis	myocardial infarction
stickleback	5×10^{-6} mol dm^{-3}	1×10^{-4} mol dm^{-3}	1.5×10^{-4} mol dm^{-3}
pike	5×10^{-7} mol dm^{-3}	2×10^{-6} mol dm^{-3}	1×10^{-5} mol dm^{-3}
catfish	1×10^{-7} mol dm^{-3}	1×10^{-6} mol dm^{-3}	5×10^{-5} mol dm^{-3}

Table 3.1

Using your answer in **b(iv)**, predict the type of health effect(s) experienced by each type of fish 24 hours after the fireworks display. Write "nil" if there is no effect.

types of fish	health effect(s)
stickleback	
pike	
catfish	

[2]

(c) Perchlorate ions can be metabolized in the tissue of stickleback fish.
The fish tissue concentration of perchlorate ions was investigated for one of the stickleback fish found in the Singapore River.

The following results was obtained.

Time/ hour	$[ClO_4^-]$ / $\times 10^{-9}$ mol dm^{-3}
0	100
4	70
8	49
12	34
16	24
20	17
24	12

Table 3.2

For Examiner's Use

(i) Plot the data from Table 3.2 on the grid provided and use your graph to prove that the order of reaction with respect to perchlorate is one.

[3]

(ii) Using your graph in **c(i)**, determine the rate constant, *k*. Include units in your answer.

[2]

(iii) Hence, estimate the time taken for the perchlorate ions to reach 1% of its initial concentration.

[1]

[Total : 17]

4 Alkalinity refers to the capability of water to neutralize acid. Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0.

In the ocean, dissolved carbon dioxide from the atmosphere is in equilibrium with seawater concentrations of carbonic acid, H_2CO_3 and hydrogen carbonate, HCO_3^-. The ocean has a very large buffering capacity made possible with the presence calcium carbonate rocks in lakes and streams.

Relevant chemical equations and equilibrium constants at 293K that affects the ocean's pH and buffering capacity are shown below.

$CO_2(g) \rightleftharpoons CO_2(aq)$ $K_{CO2} = 3.44 \times 10^{-2}$

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ $K_{H2CO3} = 2.00 \times 10^{-3}$

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$ K_{a1}

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$ K_{a2}

Fig 4.1 shows the molar fraction of H_2CO_3, HCO_3^- and CO_3^{2-} in a sample of river water at 293K.

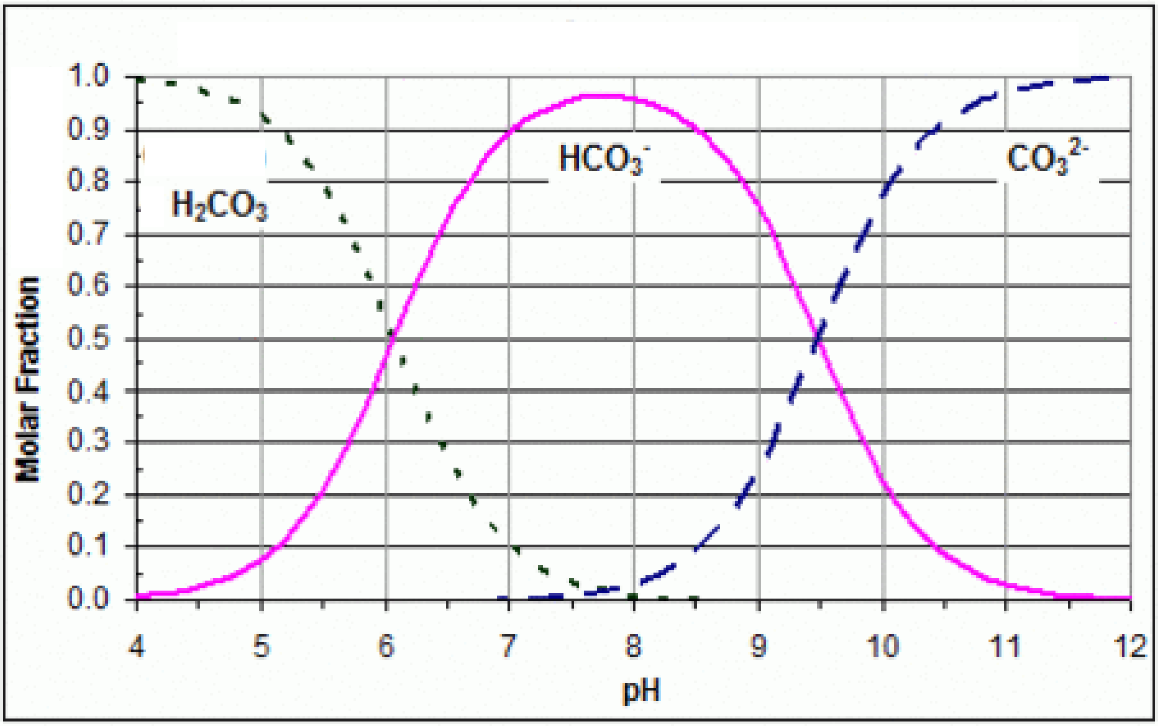

Fig 4.1

(a) **(i)** With reference to Fig 4.1, state the two pH values where the mixture are at its maximum buffering capacity.

pH of maximum buffering capacity : ……… and ……… [1]

(ii) Hence deduce the values for K_{a1} and K_{a2}.

[2]

(iii) Explain why the calculated value of K_{a1} is larger than K_{a2}?

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

………………………………………………………………………………………….[1]

(iv) Aquatic organisms survive within specific pH range.
Suggest with equations, how the hydrogen carbonate and carbonate system in natural water ensures the survival of aquatic organisms.

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

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…………………………………………………………………………………………..

…………………………………………………………………………………………..

………………………………………………………………………………………….[3]

(v) Table 4.1 gives the corresponding component of the gas in atmosphere. Determine the concentration of carbon dioxide in mol dm^{-3} in the atmosphere and hence determine the concentration of carbon dioxide dissolved in pure water at room temperature and pressure.

component in dry air	volume ratio of gas in dry air / ppm
oxygen	209 500
nitrogen	780 840
carbon dioxide	399
argon	9300

Table 4.1

[ppm refers to parts per million]

[3]

(vi) The concentration of dissolved O_2 is found to be 2.5×10^{-4} mol dm^{-3}.
With the aid of a diagram, show how oxygen can dissolve in water.

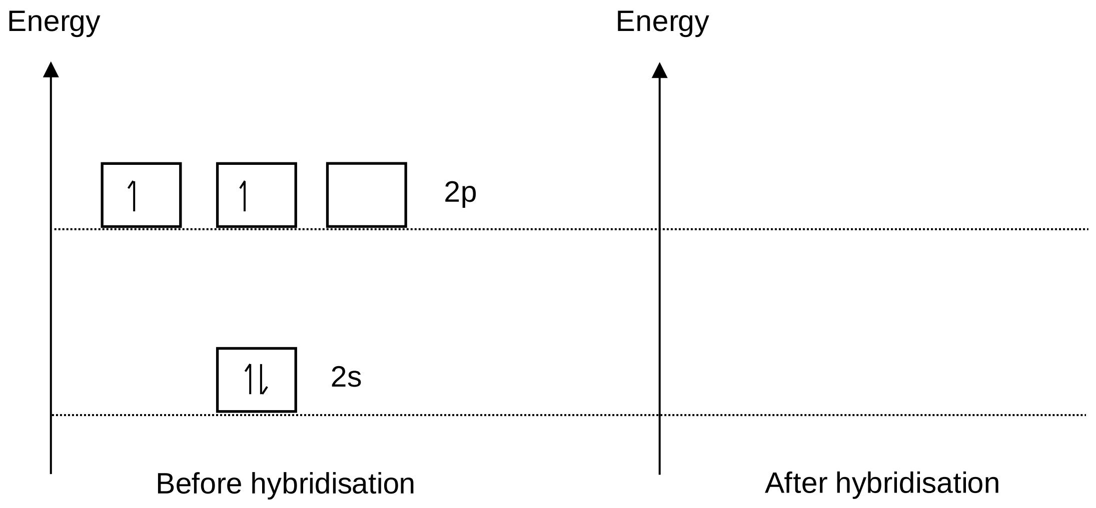
[1]

For Examiner's Use

(b) **(i)** Draw the labelled diagram to show the orbitals that form the C=O bond in CO_2, and state the type of hybridisation involved.

[2]

(ii) Indicate the energy level of the orbitals involved in the σ(sigma) and π(pi) bonding of CO_2 on the energy level diagram provided. You should use boxes to represent the orbitals and half arrows to represent electrons.



[2]

(c) Calcium carbonate is an important compound that ensures the alkalinity of river water. When calcium carbonate is heated, it decomposes according to the equation below.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of solid $CaCO_3$ to a rigid 1 dm^3 container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100K. As the container was heated, the total pressure of the $CO_2(g)$ in the container was measured over time. The data are plotted in Fig 4.2.

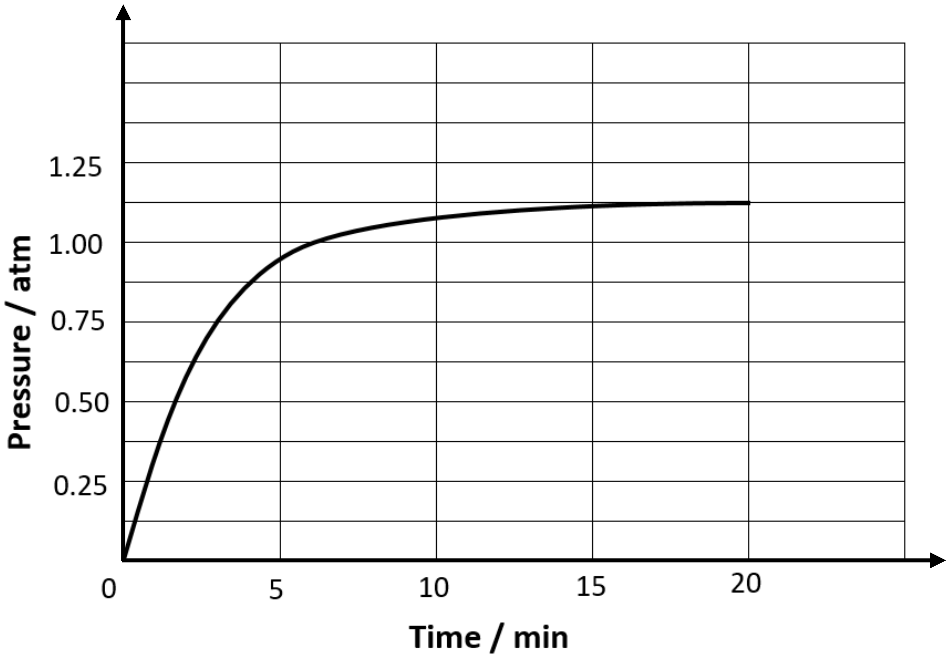


Fig 4.2

(i) The student repeated the experiment, but this time the student crushed another 50.0 g sample of $CaCO_3(s)$ into powdered form. Sketch the resultant graph **on the same axis provided in Fig 4.2**. [1]

(ii) After 20 minutes, some $CO_2(g)$ was injected into the container, initially raising the pressure to 2.5 atm while keeping the temperature constant. Would the final pressure inside the container be less than, greater than, or equal to its initial pressure at 20 minutes? Explain your reasoning.

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………….[2]

[Total : 18]

5 **(a)** Alkene can undergo oxidation with ozone, O_3, to give carbonyl compounds. This reaction is known as *ozonolysis*.

Alkene **J**, $C_{11}H_{14}$, undergoes *ozonolysis* to give compound **K**, C_8H_8O, and compound **L**, C_3H_6O.

Compound **K** gives a brick red precipitate when warmed with alkaline Cu^{2+} tartrate complex.

Compound **L** gives a yellow precipitate when warmed with alkaline I_2.

Alkene **J** gives compound **L** and benzoic acid, $C_6H_5CO_2H$, as the only organic products when heated with acidified $KMnO_4$.

(i) Suggest the structures of compounds **J**, **K** and **L**. [3]

Compound **J**	Compound **K**	Compound **L**

(ii) Write an equation for the reaction of alkene **J** with $KMnO_4$, using [O] to represent the oxidising agent.

[1]

(iii) Draw the structure of O_3 to illustrate its shape and show any dative covalent bond it may contain.

[1]

(b) Cycloalkenes can undergoes *syn* and *anti* addition as shown in Fig 5.1.

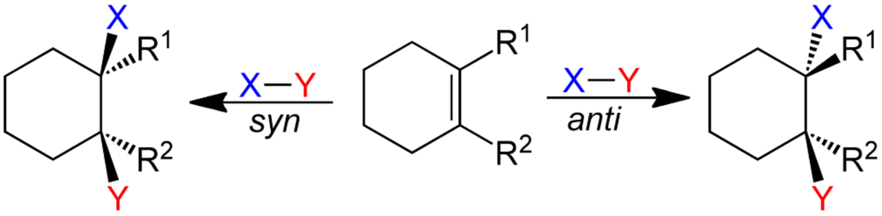


Fig 5.1

An example of *syn* addition is the oxidation of alkene to diol.
An example of *anti* addition is the bromination of alkene.

Using information from Fig 5.1, suggest the structure of the product for the reaction of 1,2−dimethylcyclohexene with the following reagents.

cold alkaline $KMnO_4$	
Br_2 in CCl_4	

[2]

(c) Fig 5.2 shows the reaction of cyclohexa−1,4−diene with HBr(g).

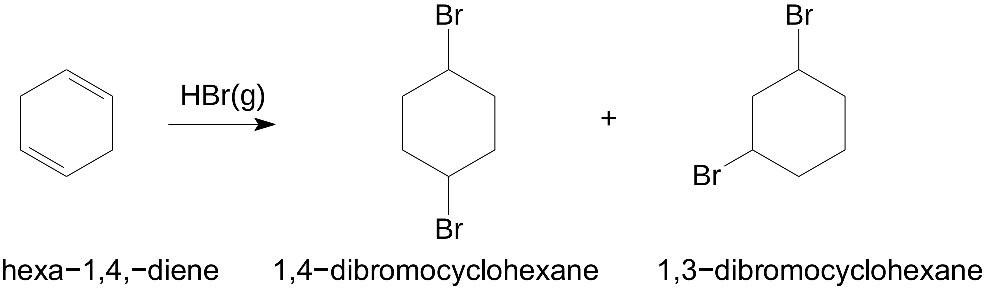


Fig 5.2

(i) 1,4−dibromocyclohexane exhibits cis-trans isomerism.

Draw the structures of the stereoisomers.

cis isomer	trans isomer

[2]

(ii) 1,3−dibromocyclohexane contains two chiral carbons. This gives rise to only three stereoisomers, of which two are optically active.

Suggest the structure of the *optically inactive* stereoisomer and explain why it has no optical activity.

………………………………………………………………………………………………

………………………………………………………………………………………………

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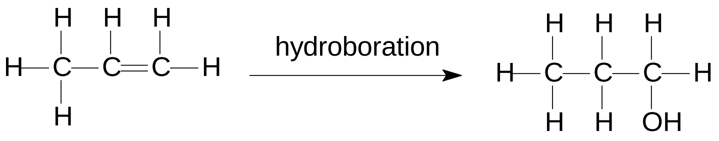
………………………………………………………………………………………………

………………………………………………………………………………………………[2]

For Examiner's Use

(d) Hydroboration can be used to convert an alkene to an alcohol.



Hydroboration involves a two-step reaction as shown in Fig 5.3:

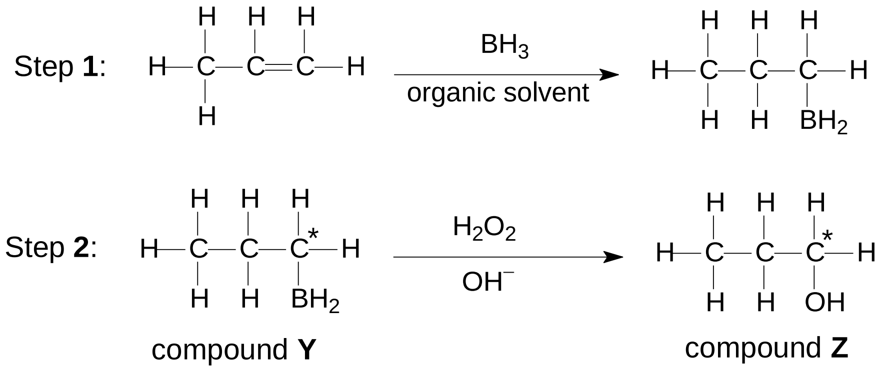


Fig 5.3

The electronegativity data for some elements are given in Table 5.1.

element	B	C	H	O
electronegativity	2.0	2.5	2.1	3.6

Table 5.1

(i) Step **1** is an electrophilic addition reaction. Draw the structure of the carbocation intermediate involved in step **1**.

[1]

(ii) State the oxidation number of the carbon atoms labelled * in compound **Y** and **Z**, and hence deduce the role of H_2O_2 in step **2**.

Oxidation number of C* in **Y** is ....

Oxidation number of C* in **Z** is ....

Role of H_2O_2: ………………………………………..

[2]

[Total : 14]

Suggested Answer for SH2 H2 Chemistry 2019 Prelim Paper 2

1 **(a)** Brass is a mixture of copper and zinc. When a piece of brass is placed in dilute hydrochloric acid, only one of the metals present dissolves.

Explain the observation and write an equation for the reaction that occurs.

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^\ominus = -0.76V$

$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^\ominus = +0.34V$

$2H^+ + 2e^- \rightleftharpoons H_2 \quad E^\ominus = 0.00\ V$

For reaction between Zn and H^+,
$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$
$= 0.00 - (-0.76)$
$= +0.76V$ (reaction is feasible)

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$ OR $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

For reaction between Cu and H^+,
$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$
$= 0.00 - (0.34)$
$= -0.34V$ (reaction is not feasible)

Note: It is essential to calculate $E^\ominus_{cell}$ between metal and H^+ to conclude whether the reaction is feasible. Some answers suggest Zn is more likely to be oxidized than Cu but that does not explain why Cu do not react with H^+.

(b) Copper and zinc are the two electrodes in a *Daniell* cell. The cell is set up as shown in Fig 1.1.

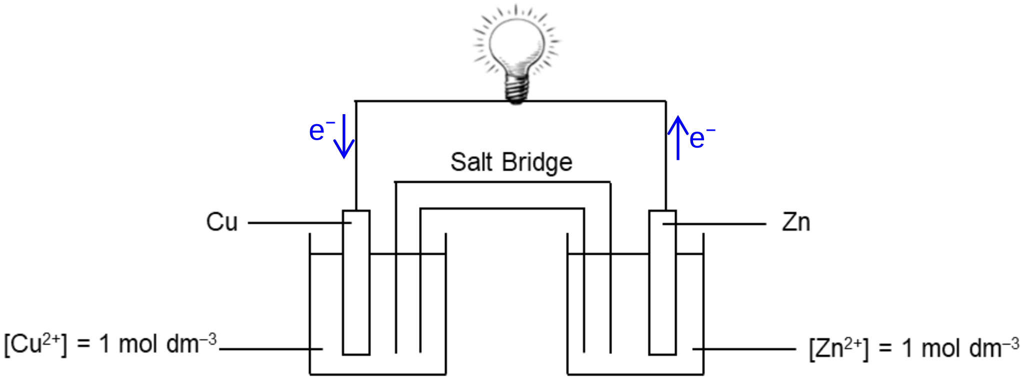


Fig 1.1

(i) Indicate the direction of electron flow **on Fig 1.1**. [1]

Note:

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^\ominus = -0.76V$

$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^\ominus = +0.34V$

Cu^{2+}/Cu half cell undergoes [R] and gain e^-
Zn^{2+}/Zn half cell undergoes [O] and lose e^-
Electrons flow from the anode (oxidation) to the cathode (reduction).

(ii) Write the equation for the reaction taking place and calculate $\Delta G^{\ominus}$ for the reaction.

$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$

$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$
$= +0.34 - (-0.76)$
$= +1.10V$

$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$
$= -2 \times 96500 \times 1.10$
$= -2.12 \times 10^5 \text{ J mol}^{-1}$

[3]

(iii) Discuss the effect of the following changes on the cell potential of the above cell.

(I) adding excess amount of aqueous ammonia into the Zn^{2+}/Zn half-cell

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^{\ominus} = -0.76V$

When excess amount of aqueous ammonia is added to Zn^{2+}/Zn half-cell, $[Zn(NH_3)_4]^{2+}$ complex ion will be formed.In order to partially offset the decrease in $[Zn^{2+}]$, oxidation of Zn is favoured to form more Zn^{2+}. Hence $E(Zn^{2+}/Zn)$ becomes more negative.

$E_{cell} = E^{\ominus}(Cu^{2+}/Cu) - E(Zn^{2+}/Zn)$

E_{cell} will become more positive.

(II) using a smaller copper electrode

Size of electrode will not affect the $E^{\ominus}$ of the reduction half-equation and E_{cell} since there is no shift in the position of the equilibrium.

Note: Solid does not affect position of equilibrium.

(iv) How many hours will it take for this galvanic cell to plate 15.0 g of metallic copper from 1 mol dm^{-3} solutions of $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ using a current of 5.0 A?

