	Catholic Junior College JC 2 Preliminary Examinations Higher 2
CANDIDATE NAME	
CLASS	2T

# **CHEMISTRY**

Paper 1 Multiple Choice

9729/01 Tuesday 3 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, class and NRIC/FIN number on the Answer Sheet in the spaces provided.

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. In a titration experiment, 15 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> phosphorous acid, H<sub>3</sub>PO<sub>3</sub> was found to react with 10 cm<sup>3</sup> of 0.30 mol dm<sup>-3</sup> sodium hydroxide, NaOH. Using this information, deduce the formula of the salt formed in this neutralisation process.

**A** NaH<sub>2</sub>PO<sub>3</sub> **C** Na<sub>3</sub>PO<sub>3</sub>

**B** Na<sub>2</sub>HPO<sub>3</sub> **D** Na<sub>3</sub>PO<sub>4</sub>

2 50 cm<sup>3</sup> of a mixture of ethene and propane gas were exploded in excess oxygen. The volume of the residual gases was found to be 200 cm<sup>3</sup>. On being shaken with potassium hydroxide, the final volume was found to be 90 cm<sup>3</sup>. What is the composition of the mixture? (*All volumes are measured at r.t.p*)

A	volume of ethene 10	volume of propane 40
В	20	30
С	30	20
D	40	10

**3** Plutonium-239 is a radioactive substance that emits a constant stream of  $\alpha$ -particles which are similar to the nucleus of <sup>4</sup>He.

Rubidium-87 is another radioactive substance that emits  $\beta$ -particles which can be considered as electrons.

A small amount of Plutonium-239 and Rubidium-87 are separately placed in an ionisation chamber to emit a constant stream of radiation and the emitted particles are passed through an electric field.



What would be the path of the emitted particles in the electric field?

	Plutonium-239	Rubidium-87
	(α–particles)	(β–particles)
Α	1	2
В	1	3
С	4	1
D	3	1

4 Diazene has a molecular formula of N<sub>2</sub>H<sub>2</sub>. Given that the nitrogen and hydrogen show their usual valencies, which of the following correctly describes the shape and bond angle around each central atom?

	shape	bond angle
Α	bent	110°
В	linear	180°
С	tetrahedral	109°
D	trigonal planar	120°

- 5 Which of the following contains delocalised electrons?
  - 1 Graphite
  - 2 Sodium
  - 3 Ethanoate ion
  - 4 Cyclohexene
  - A 1 and 2 only
  - **B** 2 and 3 only
  - **C** 1, 2 and 3 only
  - **D** 3 and 4 only
- 6 Which equation corresponds to the enthalpy change stated?

Α	$Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$	$\Delta H^{\!e}$ neutralisation
В	$Na_2SO_4(s) + aq \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$	$\Delta H^{e}_{solution}$
С	$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$	$\Delta H^{e}_{formation}$
D	$Br_2(l) \rightarrow 2Br(g)$	$\Delta H^{\!e}_{}$ atomisation

- 7 In which of the following processes will  $\Delta S$  be negative?
  - **A** photosynthesis
  - **B** electrolysis of water
  - **C** boiling of water
  - **D** dissolving solid MgSO<sub>4</sub> in water

**8** Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas?

(P = pressure,  $\rho$  = density, V = volume, T = temperature).



- A 1 only
- B 1 and 2 only
- **C** 2 and 3 only
- **D** 1, 2 and 3
- **9** A sample of HBr gas was decomposed in a sealed container at temperature T. The decomposition equation is given below.

 $2HBr(g) \Longrightarrow H_2(g) + Br_2(g)$   $\Delta H$  is positive

Which of the following statements is false?

- **A** Equal amounts of H<sub>2</sub> and Br<sub>2</sub> are formed at equilibrium.
- **B** When a catalyst is added, the rates of the forward and reverse reactions are increased by the same extent.
- **C** The  $K_c$  will decrease if the reaction is carried out at higher temperature.
- **D** The equilibrium position is unaffected when the volume of the container is decreased.

**10** The pH changes when 0.100 mol dm<sup>-3</sup> NH<sub>3</sub>(aq) is added dropwise to 25.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HC*l* as shown below.

At which point on the graph does  $pOH = pK_b$ , where  $K_b$  is the base dissociation constant of the weak base?



#### 11 Ammonia usually reacts as a base. In which reaction does it behave as an acid?

- 1  $Hg_2Cl_2 + 2NH_3 \rightarrow Hg + HgCl(NH_2) + NH_4^+ + Cl^-$
- 2  $Cu^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$
- 3  $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

Α	1, 2 and 3	В	1 and 2	С	2 and 3	D	1 only
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**12** The table shows experimental results obtained for the reaction of hydrogen peroxide with acidified iodide ions to liberate iodine.

initia rea	al concentratior actants / mol dr	initial rate of formation of iodine	
[H <sub>2</sub> O <sub>2</sub> ]	[I <sup>-</sup> ]	[H⁺]	/ mol dm <sup>-3</sup> s <sup>-1</sup>
0.010	0.010	0.010	2.0 × 10 <sup>-6</sup>
0.030	0.010	0.010	6.0 × 10 <sup>-6</sup>
0.030	0.020	0.010	1.2 × 10 <sup>−5</sup>
0.030	0.020	0.020	1.2 × 10 <sup>-5</sup>

What can be deduced from these results?