[R] $Cu^{2+} + 2e^- \rightarrow Cu$

Amount of Cu $= \dfrac{15.0}{63.5} = 0.2362$ mol

Amount of electrons = 0.4724 mol

$Q = It = n_eF$

$t = \dfrac{0.4724 \times 96500}{5.0}$
$= 9117s$
$= 2.53h$

[2]

(v) The Nernst equation is an equation that relates the cell potential, E_{cell}, of an electrochemical reaction to the standard cell potential, $E^{\ominus}_{cell}$. It can be simplified and written as

Nernst equation : $E_{cell} = E^{\ominus}_{cell} - \frac{RT}{zF}\ln Q$

where *R* is the ideal gas constant — *T* is temperature in Kelvin

z is the number of electron transferred — *F* is Faraday's constant

Q is $\frac{[Zn^{2+}]}{[Cu^{2+}]}$ for the *Daniell* cell

Using the above equation, calculate Q for the overall redox reaction of the *Daniell* cell when it reaches equilibrium at 25 °C.

At equilibrium, $E_{cell} = 0$

$$E^{\ominus}_{cell} = \frac{RT}{zF}\ln Q$$

$$1.10 = \frac{8.31 \times 298}{2 \times 96500}\ln Q$$

$$Q = 1.71 \times 10^{37}$$

[2]

(vi) In another set-up conducted at 25 °C, the concentration of Cu^{2+} ions and Zn^{2+} ions have been adjusted to 0.125 mol dm^{-3} and 0.002 mol dm^{-3} respectively.

Using the Nernst equation, calculate the e.m.f. of this cell.

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{zF}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.10 - \frac{8.31 \times 298}{2 \times 96500}\ln\frac{[0.002]}{[0.125]}$$

$$= 1.15V$$

[2]

[Total: 17]

For Examiner's Use

2 Saccharin is an artificial sweeting agent used in some soft drinks and produced in various ways. Fig 2.1 shows the original route by *Remsen and Fahlberg*, starting with methylbenzene undergoing electrophilic substitution reaction using chlorosulfonic acid, $ClSO_3H$. This is also known as aromatic sulfonation process.

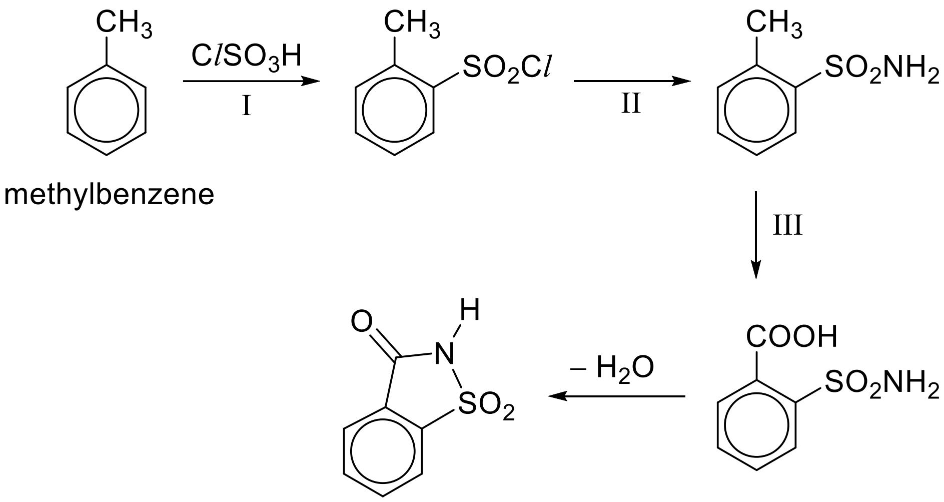
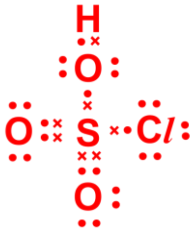


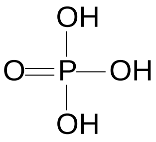
Fig 2.1

(a) Draw a dot-and-cross diagram of chlorosulfonic acid, $ClSO_3H$ and hence state the bond angle for Cl−S−O.

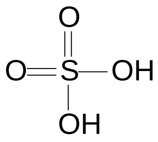


Cl−S−O bond angle : 109.5°

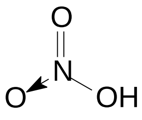
Note: All acid compounds are covalent molecule. They only dissociate into ions in aqueous state. Acids containing H&O atoms lose H^+ from the O−H bonds when ionize in water. Examples of acid molecule structures:

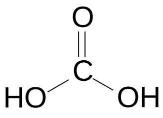


$$\mathrm{O{=}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}{-}OH}$$



$$\mathrm{O{=}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{S}}{-}OH}$$



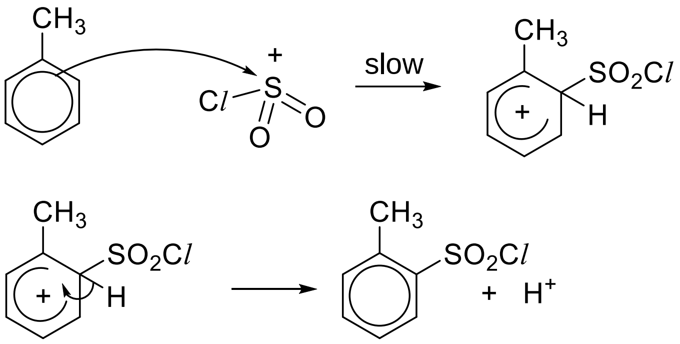


[2]

(b) **(i)** Reaction I of the aromatic sulfonation process involves the formation of an electrophile. Identify the electrophile.

Electrophile : $^{+}SO_2Cl$ [1]

(ii) Hence, describe the mechanism for reaction I of the reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



Note:
arrow from benzene π electron to S atom of the electrophile to form arenium cation
arrow from C−H bond to center of arenium cation to regenerate aromaticity and lose H^+ [2]

(iii) State the types of reaction that occur during reactions II and III.

reaction II : nucleophilic substitution / condensation

reaction III : oxidation [2]

(iv) Suggest reagents and conditions for reactions II and III.

reaction II : excess ethanolic NH_3, heat in sealed tube (behave like C−C*l*)
(also accept NH_3(g) r.t.p. as it could react similar to acyl chloride)

reaction III : $KMnO_4$, dilute H_2SO_4, heat [2]

[Total : 9]

3 Perchlorate (ClO_4^-) compounds are used as oxidisers in some fireworks to aid the combustion reaction. These perchlorates can contaminate bodies of water near fireworks displays. Elevated concentrations of perchlorate in water can affect wildlife and it may also affect human health if it contaminates drinking water.

(a) One common perchlorate present in fireworks is ammonium perchlorate, NH_4ClO_4. Given that the solubility of ammonium perchlorate is 30.6 g per 100 cm^3, express its solubility in mol dm^{-3} and hence, calculate the solubility product, K_{sp}, for NH_4ClO_4.

$$\text{Solubility, s} = \frac{30.6}{117.5} \times 10 = 2.60 \text{ mol dm}^{-3}$$

$$K_{sp} \text{ of } NH_4ClO_4 = [NH_4^+][ClO_4^-] = (s)(s) = (2.60)^2$$

$$= 6.78 \text{ mol}^2 \text{ dm}^{-6}$$

[2]

(b) A group of NJC students conducted a study to determine the perchlorate content of the water in the Singapore River before and after the fireworks display in the National Day Parade Rehearsal.

They followed the methodology described below one week before the rehearsal:

- Collect a 100.0 cm^3 sample of the river water and acidify it with 10 cm^3 of 1 mol dm^{-3} sulfuric acid.
- The resulting solution is added to an excess of 50 cm^3 of 5×10^{-5} mol dm^{-3} iron(II) sulfate solution. The mixture is then made up to 250 cm^3. This is solution **X**.
- A 25.0 cm^3 sample of solution **X** is pipetted into a conical flask.

The 25.0 cm^3 solution is titrated against 1×10^{-6} mol dm^{-3} potassium manganate(VII) to determine the amount of remaining iron(II) ions in the sample.

(i) Write the half equation for the conversion of perchlorate ions to chlorine in the acidic medium and hence the overall equation for the reaction between perchlorate and iron(II) ions.

Half equation : [R] $2ClO_4^- + 16H^+ + 14e^- \rightarrow Cl_2 + 8H_2O$

Overall equation : $2ClO_4^- + 16H^+ + 14Fe^{2+} \rightarrow Cl_2 + 14Fe^{3+} + 8H_2O$

[2]

(ii) Describe how you would recognise the endpoint of the titration.
Mixture turns first permanent pink [1]

(iii) The 25.0 cm^3 sample of solution **X** required 30.00 cm^3 of potassium manganate(VII) for complete reaction.

Calculate the concentration of perchlorate ions in the river water.

Amt of MnO_4^- = $\frac{30}{1000} \times 1 \times 10^{-6} = 3.0 \times 10^{-8}$ mol

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

Amt of Fe^{2+} in 25 cm^3 = $5 \times 3.0 \times 10^{-8} = 1.50 \times 10^{-7}$ mol

Amt of Fe^{2+} in 250 cm^3 = 1.50×10^{-6} mol

Amt of Fe^{2+} that reacted with ClO_4^- = $(\frac{50}{1000} \times 5 \times 10^{-5}) - 1.50 \times 10^{-6}$
$= 1.0 \times 10^{-6}$ mol

$2ClO_4^- + 16H^+ + 14Fe^{2+} \rightarrow Cl_2 + 14Fe^{3+} + 8H_2O$

Amt of ClO_4^- = $\frac{1.0 \times 10^{-6}}{14} \times 2 = 1.429 \times 10^{-7}$ mol

$[ClO_4^-] = \frac{1.429 \times 10^{-7}}{(^{100}/_{1000})} = 1.43 \times 10^{-6}$ mol dm^{-3}

[3]

(iv) Given that the perchlorate concentration in the Singapore River increased by 20% in the 24 hours after the fireworks display for the National Day Parade rehearsal, calculate the concentration of perchlorate ions in the river 24 hours after the fireworks display.

If you did not manage to work out an answer for **(b)(iii)**, you may assume the concentration of perchlorate ions in the river water is 2.5×10^{-6} mol dm^{-3}.

$[ClO_4^-] = 120\% \times 1.43 \times 10^{-6}$
$= 1.71 \times 10^{-6}$ mol dm^{-3}
OR
$[ClO_4^-] = 120\% \times 2.5 \times 10^{-6}$
$= 3.00 \times 10^{-6}$ mol dm^{-3}

[1]

(v) Table 3.1 shows the health effects on fishes due to varying concentration of perchlorate ion in the river.

types of fish	abnormalities in skeletal growth	increased angiogenesis	myocardial infarction
stickleback	5×10^{-6} mol dm^{-3}	1×10^{-4} mol dm^{-3}	1.5×10^{-4} mol dm^{-3}
Pike	5×10^{-7} mol dm^{-3}	2×10^{-6} mol dm^{-3}	1×10^{-5} mol dm^{-3}
catfish	1×10^{-7} mol dm^{-3}	1×10^{-6} mol dm^{-3}	5×10^{-5} mol dm^{-3}

Table 3.1

Using your answer in **b(iv)**, predict the type of health effect(s) experienced by each type of fish 24 hours after the fireworks display. Write "nil" if there is no effect.

types of fish	health effect(s)
stickleback	Nil
pike	abnormalities in skeletal growth
catfish	abnormalities in skeletal growth and increased angiogenesis

[2]

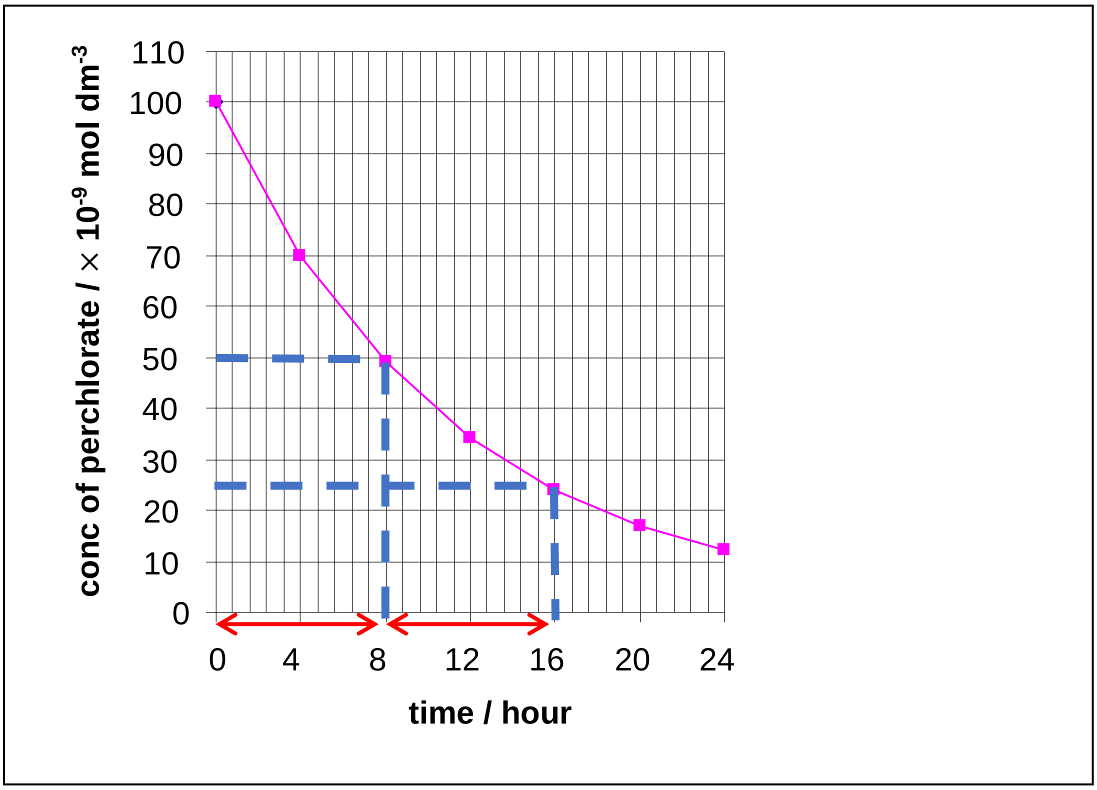
(c) Perchlorate ions can be metabolized in the tissue of stickleback fish. The fish tissue concentration of perchlorate ions was investigated for one of the stickleback fish found in the Singapore River.

The following results was obtained.

Time/ hour	$[ClO_4^-]$ / × 10^{-9} mol dm^{-3}
0	100
4	70
8	49
12	34
16	24
20	17
24	12

Table 3.2

(i) Plot the data from Table 3.2 on the grid provided and use your graph to prove that the order of reaction with respect to perchlorate is one.



Clearly labelled axis
Construction line for $t_{½}$
All points plotted correctly
Constant half-life of 8 hours, hence first order wrt perchlorate ions. [3]

(ii) Using your graph in **c(i)**, determine the rate constant, *k*. Include units in your answer.

For first order reaction, $t_{1/2} = \frac{\ln 2}{k}$

$k = 0.0866\ h^{-1}$

[2]

(iii) Hence, estimate the time taken for the perchlorate ions to reach 1% of its initial concentration.

$$\left(\frac{1}{2}\right)^n = \left(\frac{1}{100}\right)$$

n = 6.64

Time taken = 6.64 × 8 = 53.15 hours.
OR
need 7 half-lifes to reach 0.78%, time taken = 7 × 8 = 56 hours

[1]

[Total : 17]

4 Alkalinity refers to the capability of water to neutralize acid. Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0.

In the ocean, dissolved carbon dioxide from the atmosphere is in equilibrium with seawater concentrations of carbonic acid, H_2CO_3 and hydrogen carbonate, HCO_3^-. The ocean has a very large buffering capacity made possible with the presence calcium carbonate rocks in lakes and streams.

Relevant chemical equations and equilibrium constants at 293K that affects the ocean's pH and buffering capacity are shown below.

$CO_2(g) \rightleftharpoons CO_2(aq)$	$K_{CO2} = 3.44 \times 10^{-2}$
$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$	$K_{H2CO3} = 2.00 \times 10^{-3}$
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$	K_{a1}
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	K_{a2}

Fig 4.1 shows the molar fraction of H_2CO_3, HCO_3^- and CO_3^{2-} in a sample of river water at 293K.

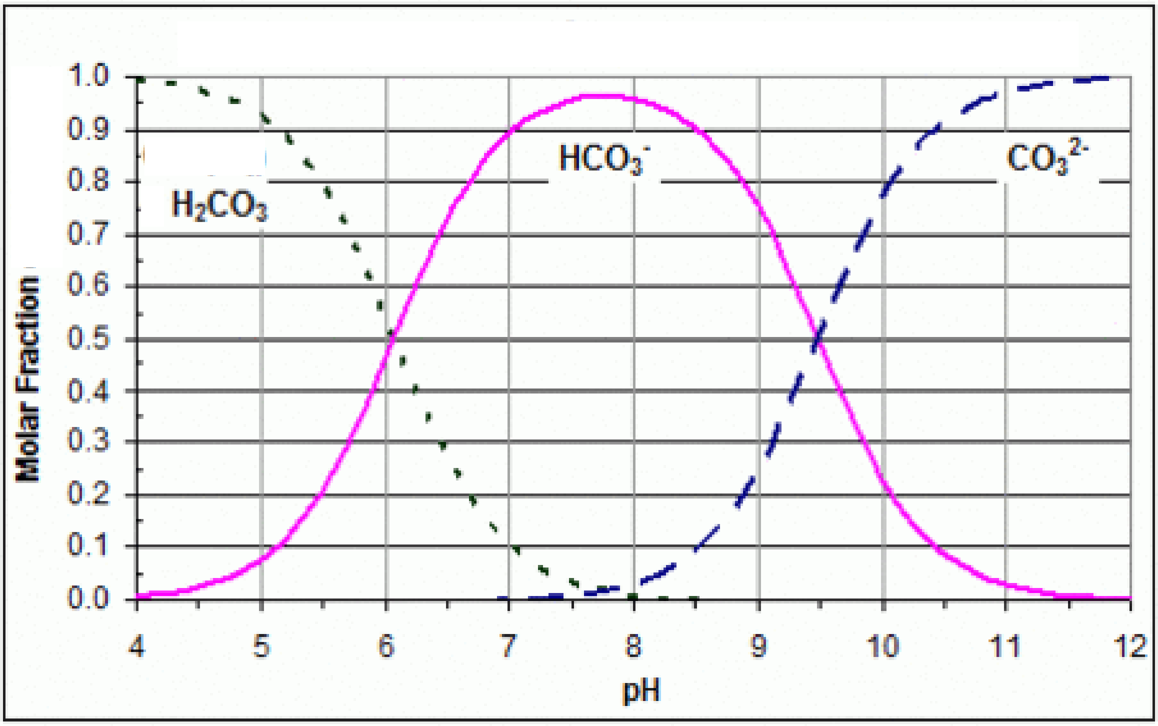


Fig 4.1

(a) **(i)** With reference to Fig 4.1, state the two pH values where the mixture are at its maximum buffering capacity.

pH of maximum buffering capacity : 6 and 9.5 [1]

(ii) Hence deduce the values for K_{a1} and K_{a2}.

pH = pK_{a1} = 6 (where [H_2CO_3] and [HCO_3^-] are equal])
$K_{a1} = 1 \times 10^{-6}$ mol dm^{-3}

pH = pK_{a2} = 9.5 (where [HCO_3^-] and [CO_3^{2-}] are equal])
$K_{a2} = 3.16 \times 10^{-10}$ mol dm^{-3}

[2]

(iii) Explain why the calculated value of K_{a1} is larger than K_{a2}?
It is **easier/less energy required** to dissociate/ give out a **positively charge H^+** ion from a **neutral molecule**, H_2CO_3, than from a negatively charged HCO_3^- ion. Thus position of equilibrium lie more to the right for K_{a1}.

(iv) Aquatic organisms survive within specific pH range.
Suggest with equations, how the hydrogen carbonate and carbonate system in natural water ensures the survival of aquatic organisms.

Large reservoir of CO_3^{2-} neutralises **small amount** of H^+ added.