- 1 The rate equation for the reaction can be written: rate =  $k[H_2O_2][I^-]$ .
- 2 The reaction is zero order with respect to acid.
- 3 The units of rate constant is  $mol^{-2} dm^6 s^{-1}$ .
- 4 Both hydrogen peroxide and iodide ions are involved in the rate-determining step.
- A 1 and 2 only
- **B** 3 and 4 only
- **C** 1, 2 and 4
- **D** 2, 3 and 4
- **13** The mechanism for a certain reaction is given below:

 $2P \longrightarrow R \text{ (fast)}$  $R + Q \Longrightarrow S \text{ (slow)}$  $S + Q \longrightarrow P_2Q_2 \text{ (fast)}$ 

What conclusion can be drawn from the above mechanism?

- **A** The rate equation is rate =  $k[P]^2[Q]$ .
- **B** The overall order of reaction is 2.
- **C** The units of the rate constant, k, is mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>.
- **D** The half-life of Q is halved when [Q] is doubled,

- **14** Four elements with atomic numbers from 11 to 17 inclusive have the following properties.
  - Chloride of **E** dissolves in water and turns moist blue litmus red.
  - Oxide of **F** is amphoteric.
  - **G** has the lowest electronegativity among these four elements.
  - **H** has the smallest atomic radius.

Which of the following is the correct sequence of the four elements in order of increasing atomic number?

- **A F**, **G**, **H**, **E**
- B F, G, E, H
- C G, F, E, H
- D G, F, H, E

**15** Use of Data Booklet is relevant to this question. Which statements about the elements chlorine, bromine and iodine are correct?

- 1 The oxidising power increases from chlorine to iodine.
- 2 The strength of the covalent bonds in the molecules decreases from chlorine to iodine.
- 3 The magnitude of the first electron affinity increases from chlorine to iodine.
- A 1 only
- B 2 only
- C 2 and 3 only
- **D** 1, 2 and 3
- 16 How many stereoisomers does compound Q exhibit?



- **17** Which of the following is a **propagation** step in the formation of 1,1-dibromopropane from the reaction between propane and bromine in the presence of ultraviolet light?
  - $\mathbf{A} \qquad \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{Br} + \mathsf{Br} \bullet \to \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\bullet + \mathsf{Br}_2$
  - $\mathbf{B} \qquad \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\bullet + \mathsf{Br}\bullet \to \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{Br}$
  - **C**  $CH_3CH_2CH_2\bullet + Br_2 \rightarrow CH_3CH_2CHBr\bullet + HBr$
  - **D**  $CH_3CH_2CHBr \bullet + Br_2 \rightarrow CH_3CH_2CHBr_2 + Br \bullet$

18 Methane is a greenhouse gas but is destroyed in the troposphere by the action of hydroxyl radicals.

•OH + CH<sub>4</sub>  $\rightarrow$  •CH<sub>3</sub> + H<sub>2</sub>O

Which statement about this reaction is correct?

- Α The reaction involves homolytic fission and  $\sigma$  bond formation.
- В The reaction involves heterolytic fission and  $\sigma$  bond formation.
- С The reaction involves heterolytic fission and  $\pi$  bond formation.
- D The total number of electrons in the two reacting species is 20.
- 19 A new industrial preparation of ethyl ethanoate has been developed using cheap sources of ethanol.



- Α electrophilic addition
- В nucleophilic substitution
- С nucleophilic addition
- D condensation

20 Compound X was subjected to the following sequence of reactions.



Which of the following could be the structure of X?



В





21 Hydrocortisone is commonly used as an active ingredient in anti-inflammatory creams and has the following structure.



#### hydrocortisone

Which of the following statements about hydrocortisone is correct?

- A When treated with an excess of hot acidified KMnO<sub>4</sub>, it forms a compound containing six carbonyl groups.
- **B** When warmed with aqueous alkaline iodine, a yellow precipitate is observed.
- **C** When treated with cold dilute KMnO<sub>4</sub>, it forms a compound containing two additional hydroxy groups.
- **D** When treated with NaBH<sub>4</sub> in the presence of methanol, it forms a compound containing seven hydroxy groups.
- 22 Compound **P**, C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, has an unbranched carbon chain. An aqueous solution of **P** has an approximate pH of 3. Compound **Q**, C<sub>3</sub>H<sub>8</sub>O, is a secondary alcohol.

**P** and **Q** are reacted together in the presence of a small amount of concentrated sulfuric acid to form **R** as the major organic product.

What is the structural formula of R?

- $A \qquad (CH_3)_2 CHCO_2 CH_2 CH_2 CH_3$
- $\mathbf{B} \qquad \mathsf{CH}_3(\mathsf{CH}_2)_2\mathsf{CO}_2\mathsf{CH}(\mathsf{CH}_3)_2$
- $C \qquad CH_3(CH_2)_2CO_2(CH_2)_2CH_3$
- $D \qquad (CH_3)_2 CHCO_2 CH(CH_3)_2$

**23** *Amygdalin* is partly responsible for the flavour of almonds. On hydrolysis, it first gives compound **X**, which is then further hydrolysed to give other products.



What are the other products formed after further hydrolysis?

- **A**  $C_6H_5CH(OH)CO_2H$  and  $NH_3$
- **B**  $C_6H_5CH_2OH$  and  $CO_2$  and  $NH_3$
- C C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>H and HCHO and NH<sub>3</sub>
- **D**  $C_6H_5OH$  and  $CH_3CN$
- **24** 5-hydroxyanthranillic acid (5-HAA) is a tryptophan metabolite that is suspected of generating oxidative stress and neuronal death.



When 5-HAA was reacted with ethanoyl chloride followed by lithium aluminium hydride,  $LiA/H_4$ , in dry ether, the product was found to give a purple colouration with neutral  $FeCl_3(aq)$ .

Which is a likely product?







A student set up an electrochemical cell as above and made the conclusion listed below. Which of the statements are correct?

- 1 The reaction is feasible and Pb electrode grows larger with time.
- 2 Electrons flow from the Sn electrode to the Pb electrode.
- 3 Sn is the positive electrode while Pb is the negative electrode.
- 4 Concentrated KC*l* is suitable to be used as salt bridge.

۸	1 and 2 only	B	2 and 3 only	C	1 2 and 3 only	П	1 2 3 and $4$
A	i anu z oniy	D	Z and S only		1, 2 and $3$ only	υ	1, Z, S anu 4

**26** Electrolysis of aqueous copper(II) sulfate was carried out using copper electrodes and a steady current. Which graph shows the change in mass of the cathode with time?



**27** Aldol condensation is used in the manufacture of pharmaceuticals. One example of such a reaction is as shown below in the presence of a base.



Under similar conditions, what would be the product X?



28 Which of the following reactions would yield the product shown?



**29** Use of Data Booklet is relevant to this question.

The following diagram shows how the d-orbitals are split in an octahedral environment.



Some transition metal ions exhibit the ability to change their electronic configuration from a 'high spin' state to a 'low spin' state.

In a 'high spin' state, the electrons occupy all the d–orbitals singly first, before starting to pair up in the lower energy d–orbitals.

In a 'low spin' state, the lower energy d–orbitals are first filled, by pairing up if necessary, before the higher energy d–orbitals are used.

Which one of the following transition metal ions is likely to be able to exhibit both spin states?

 $\begin{array}{ccc} 1 & Fe^{3+} \\ 2 & Cu^{2+} \\ 3 & Cr^{3+} \\ 4 & Co^{3+} \end{array}$ 

	уı	y	υ	2 and 3 only
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**30** The absorbance graph below shows the visible spectra of two complexes of transition metal M,  $MX_6^{n+}$  and  $MY_6^{n+}$ .

What is the colour of each complex and which ligand causes a larger d-orbital splitting?

	Colour of MX <sub>6</sub> <sup>n+</sup>	Colour of MY <sub>6</sub> <sup>n+</sup>	ligand which causes a larger d-orbital splitting
Α	Violet	Orange-red	Х
В	Red	Green-blue	Х
С	Violet	Orange-red	Y
D	Red	Green-blue	Y

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# CHEMISTRY

Paper 1 Multiple Choice

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Additional Materials: Multiple Choice Answer Sheet Data Booklet

# WORKED SOLUTIONS

- 1 In a titration experiment, 15 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> phosphorous acid, H<sub>3</sub>PO<sub>3</sub> was found to react with 10 cm<sup>3</sup> of 0.30 mol dm<sup>-3</sup> sodium hydroxide. Using this information, deduce the formula of the salt formed in this neutralisation process.
  - **A** NaH<sub>2</sub>PO<sub>3</sub> **C** Na<sub>3</sub>PO<sub>3</sub>
  - **B** Na<sub>2</sub>HPO<sub>3</sub> **D** Na<sub>3</sub>PO<sub>4</sub>