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \text{ with full arrow}$$

Large reservoir of HCO_3^- neutralises **small amount** of OH^- added

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \text{ with full arrow}$$

Hence **pH of the buffer** solution remains **approximately the same.**

(v) Table 4.1 gives the corresponding component of the gas in atmosphere. Determine the concentration of carbon dioxide in mol dm^{-3} in the atmosphere and hence determine the concentration of carbon dioxide dissolved in pure water at room temperature and pressure.

component in dry air	volume ratio of gas in dry air / ppm
oxygen	209 500
nitrogen	780 840
carbon dioxide	399
argon	9300

Table 4.1

[ppm refers to parts per million]

In 1 dm^3 of air,

$$\text{vol. of } CO_2(g) = \frac{399}{1000000} \times 1 = 3.99 \times 10^{-4} \text{ dm}^3$$

$$\text{amount of } CO_2(g) = \frac{3.99 \times 10^{-4}}{24} = 1.663 \times 10^{-5} \text{ mol}$$

$$\text{concentration of } CO_2(g) = 1.663 \times 10^{-5} \text{ mol dm}^{-3}$$

$$3.44 \times 10^{-2} = \frac{[CO_2(aq)]}{[CO_2(g)]}$$

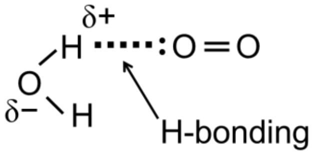
$$3.44 \times 10^{-2} = \frac{[CO_2(aq)]}{1.663 \times 10^{-5}}$$

$$[CO_2(aq)] = 5.71 \times 10^{-7} \text{ mol dm}^{-3}$$

[3]

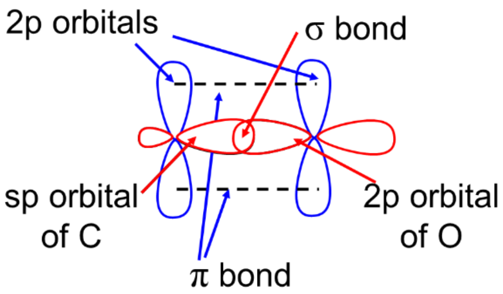
For Examiner's Use

(vi) The concentration of dissolved O_2 is found to be 2.5×10^{-4} mol dm^{-3}.
With the aid of a diagram, show how oxygen can dissolve in water.



- Lone pair electron on oxygen of O_2
- δ+ on H and δ− on O of H_2O
- Label hydrogen bonding between lone pair of O (from O_2) and the δ+ on H [1]

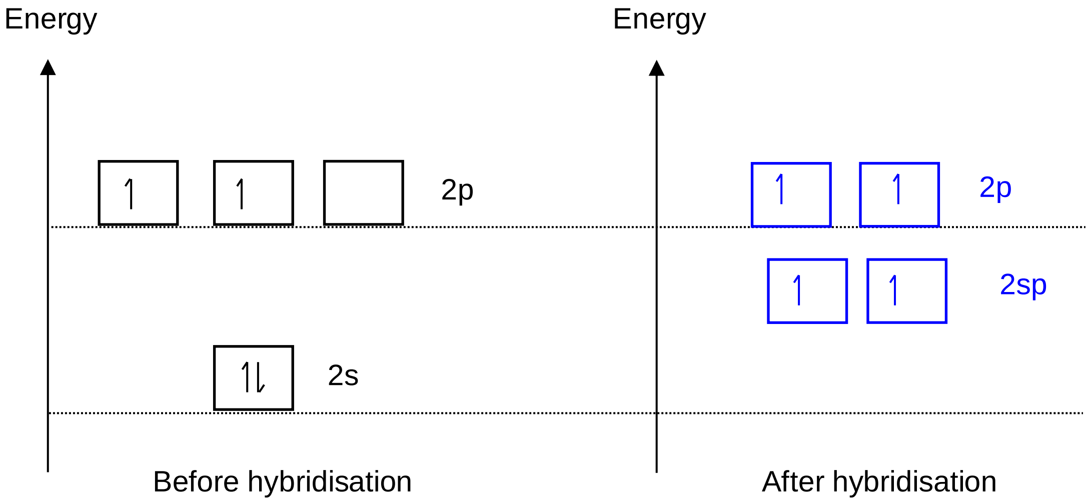
(b) **(i)** Draw the labelled diagram to show the orbitals that form the C=O bond in CO_2, and state the type of hybridisation involved.



sp hybridisation

For your information: O atom in CO_2 is actually sp^2 hybridised. For O atom, sp^2 hybrid orbital is used for sigma bonding and the unhybridised p orbital for pi bonding. However, for A level H2 Chemistry, we only study hybridisation for central atom and we can assume that terminal O atoms do not undergo hybridisation. [2]

(ii) Indicate the energy level of the orbitals involved in the σ(sigma) and π(pi) bonding of CO_2 on the energy level diagram provided. You should use boxes to represent the orbitals and half arrows to represent electrons.



Before hybridisation

After hybridisation

- Correct label of the orbitals
- Energy level of the 2 2sp hybrid orbital in between energy level of p and s orbitals
- Energy of the 2 unhybridised p orbital at the same energy level
- Correct number of electrons in each orbitals. [2]

(c) Calcium carbonate is an important compound that ensures the alkalinity of river water. When calcium carbonate is heated, it decomposes according to the equation below.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of solid $CaCO_3$ to a rigid 1 dm^3 container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100K. As the container was heated, the total pressure of the $CO_2(g)$ in the container was measured over time. The data are plotted in Fig 4.2.

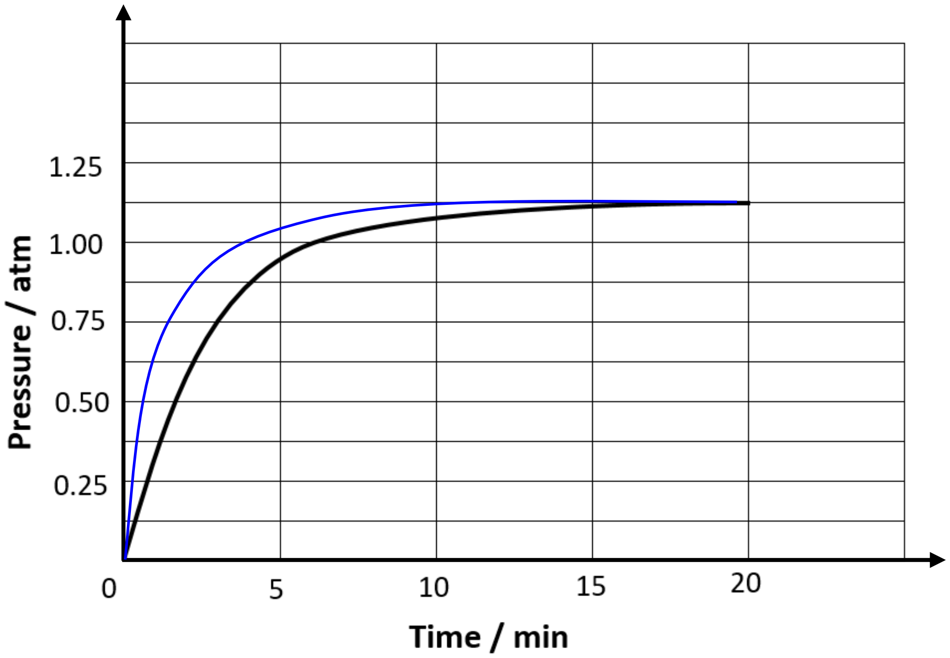


Fig 4.2

(i) The student repeated the experiment, but this time the student crushed another 50.0 g sample of $CaCO_3(s)$ into powdered form. Sketch the resultant graph **on the same axis provided in Fig 4.2**. [1]

steeper gradient but same final pressure

(ii) After 20 minutes, some $CO_2(g)$ was injected into the container, initially raising the pressure to 2.5 atm while keeping the temperature constant. Would the final pressure inside the container be less than, greater than, or equal to its initial pressure at 20 minutes? Explain your reasoning.

$K_p = P_{CO_2}$

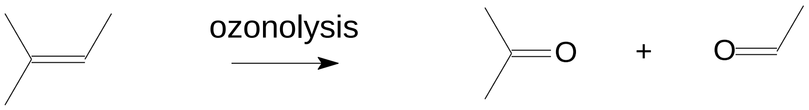
K_p changes only when temperature changes. Since **K_p only dependent on P_{CO_2} in the equation.** The final pressure after adding more CO_2 will still be **1.125atm / equal to its initial pressure at 20 minutes**.

[2]

[Total : 18]

For Examiner's Use

5 **(a)** Alkene can undergo oxidation with ozone, O_3, to give carbonyl compounds. This reaction is known as *ozonolysis*.



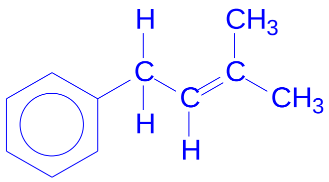
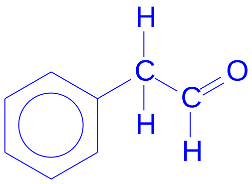
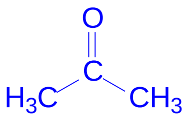
Alkene **J**, $C_{11}H_{14}$, undergoes *ozonolysis* to give compound **K**, C_8H_8O, and compound **L**, C_3H_6O.

Compound **K** gives a brick red precipitate when warmed with alkaline Cu^{2+} tartrate complex.

Compound **L** gives a yellow precipitate when warmed with alkaline I_2.

Alkene **J** gives compound **L** and benzoic acid, $C_6H_5CO_2H$, as the only organic products when heated with acidified $KMnO_4$.

(i) Suggest the structures of compounds **J**, **K** and **L**. [3]

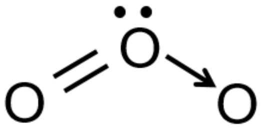
		
Compound **J**	Compound **K**	Compound **L**

(ii) Write an equation for the reaction of alkene **J** with $KMnO_4$, using [O] to represent the oxidising agent.

$C_{11}H_{14} + 6[O] \longrightarrow C_3H_6O + C_6H_5COOH + CO_2 + H_2O$

[1]

(iii) Draw the structure of O_3 to illustrate its shape and show any dative covalent bond it may contain.



bent and dative bond

[1]

(b) Cycloalkenes can undergoes *syn* and *anti* addition as shown in Fig 5.1.

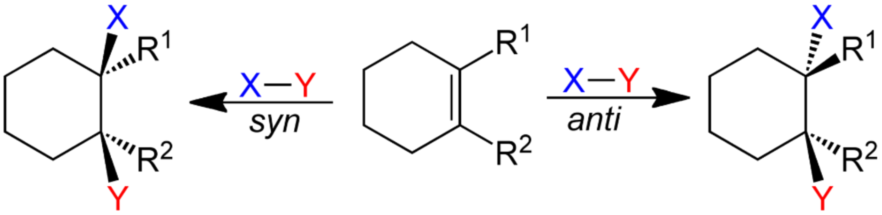
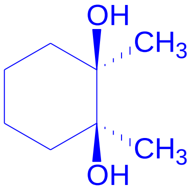
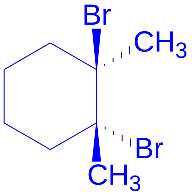


Fig 5.1

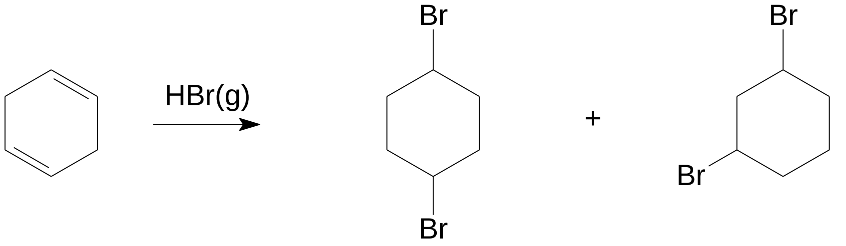
An example of *syn* addition is the oxidation of alkene to diol.
An example of *anti* addition is the bromination of alkene.

Using information from Fig 5.1, suggest the structure of the product for the reaction of 1,2−dimethylcyclohexene with the following reagents.

cold alkaline $KMnO_4$	
Br_2 in CCl_4	

[2]

(c) Fig 5.2 shows the reaction of cyclohexa−1,4−diene with HBr(g).

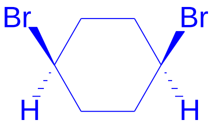
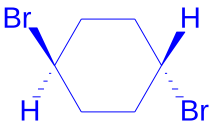


Cyclohexa−1,4,−diene 1,4−dibromocyclohexane 1,3−dibromocyclohexane

Fig 5.2

(i) 1,4−dibromocyclohexane exhibits cis-trans isomerism.

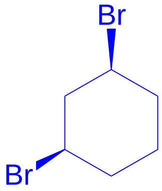
Draw the structures of the stereoisomers.

cis isomer	trans isomer
	

[2]

(ii) 1,3−dibromocyclohexane contains two chiral carbons. This gives rise to only three stereoisomers, of which two are optically active.

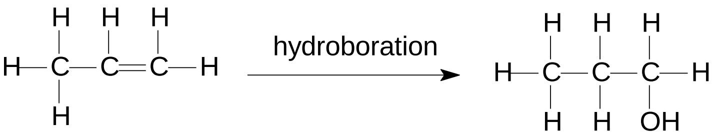
Suggest the structure of the *optically inactive* stereoisomer and explain why it has no optical activity.



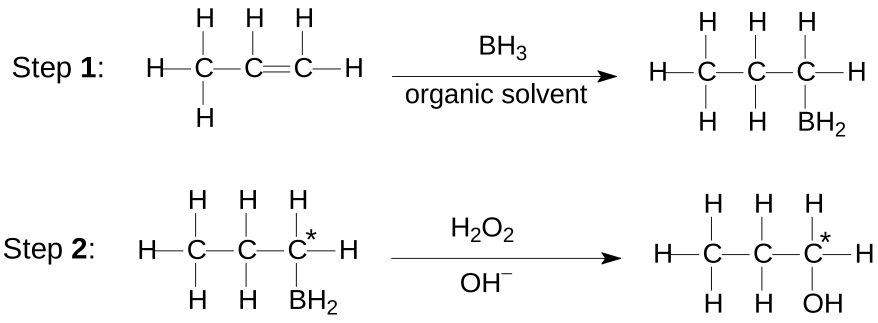
This stereoisomer contains an internal plane of symmetry. **The rotation of plane polarised light by each chiral carbon is completely cancelled out by the other chiral carbon.**

[2]

(d) Hydroboration can be used to convert an alkene to an alcohol.



Hydroboration involves a two-step reaction as shown in Fig 5.3:



compound **Y**

compound **Z**

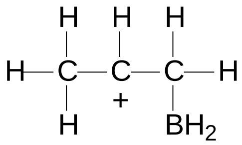
Fig 5.3

The electronegativity data for some elements are given in Table 5.1.

element	B	C	H	O
electronegativity	2.0	2.5	2.1	3.6

Table 5.1

(i) Step **1** is an electrophilic addition reaction. Draw the structure of the carbocation intermediate involved in step **1**.



Note: Based on the data on electronegativity, B is δ+ and H is δ– (B is less electronegative than H). Thus BH_2^+/BH_3 is the electrophile.

[1]

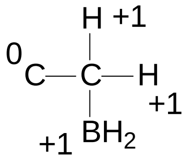
(ii) State the oxidation number of the carbon atoms labelled * in compound **Y** and **Z**, and hence deduce the role of H_2O_2 in step **2**.

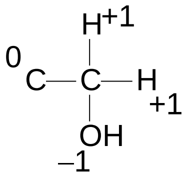
Oxidation number of C* in **Y** is −3

Oxidation number of C* in **Z** is −1

Role of H_2O_2: as oxidising agent

Note:
Oxidation number of C atom in organic compound is obtained by looking at the atoms surrounding the C atom.





H and B atoms are less electronegative than C atom, the single bonded H and B atoms would be assigned an oxidation number of +1 relative to the C atom.
O is more electronegative than C, the single bonded O is assigned O.N of −1 relative to the C.

[2]

[Total : 14]

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY **9729/03**

Paper 3 Free Response **Wednesday 18 September 2019**
2 hours

Candidates answer on separate paper.
Additional Materials: Answer Paper
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.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

This document consists of **11** printed pages and **1** blank page.

[Turn over

Section A

Answer **all** the questions from this section.

1 Potassium is an element found in Period 4 of the Periodic Table.

(a) **(i)** Write an equation for the second ionisation energy of potassium. [1]

(ii) Fig 1.1 shows the second ionisation energy for the consecutive elements from Period 3 and Period 4.

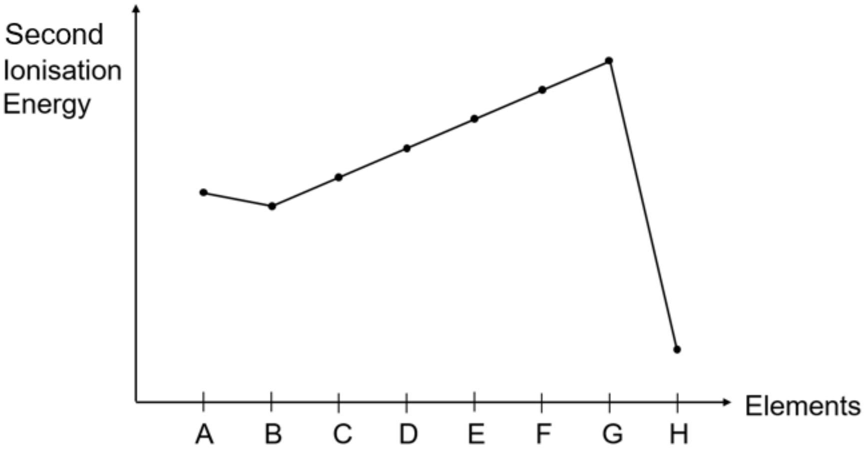


Fig 1.1

Suggest which of the above elements, **A** to **H**, is potassium. [2]

(b) When 0.400 g of potassium dichromate(VI), $K_2Cr_2O_7$, was heated using a strong flame, a yellowish green solid mixture was obtained and a gas was evolved. The gas collected ignited a glowing splint. Upon adding water to the yellowish green solid, part of the solid dissolved to give a yellow solution of K_2CrO_4, leaving a green solid.

(i) State the identity of the gas. [1]

(ii) The green solid that remained was collected and dried. It weighed 0.052 g and was found to be 68.4% chromium by mass and contains only chromium and oxygen.

Determine the chemical formula of the green solid. [2]

(iii) Using your answers to **b(i)** and **b(ii)**, write the equation for the decomposition of potassium dichromate(VI). [1]

(c) State **two** physical properties of chromium that differs from calcium.
Explain the reasons for those differences. [2]

(d) Vanadate(V) ion, VO_3^-, changes into pale yellow oxovanadium(V) ions, VO_2^+, when acid is added. Upon addition of excess zinc, the pale yellow solution changes to blue, to green and finally to violet.

(i) With the aid of an equation, explain the type of reaction that occurs when vanadate(V) ion changes into oxovanadium(V) ions. [2]

(ii) Explain why vanadium is able to exhibit variable oxidation states. [1]

(iii) With the aid of the *Data Booklet*, deduce the final oxidation state of vanadium in the violet solution. [3]

Solid vanadium(V) oxide, V_2O_5, is used as a catalyst for reaction 1.

reaction 1: $SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$

(iv) State the type of catalysis and outline the mode of action when V_2O_5 is used for reaction 1. [3]

(v) NO_2 can also act as a catalyst for reaction 1.

Write two equations to show how NO_2 acts as a catalyst in reaction 1. [2]

[Total : 20]

2 Lithium oxide, Li_2O, is used in traditional ceramic glazing to create a blue hue with copper on ceramics.

(a) Using the data below and any appropriate data from the *Data Booklet*, construct a labelled energy level diagram to calculate the standard enthalpy change of formation of Li_2O(s).

	/ kJ mol^{-1}
first electron affinity of oxygen	–141
second electron affinity of oxygen	+798
lattice energy of lithium oxide	–2863
standard enthalpy change of atomisation of lithium	+159

[5]

(b) Lithium oxide is produced during the thermal decomposition of lithium peroxide, Li_2O_2, at 450 °C.

$$Li_2O_2(l) \longrightarrow Li_2O(s) + \frac{1}{2}O_2(g)$$

(i) Given that the standard enthalpy change of formation of Li_2O_2(l) is –606 kJ mol^{-1} and using your answer in **(a)**, calculate the enthalpy change for the thermal decomposition of Li_2O_2. [1]

(ii) Explain why the thermal decomposition of Li_2O_2 is feasible. [2]

(c) Table 2.1 gives the melting points of two lithium ionic compounds.

compound	melting point / °C
Li_2O	1400
Li_2O_2	195

Table 2.1

Explain the difference in the melting points. [2]

(d) Similar to lithium peroxide, Li_2O_2, lithium nitrate, $LiNO_3$(s), undergoes thermal decomposition to produce oxygen and a brown gas.

(i) Write a balance equation, with state symbols, for the thermal decomposition of lithium nitrate. [2]

(ii) Among the Group 1 metal nitrates, only lithium nitrate undergoes thermal decomposition.

Explain why lithium nitrate can undergo thermal decomposition. [2]

(e) Ethylenediamine tetraacetate, $[EDTA]^{4-}$, is a chelating agent that is widely used to remove transition metal ions such as copper(II) ions from aqueous solutions.

(i) Suggest a synthesis of ethylenediamine tetraacetate, $[EDTA]^{4-}$, starting from methanal and 1,2−diaminoethane ($NH_2CH_2CH_2NH_2$), according to the scheme in Fig. 2.1. Deduce the structure of compound **A**. Include reagents and conditions for all reactions, and the structures of all other intermediate compounds, in your answer.