# Concept: MCS, Acid-base reaction Answer: B

Amount of  $H_3PO_3$  used in experiment =  $0.015 \times 0.10 = 1.50 \times 10^{-3}$  mol Amount of NaOH neutralised =  $0.010 \times 0.30 = 3.00 \times 10^{-3}$  mol  $H_3PO_3 \equiv 2$  NaOH 2 mol of NaOH neutralise 2 mol of H<sup>+</sup> 1 mol of H<sup>+</sup> is left unreacted in 1 mol  $H_3PO_3$  (since  $H_3PO_3 \equiv 3H^+$ ) Salt formed contains 1 mol of H<sup>+</sup>

2 50 cm<sup>3</sup> of a mixture of ethene and propane gas were exploded in excess oxygen. The volume of the residual gases was found to be 200 cm<sup>3</sup>. On being shaken with potassium hydroxide, the final volume was found to be 90 cm<sup>3</sup>. What is the composition of the mixture? (*All volumes are measured at r.t.p*)

Α	volume of ethene 10	volume of propane 40
В	20	30
С	30	20
D	<mark>40</mark>	<mark>10</mark>

Concept: MCS, calculations involving volume of gases (involving hydrocarbons) Answer: D

 $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$  $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$ 

5 6 2 2 2

Let vol of ethene  $(C_2H_4)$  be x.

∴ vol of propane ( $C_3H_8$ ) = 50 - x

Vol of CO<sub>2</sub> gas formed in total = 2x + 3(50 - x) = 150 - x

Change in vol of residual gases after passing through KOH = vol of CO<sub>2</sub> formed

 $= 200 - 90 = 110 \text{ cm}^3$ 

Hence, 150 - x = 110

 $x = 40 \text{ cm}^3$  Vol of ethene = 40 cm<sup>3</sup>; vol of propane = 10 cm<sup>3</sup>

**3** Plutonium-239 is a radioactive substance that emits a constant stream of  $\alpha$ -particles which are similar to the nucleus of <sup>4</sup>He.

Rubidium-87 is another radioactive substance that emits  $\beta$ -particles which can be considered as electrons.

A small amount of Plutonium-239 and Rubidium-87 are separately placed in an ionisation chamber to emit a constant stream of radiation and the emitted particles are passed through an electric field.



What would be the path of the emitted particles in the electric field?

	Plutonium-239	Rubidium-87
	(α–particles)	(β–particles)
Α	1	2
В	1	3
С	4	1
D	3	1

Answer: D

Angle of deflection  $\propto \frac{\text{charge of ion}}{1 + 1 + 1 + 1}$ 

Given that alpha particles ( $\alpha$ -particles) are similar to the nucleus of He (i.e. <sup>4</sup>He<sup>2+</sup>) and beta particles ( $\beta$ -particles) can be considered as electrons ( $^{0}e^{-}$ ),  $\alpha$ -particles will be deflected towards the <u>negative plate</u> and by a <u>smaller magnitude</u> (due to greater mass no.) than  $\beta$ -particles (towards positive plate). 4 Diazene has a molecular formula of N<sub>2</sub>H<sub>2</sub>. Given that the nitrogen and hydrogen show their usual valencies, which of the following correctly describes the shape and bond angle around each central atom?

4

	shape	bond angle		
A	<mark>bent</mark>	<mark>110º</mark>		
В	linear	180°		
С	tetrahedral	109°		
D	trigonal planar	120°		

#### Concept: Drawing Lewis structure, identify shape and bond angle

#### Answer: A

Around each N atom, there are 2 bonds pairs and 1 lone pair of electrons. Hence, it is bent around each N atom and the bond angle is between 109° and 120°. Hence, the most appropriate answer is 110°.

- 5 Which of the following contains delocalised electrons?
  - 1 Graphite
  - 2 Sodium
  - 3 Ethanoate ion
  - 4 Cyclohexene
  - A 1 and 2 only
  - **B** 2 and 3 only
  - C 1, 2 and 3 only
  - D 3 and 4 only

## Concept: Structure and bonding, delocalisation of electrons

Answer: C

- 1: Each C atom is bonded to 3 other C atoms and the remaining electron is delocalised along the layers of carbon atoms.
- 2: Sodium metal has a giant metallic structure, which has strong electrostatic forces of attraction between the metal ion and the sea of delocalised electrons. The valence electron is involved in delocalisation.
- 3: The negative charge on oxygen can be delocalised across the sp<sup>2</sup> hybridised carbon.



 $\Box \Delta H^{e}_{neutralisation}$ 

 $\Box \Delta H^{e}_{solution}$ 

 $\Box \Delta H^{e}_{formation}$ 

 $\Box \Delta H^{e}$  atomisation

4: The  $\pi$  electrons are localised between the 2 C in the C=C.