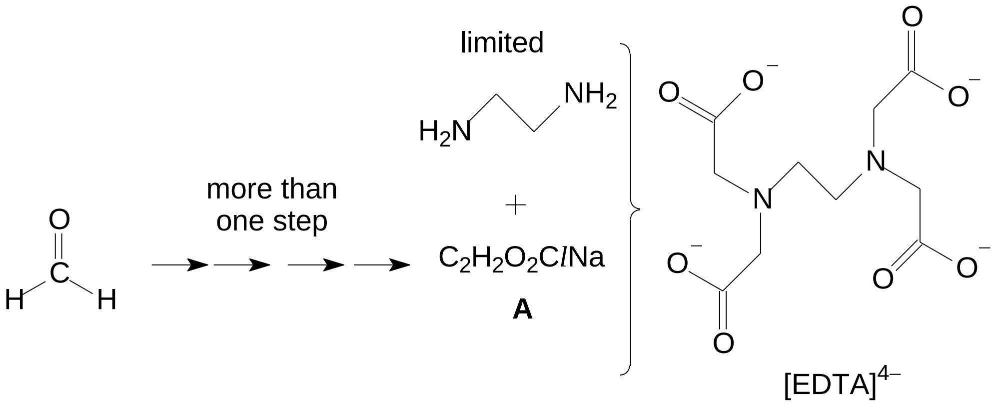


Fig 2.1

[5]

(ii) When aqueous ammonia is added to a solution of $CuSO_4$, a blue precipitate is formed which dissolves in excess aqueous ammonia to give a deep blue solution. On addition of $Na_4(EDTA)$ solid to the mixture, the colour of the solution turns light blue.

Suggest explanations for the above observations, writing equations as appropriate.

[3]

[Total : 22]

3 **(a)** Phenol is a white crystalline solid that is volatile. It is mildly acidic and requires careful handling as it can cause chemical burns.

Table 3.1 shows the physical properties for phenol and its derivatives.

compound	melting point / °C	K_a / mol dm^{-3}
phenol	41	1.12×10^{-10}
2−nitrophenol	46	5.89×10^{-8}
4−nitrophenol	114	7.08×10^{-8}

Table 3.1

(i) Explain the difference in melting points between 2−nitrophenol and 4−nitrophenol. [2]

(ii) Explain the difference in the acidities of phenol and 2−nitrophenol. [2]

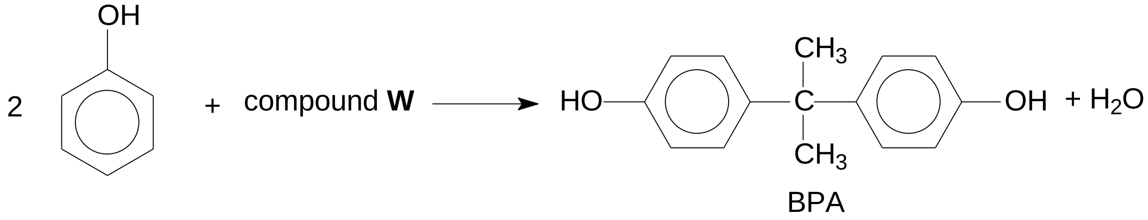
(iii) Suggest how 2,6−dibromo−4−nitrophenol can be synthesised from phenol in a 2−step synthesis. In your synthesis, you should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds. [3]

(b) When aqueous neutral $FeCl_3$ is added to a solution containing phenol, a violet solution containing the complex ion $[Fe(C_6H_5O)_6]^{3-}$ is formed.

(i) Draw the structure of the complex ion. [1]

(ii) The violet complex ion $[Fe(C_6H_5O)_6]^{3-}$ is not observed in **both** acidic and alkaline solutions. Suggest explanations for the above observation. [2]

(c) Phenol can react with compound **W** under suitable conditions to give bisphenol-A (BPA).



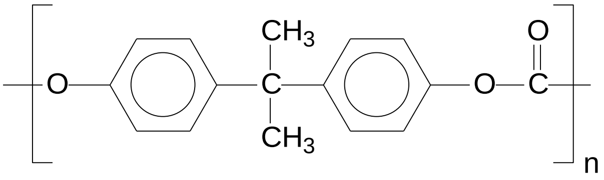
The use of the table of characteristic infra-red absorption frequencies for some selected bonds in the *Data Booklet* is relevant to this question.

Infra-red absorptions can be used to identity functional groups in organic compounds. For example, phenol shows absorption at 3200−3600 cm^{-1} due to the O−H bond.

The analysis of compound **W** shows absorptions at 1670−1740 cm^{-1}.

Identify the bond present in compound **W** and suggest its structure. [2]

(d) BPA can react with another monomer **X** to produce polycarbonates. Polycarbonates are commonly used in the manufacturing of water bottles.



Polycarbonates

(i) Identify the new functional group formed in the polycarbonates. [1]

(ii) Suggest the structure of monomer **X**. [1]

(iii) Research has shown that BPA can leach into beverages from the polycarbonate water bottles under certain conditions. Exposure to BPA is a concern because of possible health effects of BPA on the brain.

Discuss whether it is safe to consume cold lemon juice stored in a polycarbonate water bottle. [1]

(e) BPA can react with epoxides to form epoxy resins. Fig 3.1 shows the simplified equations for the reaction.

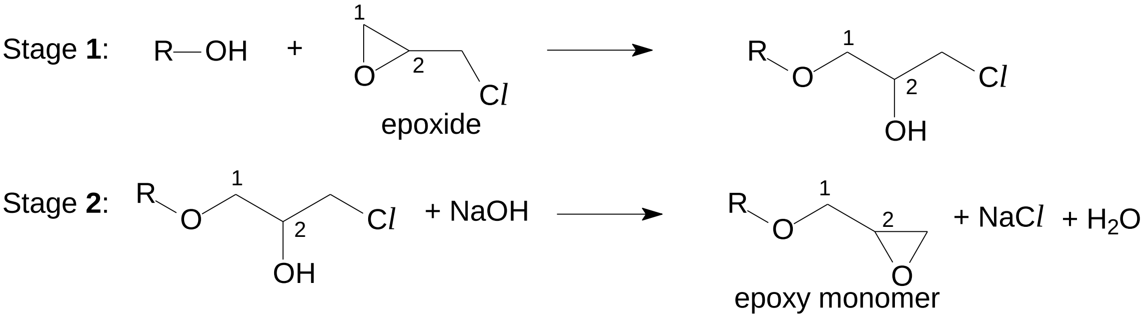


Fig 3.1

(i) For stage **1**, the phenol group of BPA acts as the nucleophile. Suggest why the nucleophile attacks C^1 instead of C^2. [1]

(ii) For stage **2**, state the type of reaction and the role of NaOH in the reaction. [2]

[Total : 18]

Section B

Answer **one** question from this section.

4 **(a)** Diphenylmethanone can be synthesized from methylbenzene in three steps as shown in Fig 4.1.

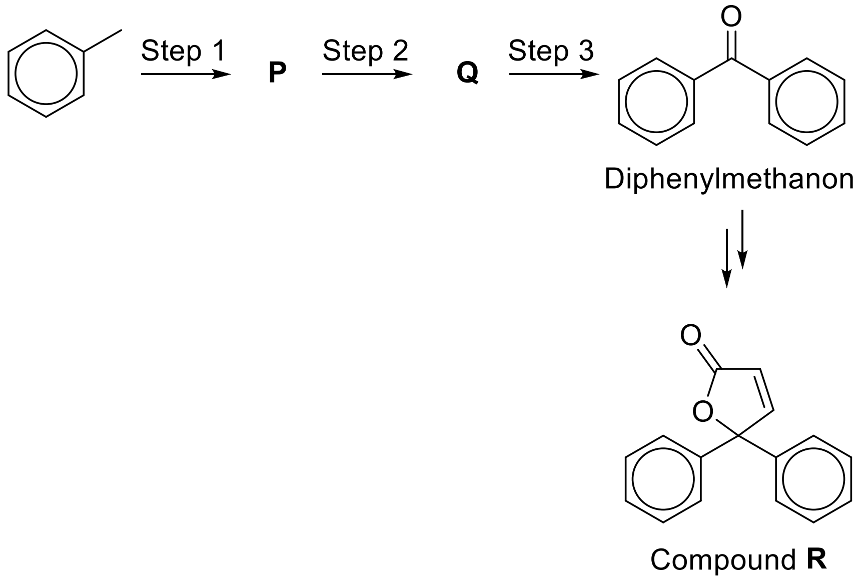
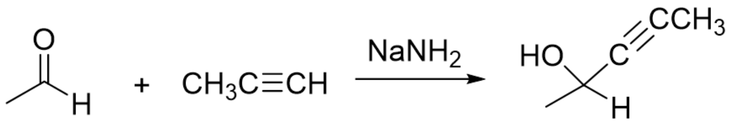


Fig 4.1

(i) Suggest the reagents and conditions for steps **1**, **2** and **3**, and draw the structures for compounds **P** and **Q**. [5]

(ii) When compound **R** is heated with acidified $KMnO_4$, compound **S** is formed as the only organic product. Suggest the structure of compound **S**. [1]

(b) Propyne, $CH_3C{\equiv}CH$, is a weak acid. It can react with an aldehyde in the presence of trace amount of strong base such as $NaNH_2$.



When propyne reacts with NH_2^-, propynyl ion, $CH_3C{\equiv}C^-$ is formed.

(i) State the type of reaction that occurred between propyne and ethanal. [1]

(ii) Describe the mechanism for this reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(iii) Suggest if the organic product formed from this reaction would rotate plane−polarised light. [2]

(c) The mechanism for the reaction between compounds **T** and **U** is as shown.

Step 1: $\mathbf{T} + \mathbf{U} \rightleftharpoons \mathbf{V}$

Step 2: $\mathbf{T} + \mathbf{V} \rightarrow \mathbf{W}$ (slow)

(i) Write a balanced overall equation for the reaction between compounds **T** and **U**. [1]

(ii) Write an expression for K_c for step 1, stating its units. [2]

(iii) Using the information given in the question and your answer to **c(ii)**, derive the rate equation for the reaction between compounds **T** and **U**. [2]

(iv) A concentration−time graph was plotted for step 1 as shown in Fig 4.2. Equilibrium was established at t_0. At t_1, a change was introduced.

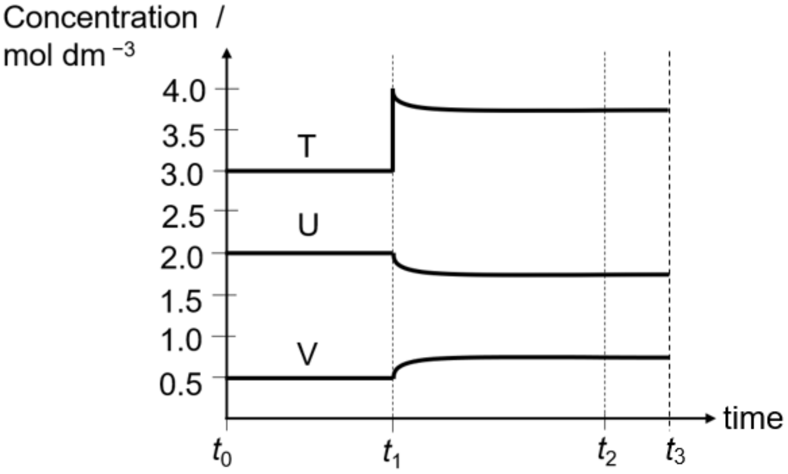


Fig 4.2

State the change that occurred at t_1. Explain the trend observed in the graph from t_1 to t_2. [2]

(v) Suggest whether there would be any change in the individual concentrations of compounds **T**, **U** and **V** when a catalyst is added to the reaction mixture at t_3. [2]

[Total : 20]

5 **(a)** Describe and explain the variation in volatility of the elements in Group 17. [2]

(b) *Use of the Data Booklet is relevant to this question.*

Explain the following observations in terms of the relative thermal stabilities of the hydrides of the Group 17 elements.

compound	HCl	HBr	HI
decomposition behaviour	does not decompose even on strong heating	strong heating yields reddish brown fumes of Br_2	purple fumes of I_2 obtained when red-hot rod is plunged into jar of HI

[2]

(c) State and explain the observations when separate solutions of chloride and iodide ions are mixed with aqueous silver nitrate, followed by excess aqueous ammonia. [3]

(d) Carbon monoxide in a sample of polluted air can readily be determined by passing through solid iodine(V) oxide, I_2O_5, to give carbon dioxide and iodine.

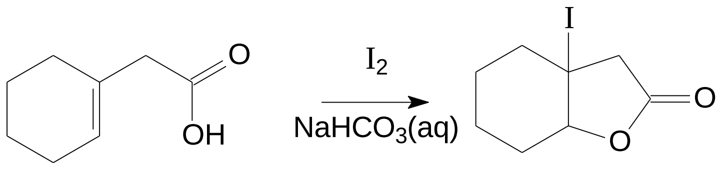
(i) Write a balanced equation for the reaction between carbon monoxide and iodine(V) oxide. [1]

(ii) The iodine produced is dissolved in a suitable solvent and titrated with aqueous sodium thiosulfate, $Na_2S_2O_3$.

1 dm^3 sample of air produced iodine that required 20.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate to discharge the iodine colour.

Calculate the mass of carbon monoxide in this sample of polluted air. [2]

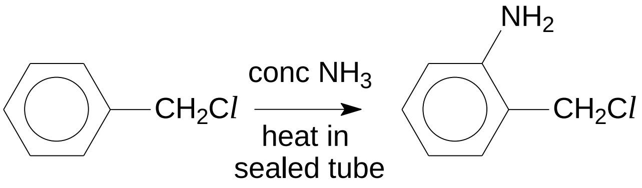
(e) In the presence of aqueous sodium hydrogencarbonate, iodine does not add across the C=C bond of compound **D** as might be expected. Instead, the following reaction occurs.



compound **D**

The first step of the mechanism involves a fast acid-carbonate reaction. Describe the mechanism for this electrophilic addition reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(f) A student attempted to make compound **E** from (chloromethyl)benzene as shown.



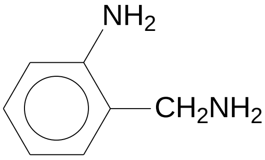
(chloromethyl)benzene compound **E**

However, a different product with molecular formula C_7H_9N was obtained.

(i) Draw the displayed formula of the product obtained from the reaction. [1]

(ii) Explain why compound **E** was not obtained. [1]

(g) The pK_b values of the two amine groups in compound **F** are 3.4 and 9.1.



compound **F**

(i) Copy the structure of compound **F** to your answer booklet and assign the pK_b values to the two amine groups. Explain your answer. [2]

(ii) Calculate the initial pH of 0.100 mol dm^{-3} of compound **F**. [2]

(h) Explain the observations when Br_2(aq) is added to the two samples.

sample	phenylamine	phenylamine dissolved in excess sulfuric acid
observations	orange Br_2 (aq) decolourises and white precipitate forms	orange Br_2 (aq) remains

[2]

[Total : 20]

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Suggested Answer for SH2 H2 Chemistry 2019 Prelim Paper 3

Section A

Answer **all** the questions from this section.

1 Potassium is an element found in Period 4 of the Periodic Table.

(a) **(i)** Write an equation for the second ionisation energy of potassium. [1]

$K^+(g) \rightarrow K^{2+}(g) + e^-$

Must show state symbol

(ii) Fig 1.1 shows the second ionisation energy for the consecutive elements from Period 3 and Period 4.

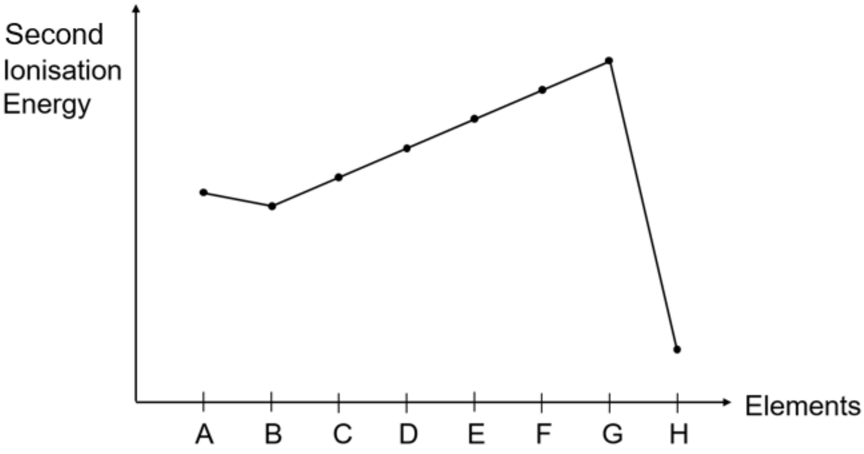


Fig 1.1

Suggest which of the above elements, **A** to **H**, is potassium. [2]

The second electron of potassium is removed from the **3p subshell (inner quantum shell)** as compared to the second electron of calcium which is removed from the **4s subshell (outer quantum shell)**. **Much more energy is required** to remove the second electron from K as compared to Ca. Hence **element G is potassium**.

Note: It is insufficient to mention that 2nd I.E. of K is much higher than 1st I.E. as the comparison with 1st I.E. is not reflected in Fig 1.1

(b) When 0.400 g of potassium dichromate(VI), $K_2Cr_2O_7$, was heated using a strong flame, a yellowish green solid mixture was obtained and a gas was evolved. The gas collected ignited a glowing splint. Upon adding water to the yellowish green solid, part of the solid dissolved to give a yellow solution of K_2CrO_4, leaving a green solid.

(i) State the identity of the gas. [1]

Oxygen gas.

(ii) The green solid that remained was collected and dried. It weighed 0.052 g and was found to be 68.4% chromium by mass and contains only chromium and oxygen.

Determine the chemical formula of the green solid. [2]

	Cr	O
Mass	$\frac{68.4}{100} \times 0.052 =$ 0.03557	$\frac{31.6}{100} \times 0.052 =$ 0.01643
A_r	52.0	16.0
Moles	0.000684	0.001027
÷ by smallest no.	1	1.5
Mol ratio	2	3

Hence chemical formula is Cr_2O_3

(iii) Using your answers to **b(i)** and **b(ii)**, write the equation for the decomposition of potassium dichromate(VI). [1]

$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$

(c) State **two** physical properties of chromium that differs from calcium.
Explain the reasons for those differences. [2]

TM has **higher density** due to **larger atomic mass and smaller radius giving rise to dense close-packed structure** (allowing more small size but heavy atoms to be packed within a specific volume.)

TM has **higher melting point** due to **more delocalised electrons contributed from 3d and 4s subshells**, resulting in **stronger metallic bonding**.

TM has **higher electrical/heat conductivities** due to **more delocalised electrons contributed from 3d and 4s subshells**.

Note: Variable oxidation states and reactions to give coloured complexes are **chemical** properties.

(d) Vanadate(V) ion, VO_3^-, changes into pale yellow oxovanadium(V) ions, VO_2^+, when acid is added. Upon addition of excess zinc, the pale yellow solution changes to blue, to green and finally to violet.

(i) With the aid of an equation, explain the type of reaction that occurs when vanadate(V) ion changes into oxovanadium(V) ions. [2]

$VO_3^- + 2H^+ \rightarrow VO_2^+ + H_2O$

Acid-base reaction

(ii) Explain why vanadium is able to exhibit variable oxidation states. [1]

Because of the **close proximity** in energy of the 4s and 3d electron in V, it is able to **lose electrons from both the 3d and 4s subshells**, hence it can exhibit variable oxidation states.

(iii) With the aid of the *Data Booklet*, deduce the final oxidation state of vanadium in the violet solution. [3]

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$ V

$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$ $E^\ominus = +1.00$ V

Reaction between VO_2^+ and Zn,
$E^\ominus = +1.00 - (-0.76)$
$= +1.76$ V > 0 (reaction is feasible)

$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$ $E^\ominus = +0.34$ V

Reaction between VO^{2+} and Zn,
$E^\ominus = +0.34 - (-0.76)$
$= +1.10$ V > 0 (reaction is feasible)

$V^{3+} + e^- \rightleftharpoons V^{2+}$ $E^\ominus = -0.26$ V

Reaction between V^{3+} and Zn,
$E^\ominus = -0.26 - (-0.76)$
$= +0.50$ V > 0 (reaction is feasible)

$V^{2+} + 2e \rightleftharpoons V$ $E^\ominus = -1.20$ V

Reaction between V^{2+} and Zn,
$E^\ominus = -1.20 - (-0.76)$
$= -0.44$ V < 0 (reaction is NOT feasible)

Hence final oxidation state of V is +2

Note: It is important to show that V^{2+} do not undergo further reduction when excess Zn is present.

Solid vanadium(V) oxide, V_2O_5, is used as a catalyst for reaction 1.

reaction 1: $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$

(iv) State the type of catalysis and outline the mode of action when V_2O_5 is used for reaction 1. [3]

Heterogeneous catalysis is involved in the reaction:

Reactants are **adsorbed** on the surface of the catalyst; the reactant molecules are **brought closer together with correct orientation** and the **bonds to be broken are weakened, thus E_a for the reaction is lowered**.

The products formed **desorb** and leave the surface of the catalyst.

(v) NO_2 can also act as a catalyst for reaction 1.

Write two equations to show how NO_2 acts as a catalyst in reaction 1. [2]

$NO_2 + SO_2 \rightarrow SO_3 + NO$
$NO + \frac{1}{2} O_2 \rightarrow NO_2$

Note: Eqns can be found under Org Book 1 > Alkane > Environmental pollutants.
NO_2 is acting as a homogeneous catalyst and it should produce a gaseous intermediate during catalysis.

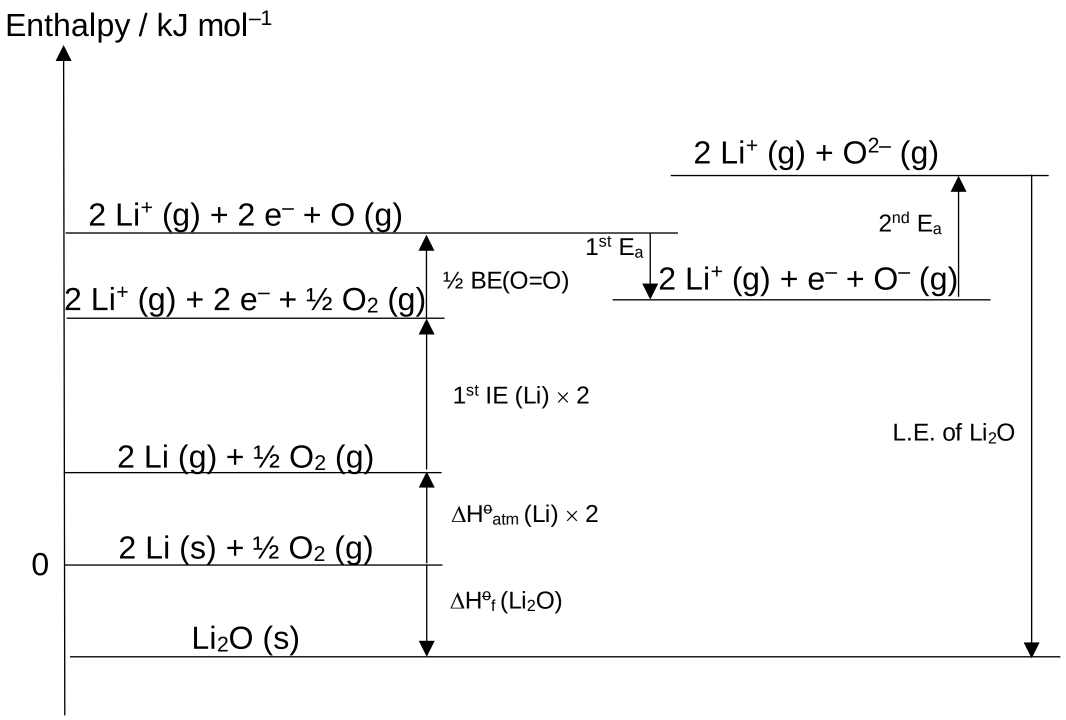
[Total : 20]

2 Lithium oxide, Li_2O, is used in traditional ceramic glazing to create a blue hue with copper on ceramics.

(a) Using the data below and any appropriate data from the *Data Booklet*, construct a labelled energy level diagram to calculate the standard enthalpy change of formation of $Li_2O(s)$.

	/ kJ mol^{-1}
first electron affinity of oxygen	–141
second electron affinity of oxygen	+798
lattice energy of lithium oxide	–2863
standard enthalpy change of atomisation of lithium	+159

[5]



- **State symbol**
- **Balanced equation**
- **Correct enthalpy change**

By Hess' Law,

$\Delta H^\ominus_f (Li_2O) = 2[\Delta H^\ominus_{atm} (Li)] + 2[1^{st}\ IE\ (Li)] + \Delta H_{atm} (O_2) + 1^{st}\ E_a (O) + 2^{nd}\ Ea\ (O) + L.E.$

$= 2(+159) + 2(+519) + ½\ (+496) + (–141) + (+798) + (–2863)$

$= –602\ kJ\ mol^{-1}$

(b) Lithium oxide is produced during the thermal decomposition of lithium peroxide, Li_2O_2, at 450 °C.

$$Li_2O_2(l) \longrightarrow Li_2O(s) + \frac{1}{2}O_2(g)$$

(i) Given that the standard enthalpy change of formation of $Li_2O_2(l)$ is –606 kJ mol^{-1} and using your answer in **(a)**, calculate the enthalpy change for the thermal decomposition of Li_2O_2. [1]

enthalpy change for the thermal decomposition of Li_2O_2
$= \sum\Delta H^{\theta}_{f}$ (products) $- \sum\Delta H^{\theta}_{f}$ (reactants)
$= \Delta H^{\theta}_{f}(Li_2O) + \Delta H_{f}(O_2) - \Delta H^{\theta}_{f}(Li_2O)$
$= (-602) + 0 - (-606)$
$= +4$ kJ mol^{-1}

(ii) Explain why the thermal decomposition of Li_2O_2 is feasible. [2]

$\Delta G = \Delta H - T\Delta S$

The increase in the entropy ($\Delta S > 0$) from the production of O_2 gas and the elevated temperature readily offset the slightly endothermic enthalpy change causing ΔG to be negative, hence the reaction is feasible.

(c) Table 2.1 gives the melting points of two lithium ionic compounds.

compound	melting point / °C
Li_2O	1400
Li_2O_2	195

Table 2.1

Explain the difference in the melting points. [2]

$|L.E| \propto \frac{q_+ \times q_-}{r_+ + r_-}$

Both Li_2O and Li_2O_2 have the **same Li^+ cation**, but different anion. Since $\mathbf{O_2^{2-}}$ in Li_2O_2 has a **larger ionic radius** as compared to the $\mathbf{O^{2-}}$ in Li_2O with a **smaller ionic radius**, the **magnitude of the lattice energy of Li_2O_2** is **smaller** **(or lattice energy of Li_2O_2 is less exothermic)** than that of Li_2O. Hence, **less energy is need to overcome the weaker ionic bond** in Li_2O_2 resulting in lower melting point.

(d) Similar to lithium peroxide, Li_2O_2, lithium nitrate, $LiNO_3(s)$, undergoes thermal decomposition to produce oxygen and a brown gas.

(i) Write a balance equation, with state symbols, for the thermal decomposition of lithium nitrate. [2]

$2LiNO_3(s) \rightarrow Li_2O(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

(ii) Among the Group 1 metal nitrates, only lithium nitrate undergoes thermal decomposition.

Explain why lithium nitrate can undergo thermal decomposition. [2]

Although Li^+ ion has a singly positively charge, but it has the **smallest ionic radius** among the Group 1 metal ions. Therefore, Li^+ ion, with a **high** $\frac{\textbf{charge}}{\textbf{size}}$ **ratio, polarises/distorts the electron cloud of NO_3^- anion** and **weakens the N–O bond** in NO_3^-. Hence, $LiNO_3$ undergoes thermal decomposition, but not other Group 1 metal nitrate.

(e) Ethylenediamine tetraacetate, $[EDTA]^{4-}$, is a chelating agent that is widely used to remove transition metal ions such as copper(II) ions from aqueous solutions.

(i) Suggest a synthesis of ethylenediamine tetraacetate, $[EDTA]^{4-}$, starting from methanal and 1,2−diaminoethane ($NH_2CH_2CH_2NH_2$), according to the scheme in Fig. 2.1. Deduce the structure of compound **A**. Include reagents and conditions for all reactions, and the structures of all other intermediate compounds, in your answer.

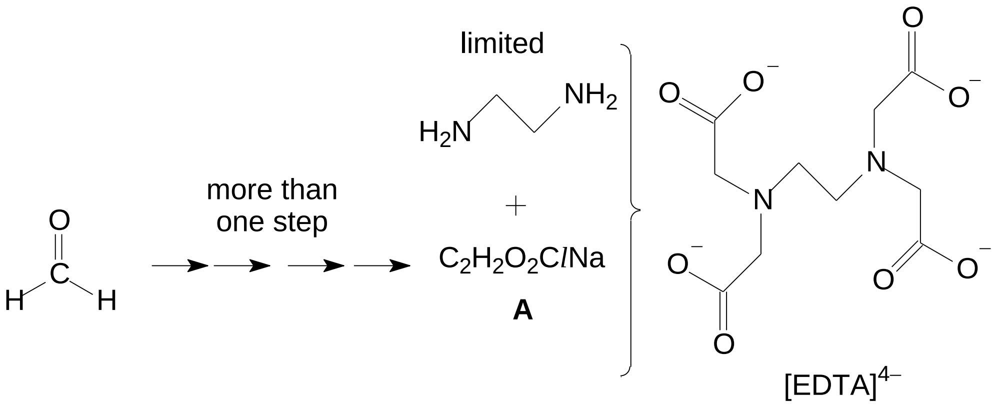
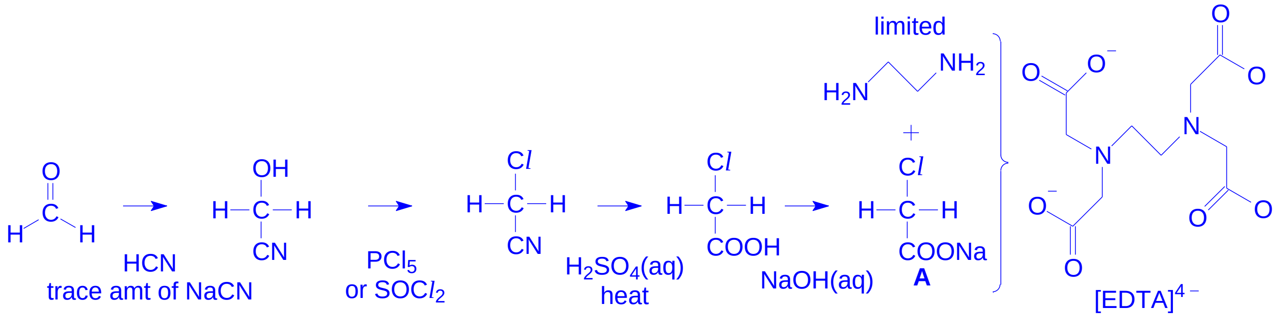


Fig 2.1

[5]



(ii) When aqueous ammonia is added to a solution of $CuSO_4$, a blue precipitate is formed which dissolves in excess aqueous ammonia to give a deep blue solution. On addition of $Na_4(EDTA)$ solid to the mixture, the colour of the solution turns light blue.

Suggest explanations for the above observations, writing equations as appropriate. [3]

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Precipitation of $Cu(OH)_2(s)$ occurs.
$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s) + 6H_2O(l)$ ---- Eqm (1)
blue soln blue ppt

Blue ppt dissolves due to formation of tetraamine copper(II) complex
$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$
blue ppt deep blue

or
$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 6H_2O(l)$
deep blue
$[Cu(H_2O)_6]^{2+}$ decreases causing the eqm (1) to shift left and $Cu(OH)_2$ (s) dissolves.

Ligand exchange results in the deep blue solution turning to light blue
$[Cu(NH_3)_4]^{2+}(aq) + [EDTA]^{4-}(aq) \rightleftharpoons [Cu(EDTA)]^{2-}(aq) + 4NH_3(aq)$
deep blue soln light blue soln

[Total : 22]

3 (a) Phenol is a white crystalline solid that is volatile. It is mildly acidic and requires careful handling as it can cause chemical burns.

Table 3.1 shows the physical properties for phenol and its derivatives.

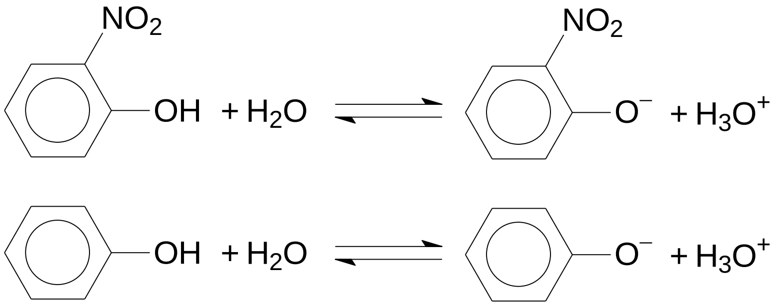
compound	melting point / °C	K_a / mol dm^{-3}
phenol	41	1.12×10^{-10}
2−nitrophenol	46	5.89×10^{-8}
4−nitrophenol	114	7.08×10^{-8}

Table 3.1

(i) Explain the difference in melting points between 2−nitrophenol and 4−nitrophenol. [2]

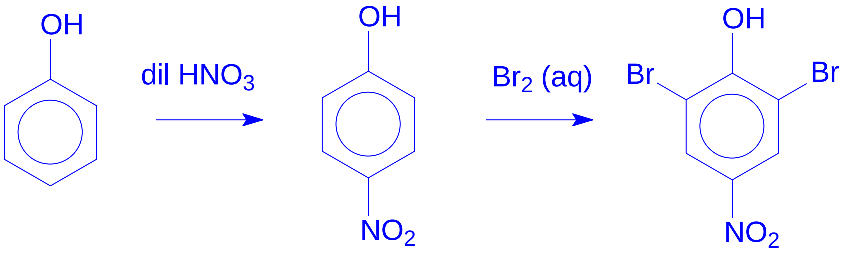
2−nitrophenol can exhibit **intramolecular H-bonding** and hence there are **less extensive intermolecular H-bonding** as compared to 4−nitrophenol.
Less energy is needed to overcome the weaker intermolecular forces of attractions between molecules of 2−nitrophenol, hence its melting point is lower than 4−nitrophenol.

(ii) Explain the difference in the acidities of phenol and 2−nitrophenol. [2]



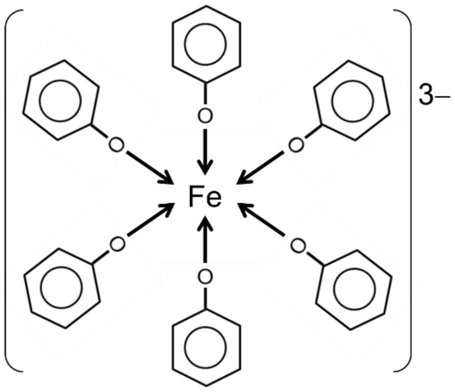
<u>Electron-withdrawing –NO_2 groups decrease the intensity of the negative charge/disperse negative charge</u> on the conjugate base and **<u>stabilises it</u>**, thus the **<u>dissociation</u>** of 2−nitrophenol into H^+ and conjugate base is **<u>more favourable (or position of equilibrium shifts to the right)</u>**. Hence 2−nitrophenol is more acidic than phenol.

(iii) Suggest how 2,6−dibromo−4−nitrophenol can be synthesised from phenol in a 2−step synthesis. In your synthesis, you should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds. [3]



(b) When aqueous neutral $FeCl_3$ is added to a solution containing phenol, a violet solution containing the complex ion $[Fe(C_6H_5O)_6]^{3-}$ is formed.

(i) Draw the structure of the complex ion. [1]

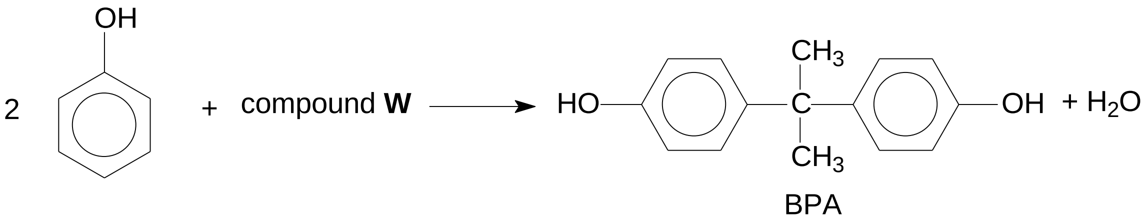


(ii) The violet complex ion $[Fe(C_6H_5O)_6]^{3-}$ is not observed in **both** acidic and alkaline solutions. Suggest explanations for the above observation. [2]

In acidic solution, the **phenoxide ligands gain H^+** to become phenol, there are no phenoxide ligands.

In alkaline solution, Fe^{3+} would react with OH^- to **give $Fe(OH)_3$ red brown ppt instead.**

(c) Phenol can react with compound **W** under suitable conditions to give bisphenol-A (BPA).



The use of the table of characteristic infra-red absorption frequencies for some selected bonds in the *Data Booklet* is relevant to this question.

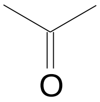
Infra-red absorptions can be used to identity functional groups in organic compounds. For example, phenol shows absorption at 3200−3600 cm^{-1} due to the O−H bond.

The analysis of compound **W** shows absorptions at 1670−1740 cm^{-1}.

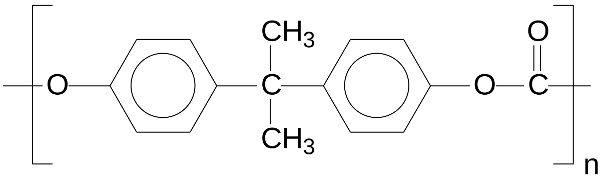
Identify the bond present in compound **W** and suggest its structure. [2]

Bond present is C=O

Based on the balanced equation, we can conclude that compound **W** has molecular formula of C_3H_6O. Compound **W** is propanone.



(d) BPA can react with another monomer **X** to produce polycarbonates. Polycarbonates are commonly used in the manufacturing of water bottles.

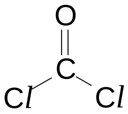


polycarbonates

(i) Identify the new functional group formed in the polycarbonates. [1]

Ester

(ii) Suggest the structure of monomer **X**. [1]



Note: Phenol reacts with acyl chloride to form ester

(iii) Research has shown that BPA can leach into beverages from the polycarbonate water bottles under certain conditions. Exposure to BPA is a concern because of possible health effects of BPA on the brain.

Discuss whether it is safe to consume cold lemon juice stored in a polycarbonate water bottle. [1]

Yes it is likely to be safe. **Complete hydrolysis of polymer into monomer BPA did not occur** and it would require **presence of concentrated acid and heating at high temperature.**

OR

No it is unsafe, eventhough rate of hydrolysis is slow, **some hydrolysis might occur and small amount of BPA** could be released into the lemon juice.

(e) BPA can react with epoxides to form epoxy resins. Fig 3.1 shows the simplified equations for the reaction.

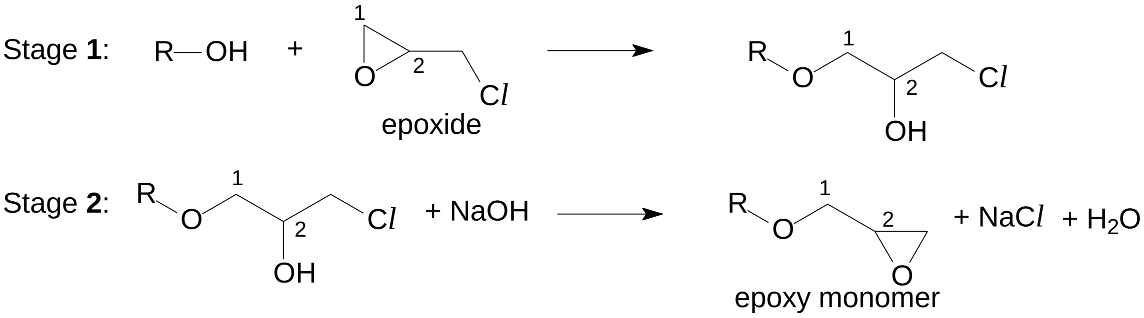


Fig 3.1

(i) For stage **1**, the phenol group of BPA acts as the nucleophile. Suggest why the nucleophile attacks C^1 instead of C^2. [1]

C^1 is less steric hindered than C^2.

(ii) For stage **2**, state the type of reaction and the role of NaOH in the reaction. [2]

Nucleophilic substitution

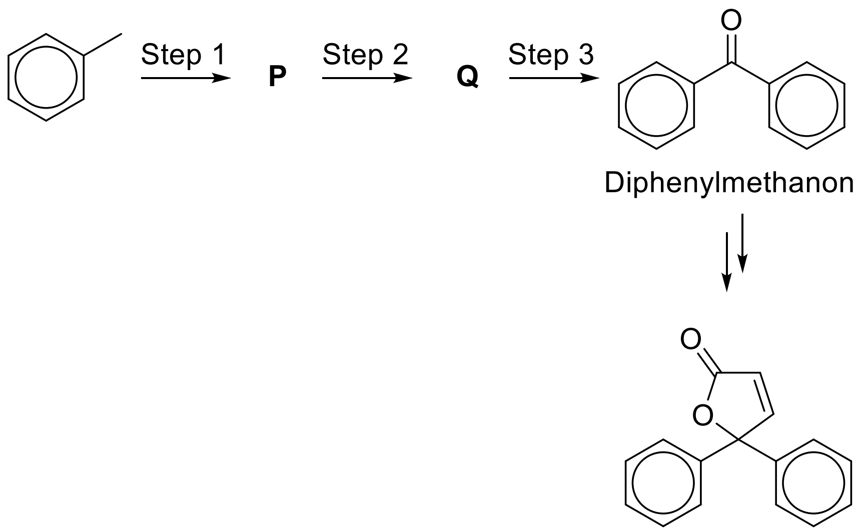
NaOH acts as a base.

[Total : 18]

Section B

Answer **one** question from this section.

4 **(a)** Diphenylmethanone can be synthesized from methylbenzene in three steps as shown in Fig 4.1.