- 6 Which equation corresponds to the enthalpy change stated?
  - $A \qquad Ba(OH)_2(aq) + 2HCI(aq) \rightarrow BaCI_2(aq) + 2H_2O(l)$ 
    - $Na_2SO_4(s) + aq \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$
  - $\mathbf{C} \qquad \mathbf{S}_8(\mathbf{s}) + \mathbf{8O}_2(\mathbf{g}) \to \mathbf{8SO}_2(\mathbf{g})$
  - **D**  $Br_2(l) \rightarrow 2Br(g)$

#### Ans: B

В

### From definitions of various enthalpy changes Errors in options given: $\Delta H^{\circ}_{neutralisation} - only 1 mol of H_2O formed (not 2 mol)$ $\Delta H^{\circ}_{formation} - only 1 mol of compound formed (not 8 mol)$

 $\Box \Delta H^{e}_{atomisation}$  – breaking of bonds in gaseous phase (not liquid phase)

7 In which of the following processes will  $\Delta S$  be negative?

#### A Photosynthesis

- B Electrolysis of water
- **C** Boiling of water
- D Dissociation of solid MgSO<sub>4</sub> in water

#### Ans: A

A:  $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \qquad \Delta S = -ve$ B:  $2H_2O + 2e^- \rightarrow H_2 + 2OH^- OR 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \Delta S = +ve$ C: phase change from liquid to solid  $\Delta S = +ve$ D: MgSO<sub>4</sub> + aq  $\rightarrow$ MgSO<sub>4</sub>(aq)  $\Delta S = +ve$ 

8 Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas?

(P = pressure,  $\rho$  = density, V = volume, T = temperature).





**9** A sample of HBr gas was decomposed in a sealed container at temperature T. The decomposition equation is given below.

 $2HBr(g) \Longrightarrow H_2(g) + Br_2(g)$   $\Delta H$  is positive

Which of the following statements is false?

- A Equal amounts of H<sub>2</sub> and Br<sub>2</sub> are formed at equilibrium.
- **B** When a catalyst is added, the rates of the forward and reverse reactions are increased by the same extent.
- **C** The  $K_c$  will decrease if reaction is carried out at higher temperature.
- **D** The equilibrium position is unaffected when the volume of the container is decreased.

#### Concept: Le Chatelier's Principle, Calculating Kc, mole fraction

When the temperature is increased, the position of equilibrium shifts to the right to favour the forward reaction which is heat-absorbing/endothermic.  $K_c$  will increase.

 $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$ 

Since the number of mole of gases on both sides of the equation are the same, there would be no change in equilibrium position when the volume of container is decreased and the pressure is increased. Hence Option D is true.

**10** The pH changes when 0.100 mol dm<sup>-3</sup> NH<sub>3</sub>(aq) is added dropwise to 25.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HC*l* as shown below.

At which point on the graph does  $pOH = pK_b$ , where  $K_b$  is the base dissociation constant of the weak base?



Concept: Chemistry of Aqueous Solutions, interpreting titration curve

#### Answer: D

For pOH = pK<sub>b</sub>, [NH<sub>4</sub><sup>+</sup>] = [NH<sub>3</sub>] HC*l* + NH<sub>3</sub>  $\rightarrow$  NH<sub>4</sub>C*l* At **A**, species present: HC*l* At **B**, species present: HC*l* and NH<sub>4</sub>C*l* At equivalence point **C**, NH<sub>4</sub><sup>+</sup> ion hydrolyses in water, NH<sub>4</sub><sup>+</sup> + H<sub>2</sub>O  $\rightleftharpoons$  NH<sub>3</sub> + H<sub>3</sub>O<sup>+</sup> At **D**, N<sub>H3</sub> = 25.00/1000 x 0.100 = 2.5 x 10<sup>-3</sup> mol n<sub>NH4C/</sub> formed = 25.0/1000 x 0.100 = 2.5 x 10<sup>-3</sup> mol At **D**, [NH<sub>4</sub><sup>+</sup>] = [NH<sub>3</sub>] 11 Ammonia usually reacts as a base. In which reaction does it behave as an acid?

1	$Hg_2Cl_2 + 2NH_3 \rightarrow Hg + HgCl(NH_2) + NH_4^+ + Cl^-$
2	$Cu^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$
3	$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

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

#### Answer: D

Option 1:  $NH_3$  donate a H<sup>+</sup> to form  $NH_2^-$ .  $\rightarrow$  Bronsted-Lowry acid

Option 2: The 4 NH<sub>3</sub> donate a pair of electrons each to the Cu<sup>2+</sup> to form an adduct through the formation of a dative bond. (complex formation – covered in JC2 Transition Metals)  $\rightarrow$  Lewis base

Option 3: Ammonia accepts a H<sup>+</sup> from HC/ to form ammonium ion (NH<sub>4</sub><sup>+</sup>).  $\rightarrow$  Bronsted-Lowry base

**12** The table shows experimental results obtained for the reaction of hydrogen peroxide with acidified iodide ions to liberate iodine.

initia rea	al concentration actants / mol dr	initial rate of formation of iodine	
[H <sub>2</sub> O <sub>2</sub> ]	[I <sup>-</sup> ]	[H+]	/ mol dm <sup>-3</sup> s <sup>-1</sup>
0.010	0.010	0.010	2.0 × 10 <sup>-6</sup>
0.030	0.010	0.010	$6.0  imes 10^{-6}$
0.030	0.020	0.010	1.2 × 10 <sup>-5</sup>
0.030	0.020	0.020	$1.2 \times 10^{-5}$

What can be deduced from these results?