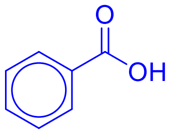
Compound **R**

Fig 4.1

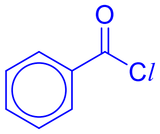
(i) Suggest the reagents and conditions for steps **1**, **2** and **3**, and draw the structures for compounds **P** and **Q**. [5]

Step 1: $KMnO_4$, H_2SO_4(aq), heat
Step 2: anhydrous $SOCl_2$ or anhydrous PCl_3 or anhydrous PCl_5
Step 3: anhydrous $FeCl_3$, benzene

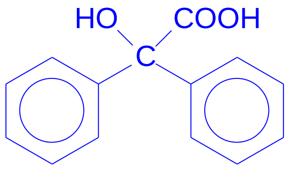
P:



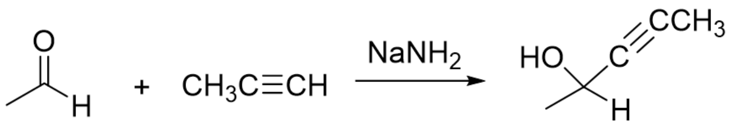
Q:



(ii) When compound **R** is heated with acidified $KMnO_4$, compound **S** is formed as the only organic product. Suggest the structure of compound **S**. [1]



(b) Propyne, $CH_3C{\equiv}CH$, is a weak acid. It can react with an aldehyde in the presence of trace amount of strong base such as $NaNH_2$.



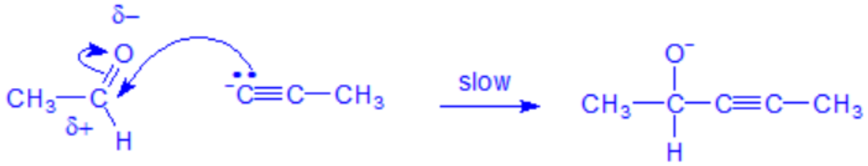
When propyne reacts with NH_2^-, propynyl ion, $CH_3C{\equiv}C^-$ is formed.

(i) State the type of reaction that occurred between propyne and ethanal. [1]

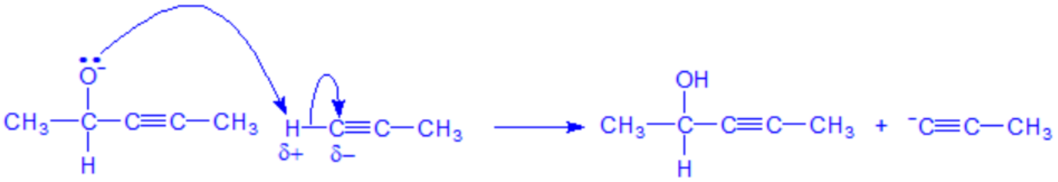
Nucleophilic addition

(ii) Describe the mechanism for this reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

Step 1:



Step 2:



(iii) Suggest if the organic product formed from this reaction would rotate plane−polarised light. [2]

Trigonal planar carbonyl C is **attacked by the nucleophile from either side of the plane with equal probability**. The **two enantiomers are formed in equal amount**. The product is a racemic mixture where the **rotation of plane−polarised light by one enantiomer is completely cancelled out by the other enantiomer**. Hence the organic product formed **would not rotate plane−polarised light.**

(c) The mechanism for the reaction between compounds **T** and **U** is as shown.

Step 1: $\mathbf{T} + \mathbf{U} \rightleftharpoons \mathbf{V}$

Step 2: $\mathbf{T} + \mathbf{V} \rightarrow \mathbf{W}$ (slow)

(i) Write a balanced overall equation for the reaction between compounds **T** and **U**. [1]

$2\mathbf{T} + \mathbf{U} \longrightarrow \mathbf{W}$

(ii) Write an expression for K_c for step 1, stating its units. [2]

$K_c = \frac{[V]}{[T][U]}$ units = $mol^{-1}dm^3$

(iii) Using the information given in the question and your answer to **c(ii)**, derive the rate equation for the reaction between compounds **T** and **U**. [2]

$[V] = K_c[T][U]$

Rate = $k[T][V]$

$= k[T](K_c[T][U]) = kK_c[T]^2[U]$ or $k'[T]^2[U]$

(iv) A concentration−time graph was plotted for step 1 as shown in Fig 4.2. Equilibrium was established at t_0. At t_1, a change was introduced.

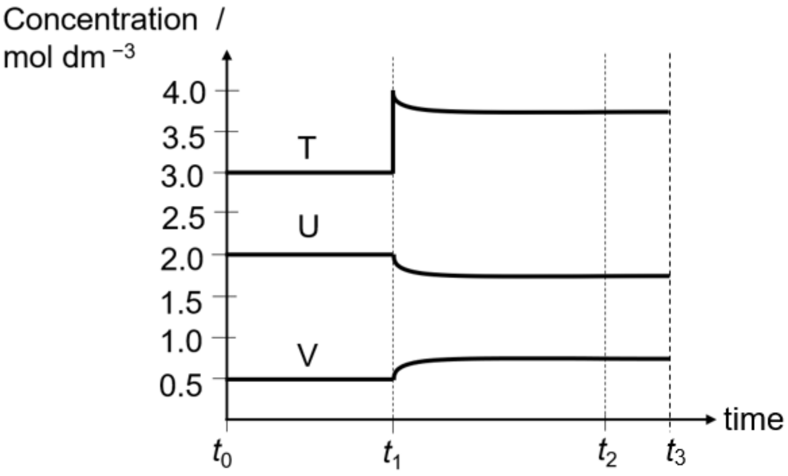


Fig 4.2

State the change that occurred at t_1. Explain the trend observed in the graph from t_1 to t_2. [2]

Concentration of **T** was increased at t_1.

By Le Chatelier's Principle, the equilibrium position will shift to the right to partially decrease the concentration of **T** and **U** and cause partial increase in concentration of **V**.

(v) Suggest whether there would be any change in the individual concentrations of compounds **T**, **U** and **V** when a catalyst is added to the reaction mixture at t_3. [2]

Catalyst increases both the rate of forward and backward reaction by the same extent but not the equilibrium position. Hence, there will be no change in K_c. The proportion of compound T, U and V remains unchanged.

[Total : 20]

5 **(a)** Describe and explain the variation in volatility of the elements in Group 17. [2]

Down the Group, ***volatility*** of the halogens ***decreases***.

Cl_2, Br_2 and I_2 are non-polar molecules with weak **temporary dipole- induced dipole interactions (td-id)** between the molecules.

Down the Group, the total no. of electrons in the molecules or relative molecular mass increases, **size of electron cloud increases and is thus more easily distorted**.

Increasing amount of energy is required to overcome the increasingly stronger td-id intermolecular forces.

(b) *Use of the Data Booklet is relevant to this question.*

Explain the following observations in terms of the relative thermal stabilities of the hydrides of the Group 17 elements.

compound	HC*l*	HBr	HI
decomposition behaviour	does not decompose even on strong heating	strong heating yields reddish brown fumes of Br_2	purple fumes of I_2 obtained when red-hot rod is plunged into jar of HI

[2]

Thermal stability of the hydrogen halides **decreases down the Group.**

The thermal stability of the hydrogen halide depends on the **strength of the H-X bond**.

BE(H−C*l*) = 431 kJ mol^{-1}, BE(H−Br) = 366 kJ mol^{-1}, BE(H−I) = 298 kJ mol^{-1}.

and hence **less energy is needed to overcome the bond** and the HX decomposes more readily.

(c) State and explain the observations when separate solutions of chloride and iodide ions are mixed with aqueous silver nitrate, followed by excess aqueous ammonia. [3]

White AgC*l* ppt, soluble in excess NH_3

Yellow AgI ppt, insoluble in excess NH_3

In the presence of excess NH_3, $Ag^+(aq)$ forms complex with NH_3, thus decreasing $[Ag^+]$.

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ \text{ ....(1)}$$

When $[Ag^+]$ decreases, ionic products for silver chloride & silver iodide decrease, but since **silver chloride has a larger K_{sp}** than silver iodide, ionic product of silver chloride becomes less than its K_{sp} and it dissolves in aqueous ammonia while silver iodide does not.

(d) Carbon monoxide in a sample of polluted air can readily be determined by passing through solid iodine(V) oxide, I_2O_5, to give carbon dioxide and iodine.

(i) Write a balanced equation for the reaction between carbon monoxide and iodine(V) oxide. [1]

$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$

(ii) The iodine produced is dissolved in a suitable solvent and titrated with aqueous sodium thiosulfate, $Na_2S_2O_3$.

1 dm^3 sample of air produced iodine that required 20.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate to discharge the iodine colour.

Calculate the mass of carbon monoxide in this sample of polluted air. [2]

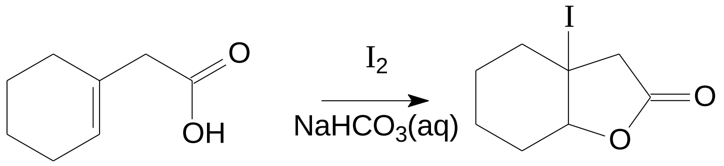
$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

No. of moles of $S_2O_3^{2-} = 0.10 \times \frac{20}{1000}$
$= 2.00 \times 10^{-3}$

$2S_2O_3^{2-} \equiv I_2 \equiv 5CO$
No. of moles of $I_2 = 1.00 \times 10^{-3}$
No. of moles of $CO = 5.00 \times 10^{-3}$

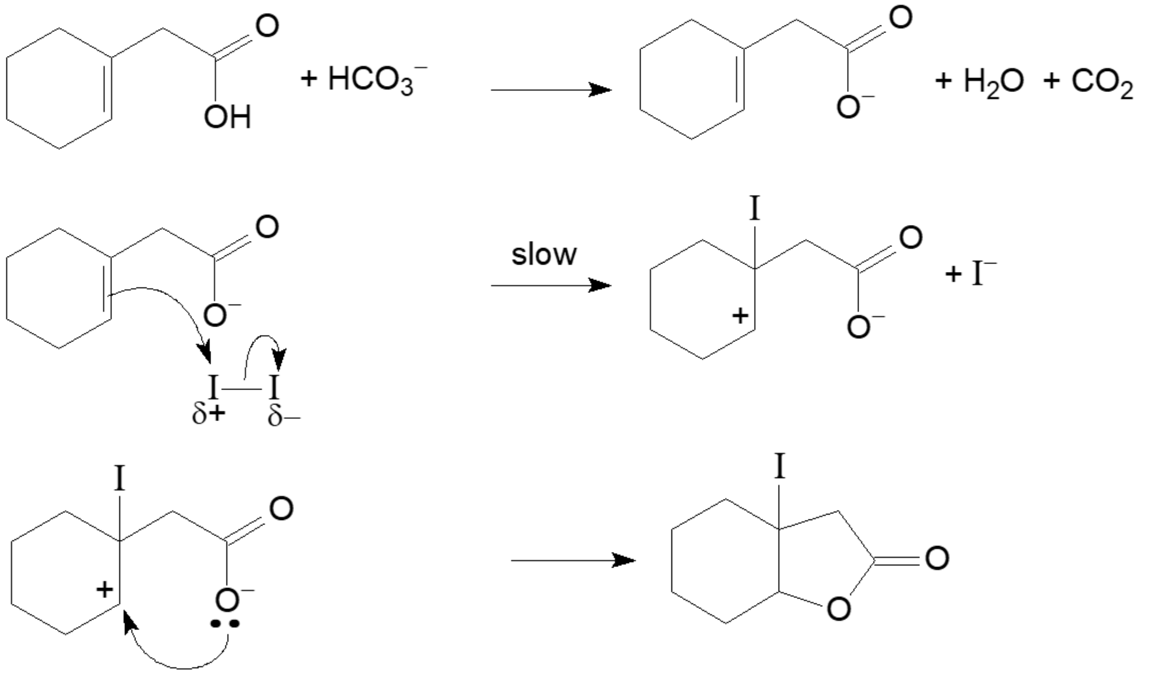
Mass of CO $= 5.00 \times 10^{-3} \times 28.0$
$= 0.140$ g

(e) In the presence of aqueous sodium hydrogencarbonate, iodine does not add across the C=C bond of compound **D** as might be expected. Instead, the following reaction occurs.

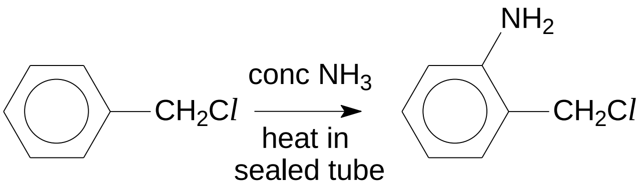


compound **D**

The first step of the mechanism involves a fast acid-carbonate reaction. Describe the mechanism for this electrophilic addition reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]



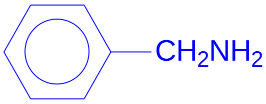
(f) A student attempted to make compound **E** from (chloromethyl)benzene as shown.



(chloromethyl)benzene compound **E**

However, a different product with molecular formula C_7H_9N was obtained.

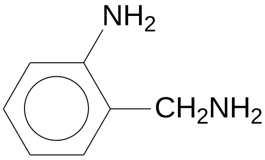
(i) Draw the displayed formula of the product obtained from the reaction. [1]



(ii) Explain why compound **E** was not obtained. [1]

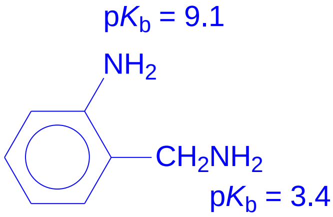
NH_3 is an electron rich nucleophile. NH_3 undergoes nucleophilic substitution at C-C*l* bond instead of attacking the electron rich benzene ring for electrophilic substitution.

(g) The pK_b values of the two amine groups in compound **F** are 3.4 and 9.1.



compound **F**

(i) Copy the structure of compound **F** to your answer booklet and assign the pK_b values to the two amine groups. Explain your answer. [2]



Phenylamine is a weaker base with higher pK_b value. The lone pair electron on N is delocalized into the π electron cloud of the benzene ring. Hence the N atom is less likely to accept an H^+.

(ii) Calculate the initial pH of 0.100 mol dm^{-3} of compound **F**. [2]

Let compound F be **B**

pK_b = 3.4 => K_b = $10^{-3.4}$

Method 1: Weak base, use ICE and K_b to calculate OH^- dissociated

	B	+ H_2O	$\rightleftharpoons$	BH^+	+ OH^-
Initial / mol dm^{-3}	0.1	-		0	0
Change / mol dm^{-3}	$-x$	-		$+x$	$+x$
Eqm / mol dm^{-3}	$0.1-x$	-		x	x

Base dissociation constant, $K_b = \frac{[BH^+][OH^-]}{[B]} = 10^{-3.4}$

$$\frac{x^2}{0.1-x} = 10^{-3.4}$$

Since B is a weak base, x << 0.1 and we can assume that $(0.1-x) \approx 0.1$

$$\frac{x^2}{0.1} = 10^{-3.4}$$

x = 0.006310 mol dm^{-3} = $[OH^-]_{eqm}$

pOH = 2.20

pH = 14 – 2.20 = **11.80 (2d.p.)**

Method 2: Weak base, use formula to calculate OH^- dissociated

Weak base,

$[OH^-] = \sqrt{K_b \times [weak\ base]} = \sqrt{10^{-3.4} \times 0.10}$

$[OH^-]$ = 0.006310 mol dm^{-3}

pOH = 2.20

pH = 14 – 2.20 = **11.80 (2d.p.)**

(h) Explain the observations when Br_2(aq) is added to the two samples.

sample	phenylamine	phenylamine dissolved in excess sulfuric acid
observations	orange Br_2 (aq) decolourises and white precipitate forms	orange Br_2 (aq) remains

[2]

Phenylamine undergoes electrophilic substitution with Br_2(aq) as N atom **donates lone pair of electrons into the ring (OR –NH_2 is a strong activating group)** which increases the electron density of the benzene ring, making it more susceptible to the electrophilic attack.

White ppt of 2,4,6-tribromophenylamine is produced.

In the presence of sulfuric acid, -NH_2 group, a base, **is protonated to form -NH_3^+** (which is a deactivating group), hence the **benzene ring is no longer activated** and cannot react with Br_2(aq).

NATIONAL JUNIOR COLLEGE
SH 2 Year – End Practical Examination
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY **9729/04**

Paper 4 Practical **Tuesday 20 August 2019**

Candidate answer on the Question paper. **2 hours 30 minutes**

READ THE INSTRUCTIONS FIRST
Write your identification number and name. Circle the practical shift and laboratory where appropriate, in the boxes provided.

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, 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 19 and 20.

At the end of the examination, submit the question paper.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift		
1	**2**	**3**

Laboratory			
CM41	**CM42**	**CM43**	**CM44**
PH31	**PH32**	**PH33**	
BI23	**BI24**		

For Examiner's Use	
1	**/ 12**
2	**/ 21**
3	**/ 14**
4	**/ 8**
Total	**/ 55**

This document consists of **19** printed pages and **1** blank page.

1 Determination of the solubility product of calcium iodate(V)

When solid calcium iodate(V) is added to water to form a saturated solution, an equilibrium between the undissolved salt and its aqueous ions is established.

$$Ca(IO_3)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2IO_3^{-}\,(aq)$$

The solubility product, K_{sp} , of calcium iodate(V) is expressed as follows.

$$K_{sp} = [Ca^{2+}(aq)]\,[IO_3^{-}(aq)]^2$$

The solubility product can be found by determining the equilibrium concentration of IO_3^- ions in a saturated solution of calcium iodate(V) through a redox titration.

Iodate(V) ions, IO_3^-, react with iodide ions according to the following equation.

$$IO_3^-\,(aq) + 5I^-(aq) + 6H^+\,(aq) \longrightarrow 3I_2\,(aq) + 3H_2O\,(l)$$

The iodine produced in this reaction may be titrated against sodium thiosulfate using starch solution as indicator. Thiosulfate ions react with iodine according to the following equation:

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

In this question, you will prepare a saturated solution of calcium iodate(V) to carry out the redox titration. Using the experimental results, you will determine the solubility product of calcium iodate(V).

You are provided with:
FA 1 is solid calcium iodate(V), $Ca(IO_3)_2$

FA 2 is 0.05 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

FA 3 is 0.50 mol dm^{-3} potassium iodide, KI

FA 4 is 0.50 mol dm^{-3} sulfuric acid, H_2SO_4

FA 5 is starch indicator

Preparation of a saturated solution of calcium iodate (V), FA 6

(a) Procedure

1. Use a 100 cm^3 measuring cylinder to transfer 80.0 cm^3 of deionised water into a 250 cm^3 beaker.

2. Transfer all **FA 1** from the weighing bottle into the beaker. Stir for 1 to 2 minutes and leave to stand for **5 minutes**. There will be some $Ca(IO_3)_2$ solids left undissolved.

3. Use a 0.2 ^oC division thermometer, record the temperature of the solution in the beaker.

4. To remove the undissolved solids, filter the saturated solution into another clean and **dry** 250 cm^3 beaker using a **dry** filter paper and **dry** funnel. Label this solution as **FA 6**.

Titration

(b) **Procedure**

(i)
1. Fill a burette with **FA 2**.
2. Pipette 10.0 cm^3 of **FA 6** into a conical flask.
3. Use a 10 cm^3 measuring cylinder to add 5.0 cm^3 of **FA 3**, followed by 5.0 cm^3 of **FA 4** to the same conical flask and swirl quickly.
4. Titrate the iodine in the conical flask with **FA 2** until the brown colour of the iodine becomes pale yellow.
5. Add about 10 drops of starch solution to the flask and continue adding **FA 2** until the blue-black colour just disappears.
6. Repeat the titration as many times as you think necessary to obtain consistent results. Record your titration results in the space below.

Results

[4]

(ii) From your titres, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

10.0 cm^3 of **FA 6** produced an amount of iodine which required ……...… cm^3 of **FA 2**.
[1]

(c) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** part.

(i) Calculate the number of moles of $S_2O_3^{2-}$ in the volume of **FA 2** recorded in **1b(ii)**, and hence determine the molar concentration of IO_3^- ions in **FA 6**.

number of moles of $S_2O_3^{2-}$ =……………………………..

concentration of IO_3^- ions in **FA 6** =……………………………..

[2]

(ii) Determine the molar concentration of Ca^{2+} in **FA 6** and hence, calculate the solubility product, K_{sp}, of calcium iodate(V), stating the units.

concentration of Ca^{2+} ions in **FA 6** = ……………………………..

solubility product of $Ca(IO_3)_2$ = ……………………………..

[2]

(d) Explain why it was necessary to use the **dry** apparatus (e.g. beaker, filter paper and funnel) in the preparation of **FA 6**, and what effect failing to do it would have on the titre values?

………

………[1]

(e) A literature value for the solubility product of calcium iodate(V) is found to be 6.15×10^{-6} at 20 °C.

State a possible reason for the difference in the K_{sp} value that you have calculated and suggest an improvement that might allow a value closer to the literature value to be obtained.

………

………

………

………

………[2]

[Total: 12]

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2 **Determination of the enthalpy change of neutralisation, ΔH_n**

FA 7 is a solution of HC*l* of unknown concentration

FA 8 is a solution of 1.0 mol dm^{-3} of NaOH

In this question, you will carry out a series of experiments where different volumes of **FA 7** and **FA 8** are mixed together.

You will determine the temperature change of the reaction mixture, ΔT, of each experiment and then analyse your results graphically in order to determine the

- concentration of HC*l* in **FA 7**
- maximum temperature change, ΔT_{max}
- value for the enthalpy change of neutralisation, ΔH_n

(a) **Determining the change in temperature for a series of reactions between FA 7 and FA 8**

(i) **Experiment 1**

1. Place a Styrofoam cup inside a second Styrofoam cup held in a 250 cm^3 beaker to prevent it from tipping over.

2. Using a measuring cylinder, transfer 20.0 cm^3 of **FA 7** into the Styrofoam cup.

3. Measure the temperature of **FA 7** in the Styrofoam cup. Record the initial temperature of the solution of **FA 7** as $T_{FA\,7}$.

4. Rinse and dry the thermometer.

5. Measure 50.0 cm^3 of **FA 8** using another measuring cylinder. Record the initial temperature of the solution of **FA 8** as $T_{FA\,8}$.

6. Transfer the **FA 8** into the cup containing **FA 7**. Stir and record the maximum temperature of the reaction as T_{max}.

7. Rinse and dry the Styrofoam cup and thermometer.

Experiment 2

Repeat steps 2 to 7 using 50.0 cm^3 of **FA 7** and 20.0 cm^3 **FA 8**.

Experiments 3 to 6

Carry out **four** further experiments to investigate how the T_{max} changes with different volumes of **FA 7** and **FA 8**. In each case, the total volume of the reaction mixture must be 70.0 cm^3 and the volume of each reagent should not be less than 20.0 cm^3.

In an appropriate format in the space provided on next page, record

- all measurements of volumes used,
- all temperatures measured, $T_{weighted\ initial}$ and ΔT

$\Delta T = T_{max} - T_{weighted\ initial}$

$$T_{weighted\ initial} = \frac{(\text{Volume of FA 7} \times T_{FA\,7}) + (\text{Volume of FA 8} \times T_{FA\,8})}{\text{Volume of FA 7} + \text{Volume of FA 8}}$$

Results

[4]

(ii) Plot a graph of ΔT (*y*–axis) against volume of **FA 7** used (*x*–axis) on the grid in Fig. 2.1 using the data you have obtained in **2a(i)**.

Fig. 2.1 [3]

(iii) Draw two best-fit straight lines, the first should be drawn using the plotted points where ΔT is increasing and the second should be drawn using the plotted points where ΔT is decreasing. Extrapolate (extend) both lines until they intercept.

[1]

(iv) From your graph in Fig. 2.1, determine the maximum temperature change, ΔT_{max}, and the volume, V_{max}, of **FA 7** required to obtain this.

ΔT_{max} = ………………………….°C V_{max} = ……………………………cm^3 [2]

(b) **Calculation**
Show your working and appropriate significant figures in the final answer to **each** part.

Using your answers in **2a(iv)**, calculate

(i) the concentration, in mol dm^{-3}, of HC*l* in **FA 7**.

concentration of HC*l* in **FA 7** = …………………………….. [2]

(ii) the heat change for the neutralisation reaction at $\Delta T_{max.}$.

You may assume that the specific heat capacity of the reaction mixture is 4.18 J g^{-1} K^{-1} and that the density is 1.00 g cm^{-3}.

heat change = …………………………….. [1]

(iii) Hence, calculate the enthalpy change of neutralisation, ΔH_n.

ΔH_n = …………………………….. [1]

(c) In another similar experiment, 1.0 mol dm^{-3} aqueous ammonia was used instead of 1.0 mol dm^{-3} NaOH. A graph of change in temperature, ΔT, against volume of **FA 7** was plotted.

Suggest how would the ΔT_{max} and volume, V_{max}, of **FA 7** from this experiment be compared to your result obtained in **2a(iv)** .

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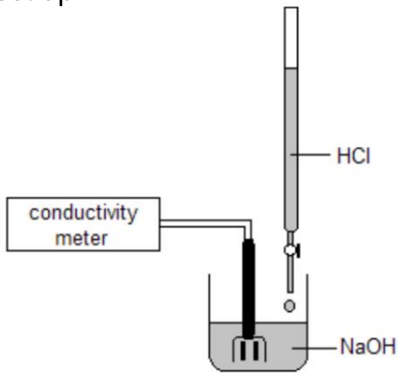
……………………………………………………………………………………………………[2]

(d) A student employed another method to determine the concentration of the HC*l* in **FA 7** through the use of conductometry. Conductometry is the measurement of the electrolytic conductivity to monitor the progress of a chemical reaction due to ions being produced or reacted away. The equivalence point can then be determined for the acid – base reaction by plotting the conductivity against the volume of the HC*l* added.

$$H^+ + OH^- \longrightarrow H_2O$$

The following apparatus were set up.



The student measured the conductivity of the solution in the beaker with each addition of a small fixed volume of HC*l* and obtained the following graph.

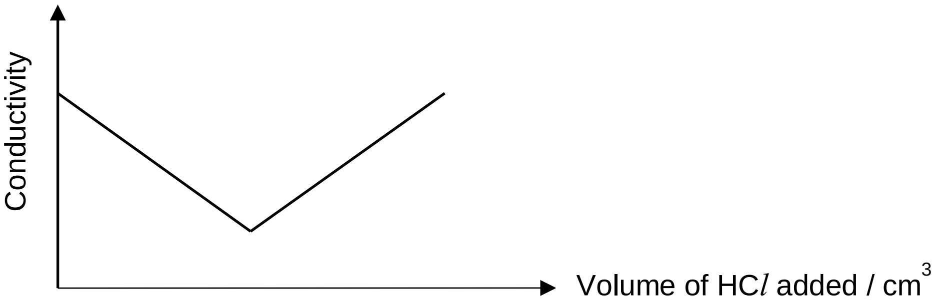


Fig. 2.2

(i) Indicate on the graph (Fig. 2.2), the point which marks the volume of HC*l* needed for complete reaction. [1]

(ii) Explain the shape of the graph in Fig. 2.2.

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…………………………………………………………………………………………….[3]

(iii) With reference to your experiment in **2(a)**, suggest which method (calorimetry or conductometry) is more accurate for the determination of the concentration of HCl in **FA 7**.

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…………………………………………………………………………………………….[1]

[Total: 21]

3 Identification of ions

FA 9 is a solution containing a mixture of two salts.

You are to perform the tests described in Table 3.1 and record your observations in the table.

In all tests, the reagents should be added gradually until no further change is observed unless you are instructed otherwise. You should indicate clearly at which stage in a test a change occurs, recording your observations alongside the relevant tests.

The volumes given below are approximate and should be estimated rather than measured, unless otherwise stated. If there is no observable change, write **no observable change**.

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

Table 3.1

	Test	*Observation*
(a)	Place about 3 cm depth of **FA 9** in a test-tube, add equal volume of aqueous sodium hydroxide. Warm the contents in the tube.	
(b)	Filter the mixture from **3(a)** and collect the filtrate in a test-tube. Label the filtrate as **FA 10** and retain it for tests **3(c)** and **3(d)**. Leave the residue in the filter paper and observe it again after 5 minutes.	
(c)	Place 2 cm depth of **FA 10** in a test-tube and add nitric acid until no further change is seen. Label the solution as **FA 11** and retain it for test **3(e)**.	
(d)	Place 1 cm depth of **FA 10** in a test-tube. Add half a spatula of zinc powder. Warm the contents in the tube cautiously.	

	Test	*Observation*
(e)	Place 2 cm depth of <u>**FA 11**</u> in a test-tube, add equal depth of aqueous ammonia. <u>Add</u> excess dilute nitric acid followed by aqueous silver nitrate.	
(f)	Place 1 cm depth of **FA 9** in a test-tube. Add dilute hydrochloric acid followed by aqueous barium chloride.	

[6]

(g) **(i)** Identify the **two** cations and **two** anions present in **FA 9**.

cation 1: ………………………… cation 2: …………………………

anion 1: ………………………… anion 2: …………………………

[4]

(ii) Write equations, with state symbols, to illustrate the observations in **3(c)**.

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……………………………………………………………………………………………….[2]

(iii) Predict what will happen when solid ammonium nitrate is added to **FA 9** followed by aqueous ammonia.

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……………………………………………………………………………………………….[2]

[Total : 14]

4 Planning

Determination of the hardness of water in a sample.

Hard water is water that has high mineral content and is formed when water percolates through deposits of limestone, chalk and gypsum, which are largely made of calcium carbonates, bicarbonates and sulfates. The hardness of water is measured in terms of the molar concentration of Ca^{2+} in mol dm^{-3}.

In a particular sample of water, the hardness is caused by the presence of calcium chloride. The amount of Ca^{2+}, and hence the concentration of Ca^{2+}, can be determined by precipitation with an excess of oxalic acid.

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_4(s)$$

You are to design an experiment to determine the hardness of water in a sample.

You are provided with

- sample of water with estimated hardness of 0.02 mol dm^{-3}
- 0.1 mol dm^{-3} of oxalic acid $H_2C_2O_4$
- electronic balance
- common laboratory apparatus

(a) Given the K_{sp} of calcium oxalate is 2.7×10^{-9} $mol^2\,dm^{-6}$, predict what will be observed when 25.0 cm^3 of the water sample is mixed with equal volume of the 0.1 mol dm^{-3} of oxalic acid solution.

[2]

(b) Your plan should include a step-by-step description of the method, including

- the sequence of steps to ensure that the maximum amount of precipitate is recovered,
- the use of appropriate apparatus,
- the recordings using the letters A, B, C etc to represent the measurement taken and present it with an appropriate table format,
- the processing of the results to determine the molar concentration of Ca^{2+} in the water sample.

[A_r: C, 12.0; Ca, 40.1; H, 1.0; O, 16.0]

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…………………………………………………………………………………………………[6]

[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

anion	*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 A*l* foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* 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 with 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 a 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 acidified 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

NATIONAL JUNIOR COLLEGE
SH 2 Year – End Practical Examination
Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

9729/04

Paper 4 Practical
Candidate answer on the Question paper.

Tuesday 20 August 2019
2 hours 30 minutes

READ THE INSTRUCTIONS FIRST
Write your identification number and name. Circle the practical shift and laboratory where appropriate, in the boxes provided.

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
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Answer **all** questions in the spaces provided on the Question Paper.

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

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Shift			
1	**2**	**3**	
Laboratory			
CM41	**CM42**	**CM43**	**CM44**
PH31	**PH32**	**PH33**	
BI23	**BI24**		

For Examiner's Use	
1	**/ 12**
2	**/ 21**
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1 Determination of the solubility product of calcium iodate(V)

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$$Ca(IO_3)_2\ (s) \rightleftharpoons Ca^{2+}\ (aq) + 2IO_3^-\ (aq)$$

The solubility product, K_{sp} , of calcium iodate(V) is expressed as follows.

$$K_{sp} = [Ca^{2+}(aq)]\ [IO_3^-(aq)]^2$$

The solubility product can be found by determining the equilibrium concentration of IO_3^- ions in a saturated solution of calcium iodate(V) through a redox titration.

Iodate(V) ions, IO_3^-, react with iodide ions according to the following equation.

$$IO_3^-\ (aq) + 5I^-(aq) + 6H^+\ (aq) \longrightarrow 3I_2\ (aq) + 3H_2O\ (l)$$

The iodine produced in this reaction may be titrated against sodium thiosulfate using starch solution as indicator. Thiosulfate ions react with iodine according to the following equation:

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

In this question, you will prepare a saturated solution of calcium iodate(V) to carry out the redox titration. Using the experimental results, you will determine the solubility product of calcium iodate(V).

You are provided with:
FA 1 is solid calcium iodate(V), $Ca(IO_3)_2$

FA 2 is 0.05 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

FA 3 is 0.50 mol dm^{-3} potassium iodide, KI

FA 4 is 0.50 mol dm^{-3} sulfuric acid, H_2SO_4

FA 5 is starch indicator

Preparation of a saturated solution of calcium iodate (V), FA 6

(a) Procedure

1. Use a 100 cm^3 measuring cylinder to transfer 80.0 cm^3 of deionised water into a 250 cm^3 beaker.
2. Transfer all **FA 1** from the weighing bottle into the beaker. Stir for 1 to 2 minutes and leave to stand for **5 minutes**. There will be some $Ca(IO_3)_2$ solids left undissolved.
3. Use a 0.2 °C division thermometer, record the temperature of the solution in the beaker.
4. To remove the undissolved solids, filter the saturated solution into another clean and **dry** 250 cm^3 beaker using a **dry** filter paper and **dry** funnel. Label this solution as **FA 6**.

Titration

(b) **Procedure**

(i) **1.** Fill a burette with **FA 2**.

2. Pipette 10.0 cm^3 of **FA 6** into a conical flask.

3. Use a 10 cm^3 measuring cylinder to add 5.0 cm^3 of **FA 3**, followed by 5.0 cm^3 of **FA 4** to the same conical flask and swirl quickly.

4. Titrate the iodine in the conical flask with **FA 2** until the brown colour of the iodine becomes pale yellow.

5. Add about 10 drops of starch solution to the flask and continue adding **FA 2** until the blue-black colour just disappears.

6. Repeat the titration as many times as you think necessary to obtain consistent results. Record your titration results in the space below.

Results

Temperature of the solution in the beaker = ………….. °C

	1	**2**	
Final burette reading / cm^3			
Initial burette reading / cm^3			
Volume of FA 2 used / cm^3			

[1]Record the temperature of the solution in the beaker
[1] Records all burette readings to 2 d.p including a(ii). (MMO)
[1] Has at least 2 titre values ± 0.10 cm^3 (MMO)
[1] Table has appropriate headings and units (PDO)

[-1] Incorrect calculation for volume of FA2

[4]

(ii) From your titres, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

Average vol of **FA 2** used = (x.00 +.00)/2 =x.00 cm^3 (round to 2 d.p.) **[1]**

* Do not award marks if inconsistent values used
* Do penalise if no working

10.0 cm^3 of **FA 6** produced an amount of iodine which required ……...… cm^3 of **FA 2**.
[1]

(c) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** part.

(i) Calculate the number of moles of $S_2O_3^{2-}$ in the volume of **FA 2** recorded in **b(ii)**, and hence determine the molar concentration of IO_3^- ions in **FA 6**.

Amt of $S_2O_3^{2-}$ = (ans from b(ii)/1000) x 0.05 = A mol **[1]**

$$\frac{\eta_{IO_3^-}}{\eta_{S_2O_3^{2-}}} = \frac{1}{6}$$

Amt of IO_3^- = $\frac{1}{6} \times A$ = B mol

$[IO_3^-]$ = $B \times \frac{1000}{10.0}$ = c mol dm^{-3} **[1]** **(Allow ecf)**

number of moles of $S_2O_3^{2-}$ =……………………………..

concentration of IO_3^- ions in **FA 6** =……………………………..

[2]

(ii) Determine the molar concentration of Ca^{2+} in **FA 6** and hence, calculate the solubility product, K_{sp}, of calcium iodate(V), stating the units.

$$\frac{\eta_{Ca^{2+}}}{\eta_{IO_3^-}} = \frac{1}{2}$$

$[Ca^{2+}]$= ½ $[IO_3^-]$ = ½ c mol dm^{-3} **[1]** **(Allow ecf)**

K_{sp} = $[Ca^{2+}(aq)]\,[IO_3^-(aq)]^2$
= [½ C] $[C]^2$
= ½ C^3 mol^3 dm^{-9} **[1] (Allow ecf)**
(Do not award the mark if the units is wrong)

concentration of Ca^{2+} ions in **FA 6** = ……………………………..

solubility product of $Ca(IO_3)_2$ = ……………………………..

[2]

(d) Explain why it was necessary to use the **dry** apparatus (e.g. beaker, filter paper and funnel) in the preparation of **FA 6**, and what effect failing to do it would have on the titre values?

To prevent the dilution of the saturated **FA 6** solution which results in lesser amount of

……………………………………………………………………………………………………

IO_3^- reacted during titration and hence smaller titre value **[1]**

(Do not award mark if there is no mention to the change in the titre value or change in conc of FA 6 or IO_3^-.)

[1]

(e) A literature value for the solubility product of calcium iodate(V) is found to be 6.15 × 10^{-6} at 20 °C.

State a possible reason for the difference in the K_{sp} value that you have calculated and suggest an improvement that might allow a value closer to the literature value to be obtained.

If the **calculated K_{sp} > literature K_{sp} value**, the explanation is as follow:

The experiment is not carried out at 20 °C **[1]**.
$Ca(IO_3)_2\ (s) \rightleftharpoons Ca^{2+}\ (aq) + 2IO_3^-\ (aq)$
Hence, the equilibrium position shifted to the right.

Use a thermostatically controlled **water bath maintained at 20 °C** during the preparation of **FA 6** before carrying out the filtration **[1]**.

or

If the **calculated K_{sp} < literature K_{sp} value**, the explanation is as follow:

The **salt has not dissolve to form a saturated solution** or **reach equilibrium with its dissolved ions**. **[1]**

Leave the mixture to stand for longer period and use a thermostatically controlled **water bath to maintain at 20 °C** for the salt solution to reach equilibrium / saturation. **[1]**

[Total: 12]

2 Determination of the enthalpy change of neutralisation, ΔH_n

FA 7 is a solution of HC*l* of unknown concentration
FA 8 is a solution of 1.0 mol dm^{-3} of NaOH

In this question, you will carry out a series of experiments where different volumes of **FA 7** and **FA 8** are mixed together.

You will determine the temperature change of the reaction mixture, ΔT, of each experiment and then analyse your results graphically in order to determine the

- concentration of HC*l* in **FA 7**
- maximum temperature change, ΔT_{max}
- value for the enthalpy change of neutralisation, ΔH_n

(a) Determining the change in temperature for a series of reactions between FA 7 and FA 8

(i) Experiment 1

1. Place a Styrofoam cup inside a second Styrofoam cup held in a 250 cm^3 beaker to prevent it from tipping over.

2. Using a measuring cylinder, transfer 20.0 cm^3 of **FA 7** into the Styrofoam cup.

3. Measure the temperature of **FA 7** in the Styrofoam cup. Record the initial temperature of the solution of **FA 7** as $\mathbf{T_{FA\,7}}$.

4. Rinse and dry the thermometer.

5. Measure 50.0 cm^3 of **FA 8** using another measuring cylinder. Record the initial temperature of the solution of **FA 8** as $\mathbf{T_{FA\,8}}$.

6. Transfer the **FA 8** into the cup containing **FA 7**. Stir and record the maximum temperature of the reaction as $\mathbf{T_{max}}$.

7. Rinse and dry the Styrofoam cup and thermometer.

Experiment 2
Repeat steps 2 to 7 using 50.0 cm^3 of **FA 7** and 20.0 cm^3 **FA 8**.

Experiments 3 to 6
Carry out **four** further experiments to investigate how the $\mathbf{T_{max}}$ changes with different volumes of **FA 7** and **FA 8**. In each case, the total volume of the reaction mixture must be 70.0 cm^3 and the volume of each reagent should not be less than 20.0 cm^3.

In an appropriate format in the space provided on next page, record

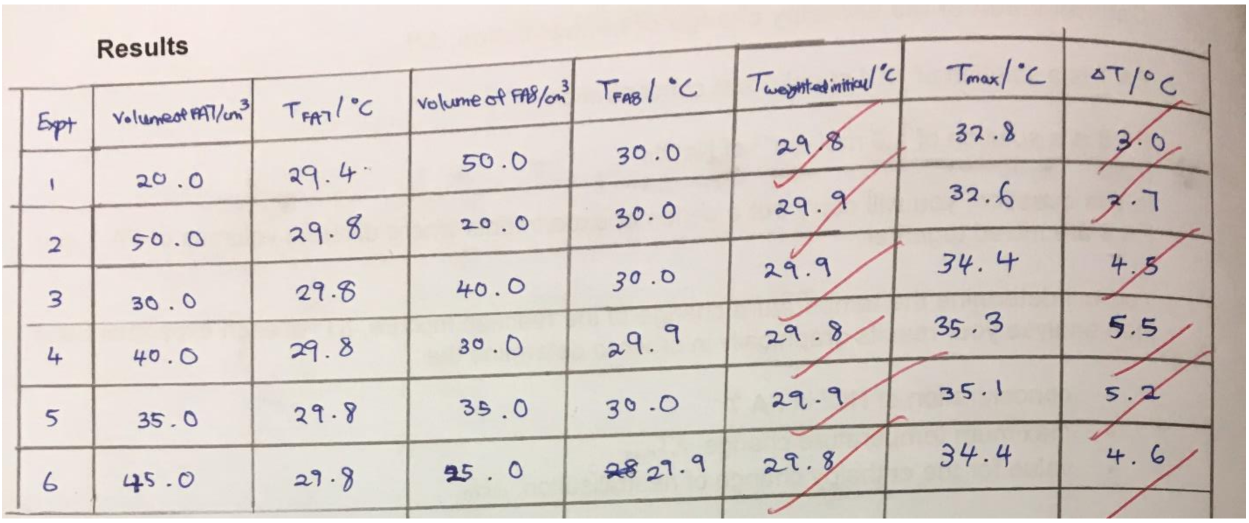
- all measurements of volumes used,
- all temperatures measured, $T_{weighted\ initial}$ and ΔT

$\mathbf{\Delta T} = \mathbf{T}_{max} - \mathbf{T}_{weighted\ initial}$

$$\mathbf{T}_{weighted\ initial} = \frac{(Volume\ of\ FA\ 7 \times T_{FA\ 7}) + (Volume\ of\ FA\ 8 \times T_{FA\ 8})}{Volume\ of\ FA\ 7 + Volume\ of\ FA\ 8}$$

Result

Expt	Vol of **FA 7** /cm^3	Vol of **FA 8** /cm^3	$T_{FA\,7}$ / °C	$T_{FA\,8}$ / °C	$T_{weighed\ initial}$ / °C	T_{may} / °C	ΔT/ °C
1							
2							
3							
4							
5							
6							



Results

Expt	Volume of FA7/cm^3	T_{FA7}/°C	Volume of FA8/cm^3	T_{FA8}/°C	$T_{weighted\ initial}$/°C	T_{max}/°C	ΔT/°C
1	20.0	29.4	50.0	30.0	29.8	32.8	3.0
2	50.0	29.8	20.0	30.0	29.9	32.6	2.7
3	30.0	29.8	40.0	30.0	29.9	34.4	4.5
4	40.0	29.8	30.0	29.9	29.8	35.3	5.5
5	35.0	29.8	35.0	30.0	29.9	35.1	5.2
6	45.0	29.8	25.0	~~28~~ 29.9	29.8	34.4	4.6

[1] Appropriate header with units

[1] Recording to correct precision

[1] Correct calculation of $T_{\text{weighted initial}}$ and ΔT_{max} in 1 d.p

[1] Proper spread of the choice of the volume used for the other 4 expts

[-1] Missing any of the experiment results

[-1] Missing the recording of $T_{\text{weighted initial}}$

[-1] Vol of either FA7 or FA8 used is less than 20.0 cm^3

[-1] Recording of data is <u>NOT IN ONE</u> table.