- 1 The rate equation for the reaction can be written: rate =  $k[H_2O_2][I^-]$ .
- 2 The reaction is zero order with respect to acid.
- 3 The units of rate constant is  $mol^{-2} dm^6 s^{-1}$ .
- 4 Both hydrogen peroxide and iodide ions are involved in the rate-determining step.
- A 1 and 2 only
- **B** 3 and 4 only
- **C** 1, 2 and 4
- **D** 2, 3 and 4

#### <u>Ans</u>: C

<u>Comparing expt 1 and 2</u>,  $[I^-]$  and  $[H^+]$  kept constant, when  $[H_2O_2]$  is tripled, initial rate is also tripled.  $\therefore$  reaction is  $1^{st}$  order w.r.t.  $H_2O_2$ .

<u>Comparing expt 2 and 3</u>,  $[H_2O_2]$  and  $[H^+]$  kept constant, when  $[I^-]$  is doubled, initial rate is also doubled.  $\therefore$  reaction is  $1^{st}$  order w.r.t.  $I^-$ . <u>Comparing expt 3 and 4</u>,  $[H_2O_2]$  and  $[I^-]$  kept constant, when  $[H^+]$  is doubled, initial rate is unchanged.  $\therefore$  reaction is zero order w.r.t.  $H^+$ . (statement 2) Hence, rate equation is rate =  $k[H_2O_2][I^-]$  (statement 1) and only  $H_2O_2$  and  $I^-$  are involved in the rate-determining step. (statement 4) From experiment 1,

units of 
$$k$$
 =  $\frac{\text{rate}}{[H_2O_2][I^-]} = \frac{\text{mol dm}^{-1} \text{ s}^{-1}}{(\text{mol dm}^{-3})^2}$   
=  $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  (not statement 3)

**13** The mechanism for a certain reaction is given below:

$$2P \longrightarrow R (fast)$$
$$R + Q \Longrightarrow S (slow)$$
$$S + Q \longrightarrow P_2Q_2 (fast)$$

What conclusion can be drawn from the above mechanism?

#### **A** The rate equation is rate = $k[P]^2[Q]$ .

- **B** The overall order of reaction is 2.
- **C** The units of the rate constant, k, is mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>.
- **D** The half-life of [Q] is halved when [Q] is doubled,

Overall equation:  $2\mathbf{P} + 2\mathbf{Q} \rightarrow \mathbf{P}_2\mathbf{Q}_2$ 

From here, we can conclude that **R** and **S** are intermediates and should not appear in the rate equation.

The second step of the reaction mechanism,  $\mathbf{R} + \mathbf{Q} = \mathbf{S}$  is a slow step. Hence, Rate = k [**R**] [**Q**].

Since R is the intermediate formed from 2 moles of **P**, Rate =  $k [P]^2 [Q]$ Thus overall order of reaction is 3.

Rate constant **k** has the units of  $\frac{moldm^{-3}s^{-1}}{(moldm^{-3})^3} = mol^{-2}dm^6s^{-1}$ 

The reaction is first-order with respect to **Q**, hence **Q** has a constant half-life that is independent of **[Q**].

Answer: Option A

- **14** Four elements with atomic numbers from 11 to 17 inclusive have the following properties.
  - Chloride of E dissolves in water and turns moist blue litmus red.
  - Oxide of **F** is amphoteric.
  - **G** has the lowest electronegativity among these four elements.
  - **H** has the smallest atomic radius.

Which of the following is the correct sequence of the four elements in order of increasing atomic number?

- A F, G, H, E B F, G, E, H
- <mark>C G, F, E, H</mark> D G, F, H, E
- Concept: The Periodic Table properties of Period 3 elements (chlorides and oxides)

Answer: C

 $MgCl_2$ ,  $A/Cl_3$ ,  $SiCl_4$  and  $PCl_5$  dissolves in water to give acidic solutions and hence turn blue litmus red. E could be Mg, Al, Si or P.

Only  $Al_2O_3$  is amphoteric. F is Al.

Across a Period, the electronegativity increases. G is the first element of give E, F, G and H.

Chlorine has the smallest atomic radius. H is chlorine.

- **15** Use of Data Booklet is relevant to this question. Which statements about the elements chlorine, bromine and iodine are correct?
  - 1 The oxidising power increases from chlorine to iodine.
  - 2 The strength of the covalent bonds in the molecules decreases from chlorine to iodine.
  - 3 The magnitude of the first electron affinity increases from chlorine to iodine.
  - A 1 only
  - B 2 only
  - **C** 2 and 3 only
  - **D** 1, 2 and 3

Concept: The Periodic Table – properties of Group 17 Answer: B

Statement 1: Group 17 elements, X<sub>2</sub>, have positive  $E^{\circ}$  values, which indicates that they are oxidising in nature. They tend to be reduced to form X<sup>-</sup> ions.  $Cl_2 + 2e \rightleftharpoons 2Cl^ E^{\circ} = +1.36$  V  $\begin{array}{ll} \mathsf{Br}_2 + 2\mathsf{e} \rightleftharpoons 2\mathsf{Br}^- & E^\mathsf{e} = +1.07 \ \mathsf{V} \\ \mathsf{I}_2 + 2\mathsf{e} \rightleftharpoons 2\mathsf{I}^- & E^\mathsf{e} = +0.54 \ \mathsf{V} \end{array}$ 

 $E^{\circ}$  values decreases down the group, which indicates the oxidising power of the elements decreases from  $Cl_2$  to  $I_2$ . Hence, Statement 1 is wrong.

#### Statement 2:

Cl - Cl BE = 244 kJ mol<sup>-1</sup> Br-- Br BE = 193 kJ mol<sup>-1</sup> I-- I BE = 151 kJ mol<sup>-1</sup>

Down the group, as the size of the halogen atom increases, the X–X bond length increases and is weaker. Hence, Statement 2 is correct.

#### Statement 3:

First electron affinity is the energy released when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous anions. First EA is always negative because it is an exothermic reaction, attraction is formed between nucleus and the incoming electron and hence energy is released.

#### $X(g) + e \rightleftharpoons X^{-}(g)$

Down the group, the size of halogen atom increases, the attraction between the nucleus and the incoming electron is weaker. Hence, less energy is released. Magnitude of the first EA decreases from Cl to I.

#### 16 How many stereoisomers does compound **Q** exhibit?



#### **Answer: D**

Total number of stereoisomers =  $2^n$  (Note: maximum no. of stereoisomers =  $2^n$ , where n = total no. of C=C bonds that can show Cis-trans isomerism + no. of chiral carbon centres)

Total number of stereoisomers =  $2^5 = 32$ 



- **17** Which of the following is a **propagation** step in the formation of 1,1-dibromopropane from the reaction between propane and bromine in the presence of ultraviolet light?
  - A  $CH_3CH_2CH_2Br + Br \bullet \rightarrow CH_3CH_2CH_2\bullet + Br_2$
  - $\mathbf{B} \qquad \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\bullet + \mathsf{Br}\bullet \to \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{Br}$
  - **C**  $CH_3CH_2CH_2\bullet + Br_2 \rightarrow CH_3CH_2CHBr\bullet + HBr$
  - **D**  $CH_3CH_2CHBr \bullet + Br_2 \rightarrow CH_3CH_2CHBr_2 + Br \bullet$

**Concept: Alkane, Free Radical Substitution** 

#### **Answer: D**

**Propagation** (generation of new radicals in each step):

Highly reactive bromine radicals <u>react with propane molecules</u> and abstract one <u>hydrogen atom leaving a propyl radical</u>

 $CH_3CH_2CH_3 + Br \rightarrow CH_3CH_2CH_2 + HBr$ 

#### Regeneration of bromine free radical by propyl radical

 $CH_3CH_2CH_2\bullet + Br_2 \longrightarrow CH_3CH_2CH_2Br + Br\bullet$ 

Regenerated bromine free radical reacts with 1-bromopropane and process **repeats** with 1-bromopropyl radical

 $CH_3CH_2CH_2Br + Br \rightarrow CH_3CH_2CHBr \rightarrow + HBr$ 

 $CH_{3}CH_{2}CHBr\bullet + Br_{2} \longrightarrow CH_{3}CH_{2}CHBr_{2} + Br\bullet$ 

**18** Methane is a greenhouse gas but is destroyed in the troposphere by the action of hydroxyl radicals.

$$\bullet OH + CH_4 \rightarrow \bullet CH_3 + H_2O$$

Which statement about this reaction is correct?

- **A** The reaction involves homolytic fission and  $\sigma$  bond formation.
- **B** The reaction involves heterolytic fission and  $\sigma$  bond formation.
- **C** The reaction involves heterolytic fission and  $\pi$  bond formation.
- **D** The total number of electrons in the two reacting species is 20.

Answer: A



The reaction involves the breaking of a C–H covalent bond in CH<sub>4</sub> with one of the bonded electrons going to each atom, forming two radicals (•CH<sub>3</sub> and •H)  $\Rightarrow$  homolytic fission

The unpaired electron in the hydrogen radical (•H) and that in the hydroxyl radical (•OH) then pair up to form a  $\sigma$  bond (O–H bond).

<u>(Note:</u> Heterolytic fission is the breaking of a covalent bond with both of the bonded electrons going to one of the atoms, forming a cation and an anion.)