[-1] Missing T_{FA7} and/or T_{FA8}

[4]

(ii) Plot a graph of ΔT (y–axis) against volume of **FA 7** used (x–axis) on the grid in Fig. 2.1 using the data you have obtained in **2a(i)**.

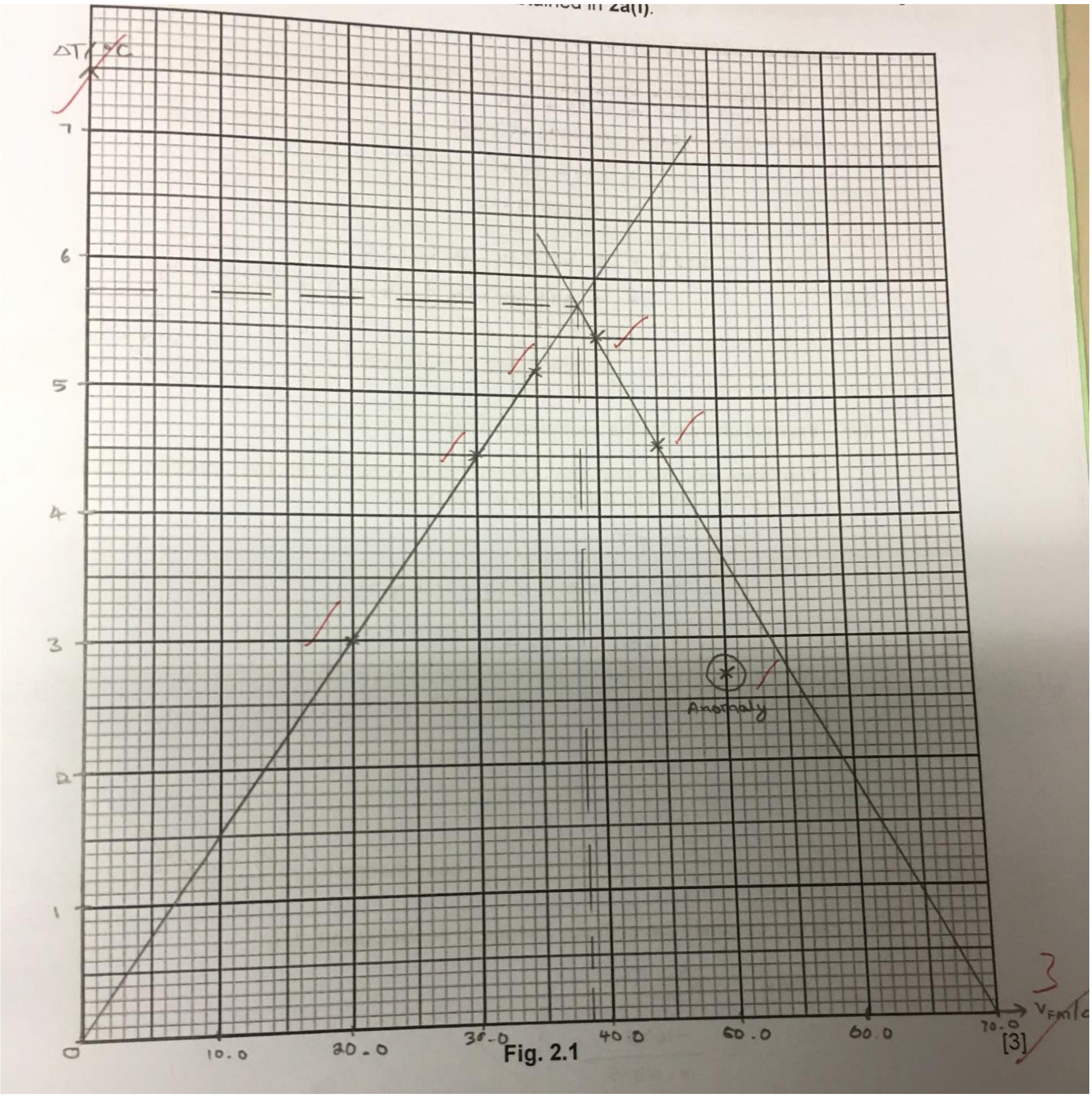


Fig. 2.1 [3]

[1] - Label of the axis with units and appropriate scale

[1] - Points plotted within half a square of 'x'

[1] –The line of best fit must include two points at x= 0 and x = 70

Note: ΔT$_{max}$ should be higher than any of the plotted points.

[-1] if ΔT$_{max}$ is lower than the plotted points .

Plotted points covers more than 50% of grids in both *x* & *y* axis

(iii) Draw two best-fit straight lines, the first should be drawn using the plotted points where ΔT is increasing and the second should be drawn using the plotted points where ΔT is decreasing. Extrapolate (extend) both lines until they intercept. [1]

[1] - Line of best fit to pass through the plotted points

(iv) From your graph in Fig. 2.1, determine the maximum temperature change, ΔT$_{max}$, and the volume, V$_{max}$, of **FA 7** required to obtain this.

Correct reading off the ΔT$_{max}$ value from the graph [1] (ignore precision)

Correct reading off the V_{max} value from the graph [1] (ignore precision)

ΔT_{max} = ……………………………°C V_{max} = ……………………………cm^3 [2]

(b) Calculation

Show your working and appropriate significant figures in the final answer to **each** part.

Using your answers in **2a(iv)**, calculate

(i) the concentration, in mol dm^{-3}, of HC*l* in **FA 7**.

$V_{NaOH} = 70 - V_{max}$ = A cm^3
Amt of NaOH = A/1000 x 1.0 = B mol **[1]**

Amount of HC*l* = B mol
Conc of HC*l* = B / (V_{max}/1000) = C mol dm^{-3} **[1] (Allow ecf)**

concentration of HC*l* in **FA 7** = …………………………….. [2]

(ii) the heat change for the neutralisation at ΔT_{max}..

You may assume that the specific heat capacity of the reaction mixture is 4.18 J g^{-1} K^{-1} and that the density is 1.00 g cm^{-3}.

$q = mc\Delta T_{max}$ = 70 x 4.18 x ΔT_{max} = D J

heat change = –D J **[1] (Accept if heat change value is positive)**

heat change = …………………………….. [1]

(iii) Hence, calculate the enthalpy change of neutralisation, ΔH_n.

Amount of H_2O = Amount of NaOH = Amount of HC*l* = B mol

ΔH_{neut} = −D / B = −E kJ mol^{-1} **[1] (Must have the <u>negative sign</u> to award the mark) (Allow ecf)**

ΔH_n = …………………………….. [1]

(c) In another similar experiment, 1.0 mol dm^{-3} aqueous ammonia was used instead of 1.0 mol dm^{-3} NaOH. A graph of maximum change in temperature, ΔT, against volume of **FA 7** was plotted.

Suggest how would the ΔT_{max} and volume, V_{max}, of **FA 7** from this experiment be compared to your result obtained in **2a(iv)** .

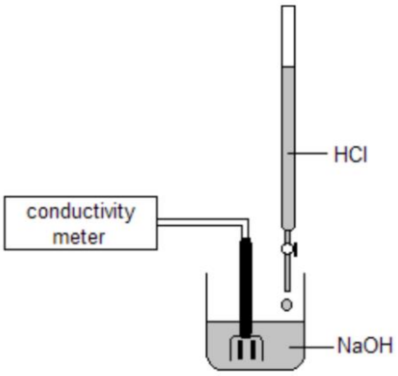
<u>Lower temperature rise, ΔT_{max}</u>, as **<u>some heat released is used to dissociate</u>** the weak base completely. **[1]**
……………………………………………………………………………………………
(Do not accept rate of reaction is less vigorous and heat lost or less water formed or the reaction is less exothermic)

……
V_{max} is the same as same number of moles of HC*l* is needed to react with the aqueous
……
NH_3 since the reacting mole ratio remains the same. **[1]**
……[2]

(d) A student employed another method to determine the concentration of the HC*l* in **FA 7** through the use of conductometry. Conductometry is the measurement of the electrolytic conductivity to monitor the progress of a chemical reaction due to ions being produced or reacted away. The equivalence point can then be determined for the acid – base reaction by plotting the conductivity against the volume of the HC*l* added.

$$H^+ + OH^- \longrightarrow H_2O$$

The following apparatus were set up.



The student measured the conductivity of the solution in the beaker with each addition of a small fixed volume of HC*l* and obtained the following graph.

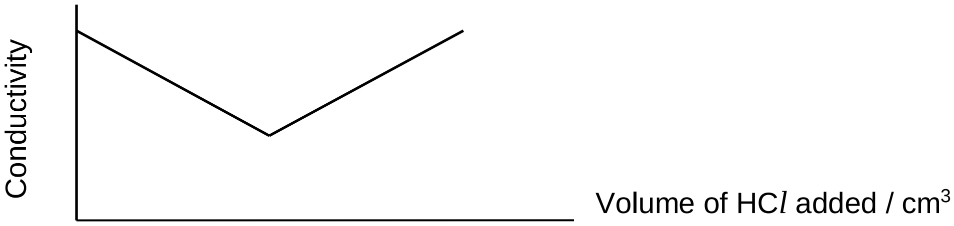
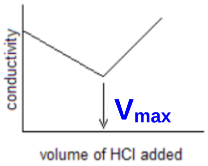


Fig. 2.2

(i) Indicate on the graph (Fig. 2.2), the point which marks the volume of HC*l* needed for complete reaction. [1]

V_{max} is the volume of HC*l* that corresponds to the minimum conductivity **[1]**



(ii) Explain the shape of the graph in Fig. 2.2.

The conductivity decreases as more HC*l* is added. This is due to the **formation of water** from H+ and OH$^-$, which **decreases the total amount of ions** in water and hence conductivity. **[1]**

The conductivity decreases to the lowest point where the equivalence volume of HC*l* is reached, as **all the NaOH has reacted** with the HC*l* .Thus. that is the **minimum amount of ions** that can be present and gives the lowest conductivity. **[1]**

After the equivalence point, **no more neutralisation** occurs. Any HC*l* that is added **dissociates and contributes to the total amount of ions** in water, thus increasing the conductivity. **[1]**

…………………………………………………………………………………………[3]

(iii) With reference to your experiment in **2(a)**, suggest which method (calorimetry or conductometry) is more accurate for the determination of the concentration of HC*l* in **FA 7**.

Conductometry is more accurate. For conductometry, there is **no heat loss to the surroundings**.

Explanation 1: For **calorimetry, the heat loss to the surroundings** will lower the ΔT_{max} and hence render the volume of HC*l* needed for complete neutralisation inaccurate

Explanation 2: For **calorimetry, the heat loss to the surroundings** will affect each ΔT plotted point, resulting in inaccurate two best-fit straight lines drawn to determine ΔT_{max} and hence volume of HC*l* needed for complete neutralisation will be inaccurate.
[1]

…………………………………………………………………………………………[1]

[Total: 21]

3 Identification of ions

FA 9 is a solution containing a mixture of two salts.

You are to perform the tests described in Table 3.1 and record your observations in the table.

In all tests, the reagents should be added gradually until no further change is observed unless you are instructed otherwise. You should indicate clearly at which stage in a test a change occurs, recording your observations alongside the relevant tests.

The volumes given below are approximate and should be estimated rather than measured, unless otherwise stated. If there is no observable change, write **no observable change**.

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

Table 3.1

	Test	*Observation*
(a)	Place about 3 cm depth of **FA 9** in a test-tube, add equal volume of aqueous sodium hydroxide. Warm the contents in the tube.	White, off-white, buff or light brown ppt. **[1]** Moist red litmus did not turn blue or no alkaline gas produced. **[1]** Ppt turned browned or darkened. **[1]**
(b)	Filter the mixture from **(a)** and collect the filtrate in a test tube. Label the filtrate as **FA 10** and retain it for tests **3(c)** and **3(d)**. Leave the residue in the filter paper and observe it again after 5 minutes.	White, off-white, buff, light brown or brown residue. [awarded once either here or in test (a) but not in both] Colourless filtrate obtained. **[1]** Residue turned brown or darkened. [awarded once either here or in test (a) but not in both]
(c)	Place 2 cm depth of **FA 10** in a test-tube and add nitric acid until no further change is seen. Label the solution as **FA 11** and retain it for test **3(e)**.	White ppt formed **[1]** Dissolved in excess nitric acid to give a colourless solution. **[1]**
(d)	Place 1 cm depth of **FA 10** in a test-tube. Add half a spatula of zinc powder. Warm the contents in the tube cautiously.	Colourless and pungent gas evolved **[1]** which turned moist red litmus paper blue. **[1]**
(e)	Place 2 cm depth of <u>**FA 11**</u> in a test-tube, add equal depth of aqueous ammonia. <u>Add</u> excess dilute nitric acid followed by aqueous silver nitrate.	White ppt formed**[1]** Soluble/dissolved in excess aqueous ammonia to form a colourless solution. **[1]** On adding HNO_3 acid, no gas evolved**[1]** White ppt formed **[1]** Dissolved in excess nitric acid to give a colourless solution. **[1]** On adding silver nitrate, no ppt observed. **[1]**

	Test	*Observation*
(f)	Place 1 cm depth of **FA 9** in a test-tube. Add dilute hydrochloric acid followed by aqueous barium chloride.	On adding acid, no observable change/ no gas liberated/ no ppt formed. **[1]** On adding barium chloride, white ppt formed. **[1]**

[6]

[6] – obtain 13 points
[5] – obtain 11 points
[4] – obtain 9 points
[3] – obtain 7 points
[2] – obtain 5 points
[1] – obtain 3 points

(g) **(i)** Identify the **two** cations and **two** anions present in **FA 9.**

cation 1: Mn^{2+} **[1]** cation 2: Zn^{2+} **[1]**

anion 1: SO_4^{2-} **[1]** anion 2: NO_3^- **[1]**

[4]

(ii) Write equations, with state symbols, to illustrate the observations in **3(c)**.

$[Zn(OH)_4]^{2-}(aq) + 2H^+(aq) \rightleftharpoons Zn(OH)_2(s) + 2H_2O(l)$ **[1]**
colourless filtrate white ppt

$Zn(OH)_2(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + 2H_2O(l)$ **[1]**
white ppt colourless solution

[2]

(iii) Predict what will happen when solid ammonium nitrate is added to **FA 9** followed by aqueous ammonia.

$NH_4NO_3 \rightarrow NH_4^+ + NO_3^-$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ ----(1)

The dissociation of ammonium nitrate produces NH_4^+ which suppressed the dissociation of NH_3 (or causes the position of equilibrium of (1) lies to the left). **[1]**

The concentration of OH^- is too low for the ppt to form or less ppt formed. **[1]**

[2]

[Total : 14]

4 Planning

Determination of the hardness of water in a sample.

Hard water is water that has high mineral content and is formed when water percolates through deposits of limestone, chalk and gypsum, which are largely made of calcium carbonates, bicarbonates and sulfates. The hardness of water is measured in terms of the molar concentration of Ca^{2+} in mol dm^{-3}.

In a particular sample of water, the hardness is caused by the presence of calcium chloride. The amount of Ca^{2+}, and hence the concentration of Ca^{2+}, can be determined by precipitation with an excess of oxalic acid.

$$Ca^{2+}\text{ (aq)} + C_2O_4^{2-}\text{ (aq)} \rightleftharpoons CaC_2O_4\text{ (s)}$$

You are to design an experiment to determine the hardness of water in a sample.

You are provided with

- sample of water with estimated hardness of 0.02 mol dm^{-3}
- 0.1 mol dm^{-3} of oxalic acid $H_2C_2O_4$
- electronic balance
- common laboratory apparatus

(a) Given the K_{sp} of calcium oxalate is 2.7×10^{-9} mol^2 dm^{-6}
, predict what will be observed when 25.0 cm^3 of the water sample is mixed with equal volume of the 0.1 mol dm^{-3} of oxalic acid solution.

$[Ca^{2+}]$ = ½(0.02) = 0.01 mol dm^{-3}
$[C_2O_4^{2-}]$ = ½(0.1) = 0.05 mol dm^{-3}
ionic product, IP = $[Ca^{2+}][C_2O_4^{2-}]$

= (0.01)(0.05)

= 5.0×10^{-4} mol^2 dm^{-6} [1]

Since IP > K_{sp}, calcium oxalate will be precipitated. [1] (Can award this mark based on correct deduction of IP against Ksp even if IP above is calculated wrongly)

[2]

(b) Your plan should include a step-by-step description of the method, including the

- sequence of steps to ensure that the maximum amount of precipitate is recovered,
- the use of appropriate apparatus,
- the recordings using the letters A, B, C etc to represent the measurement taken and present it with an appropriate table format,
- the processing of the results to determine the molar concentration of Ca^{2+} in the water sample.

[A_r: C, 12.0; Ca, 40.1; H, 1.0; O, 16.0]

Forming of precipitate

1. *Pipette out 25.0 cm^3 of the sample water with a 25.0 cm^3 pipette into a dry and clean 250 cm^3 beaker*
2. *Using a burette, transfer 25.0 cm^3 of 0.1 mol dm^{-3} of oxalic acid into the same beaker (as long as oxalic acid is in excess)*
3. *Stir the mixture thoroughly with a glass rod and leave it to stand for a few minutes for equilibrium to be reached*

Recovering of precipitate

4. *Filter the solution into a 250 cm^3 conical flask and collect the residue precipitate into a pre-weighed filter paper.*
5. *Rinse the beaker and glass rod with small volume of deionised water and transfer the washings and continue to filter.*
6. *Wash the precipitate with limited cold deionised water to get rid of aq ions adsorbed on the surface of precipitate.*
7. *Drain off excess water by pressing the solid between filter papers.*
8. *Dry the precipitate in oven at 80 - 100 °C ± 10%.*
9. *Cool and weigh the dried precipitate*
10. *Repeat the heat cool weigh process until mass is constant to ±0.01g*

Mass of filter paper	*/ g*	*A*
Mass of filter paper and residue after first heating	*/ g*	*B*
Mass of filter paper and residue after second heating	*/ g*	*C*
Mass of filter paper and residue after third heating	*/ g*	*C*
Mass of residue	*/g*	*C – A* = E

$$\text{Amount of } CaC_2O_4 = \frac{E}{40.1+2(12.0)+4(16.0)} = F \text{ mol}$$

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_4(s)$$

Amt of Ca^{2+} to form CaC_2O_4 = F mol

$$[Ca^{2+}] \text{ in mol dm}^{-3} = \frac{F}{\left(\frac{25.0}{1000}\right)} = G \text{ mol dm}^{-3}$$

Marks	Requirement	Key marking Points
L-[1]	**Logical flow** of plan	- **Pipetting out water sample into beaker followed by adding fixed solution of oxalic acid into beaker** - **Filtering out precipitate** - **Drying with filter paper and oven or IR lamp (Buchner funnel accepted)** ***Award mark for including all 3 points*****.**
A- [1]	Appropriate **apparatus** and their capacities	- **100 cm^3 beaker** - **250 cm^3 beaker** - **250 cm^3 conical flask** - **25.0 cm^3 pipette**
R-[1]	Essential experimental details to ensure **reliable results**	- **Stir mixture with glass rod and leave to stand for a few minutes** - **Repeat heat cool weigh process until mass is constant at ± 0.01g**
P-[1]	Appropriate volumes with **correct precision**	- **25.0 cm^3 of water sample** - **25.0 cm^3 of oxalic acid**
D-[1]	Appropriate table for tabulation of **data**	- **Correct headers and units** - **Letter**
M-[1]	**Manipulation** of data	- **Correct calculation for mass of residue** - **Correct calculation for the conc of Ca^{2+} in water**

[6]

[Total: 8]