The total number of electrons in the two reacting species is  $9(\bullet OH) + 10(CH_4) = 19$ . Hence, option D is incorrect.

**19** A new industrial preparation of ethyl ethanoate has been developed using cheap sources of ethanol.



Answer is **C**. Stages 1 and 3 are oxidation whereas stage 2 is nucleophilic addition with  $CH_3CH_2OH$  acting as the nucleophile. Stage 2 is not condensation as there is no loss of any molecules.

20 Compound X was subjected to the following sequence of reactions.

Compound X 
$$\begin{array}{c} 1. \text{ NaOH}(aq), \text{ heat under reflux} \\ \underline{2. \text{ Cool, acidify with HNO}_3(aq)} \\ \hline 3. \text{ AgNO}_3(aq) \end{array} \xrightarrow{} \text{ Compound Y} + \begin{array}{c} \text{white} \\ \text{precipitate} \end{array}$$

Which of the following could be the structure of **X** ?



21 Hydrocortisone is commonly used as an active ingredient in anti-inflammatory creams and has the following structure.



hydrocortisone

Which of the following statements about hydrocortisone is correct?

- **A** When treated with an excess of hot acidified KMnO<sub>4</sub>, it forms a compound containing six carbonyl groups.
- **B** When warmed with aqueous alkaline iodine, a yellow precipitate is observed.
- **C** When treated with cold dilute KMnO<sub>4</sub>, it forms a compound containing two additional hydroxy groups.
- **D** When treated with NaBH<sub>4</sub> in the presence of methanol, it forms a compound containing seven hydroxy groups.

#### **Concept: Organic reactions involving oxidation and reduction**

A The C=C, primary and secondary alcohols will undergo oxidation with hot acidified KMnO<sub>4</sub> to give the following compound. Only 4 carbonyl groups are formed.



- **B** The compound does not contain  $-CH_3CH(OH)$  or  $-COCH_3$ , hence no yellow precipitate is observed.
- **C** When reacted with cold dilute KMnO<sub>4</sub>, mild oxidation of the C=C occurs and a diol (2 alcoholic –OH groups) is formed.
- **D** When treated with NaBH<sub>4</sub>, the following compound is obtained (5 hydroxy groups are present). Note that C=C does not react with NaBH<sub>4</sub>.



22 Compound **P**, C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, has an unbranched carbon chain. An aqueous solution of **P** has an approximate pH of 3. Compound **Q**, C<sub>3</sub>H<sub>8</sub>O, is a secondary alcohol.

**P** and **Q** are reacted together in the presence of a small amount of concentrated sulfuric acid to form **R** as the major organic product.

What is the structural formula of R?

- $A \qquad (CH_3)_2 CHCO_2 CH_2 CH_2 CH_3$
- B CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>
- $\textbf{C} \qquad CH_3(CH_2)_2CO_2(CH_2)_2CH_3$
- $D \qquad (CH_3)_2 CHCO_2 CH(CH_3)_2$

<u>Ans</u>: B

- P is butanoic acid, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H, which forms an ester with Q (2° alcohol).
- ester formed contains butanoate group (.:. either B or C).
- since Q is a 2° alcohol, ester formed is not C.
- **23** *Amygdalin* is partly responsible for the flavour of almonds. On hydrolysis, it first gives compound **X**, which is then further hydrolysed to give other products.



What are the other products formed after further hydrolysis?

#### **A** $C_6H_5CH(OH)CO_2H$ and $NH_3$

- **B**  $C_6H_5CH_2OH$  and  $CO_2$  and  $NH_3$
- C C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>H and HCHO and NH<sub>3</sub>
- **D**  $C_6H_5OH$  and  $CH_3CN$

#### <u>Ans</u>: A

• The –CN group is hydrolysed to give the corresponding carboxylic acid and NH<sub>3</sub>.

**24** 5-hydroxyanthranillic acid (5-HAA) is a tryptophan metabolite that is suspected of generating oxidative stress and neuronal death.



When 5-HAA was reacted with ethanoyl chloride followed by lithium aluminium hydride,  $LiA/H_4$ , in dry ether, the product was found to give a purple colouration with neutral  $FeCl_3(aq)$ .

Which is a likely product?



# Concept: Condensation reactions with amines, phenols, distinguishing test for phenols

D Ethanoyl chloride undergoes condensation reaction with amines, alcohols and phenols. The intermediate produced contains an amide and an ester.



Lithium aluminium hydride can reduce carboxylic acid (to 1° alcohol), amide (to the corresponding amine) and ester (to the corresponding alcohols or phenol).

Since purple colouration with neutral  $FeCl_3$  (aq) is observed, this indicates that the phenol is formed from the reduction of esters.



A student set up an electrochemical cell as above and made the conclusion listed below. Which of the statements are correct?

- 1 The reaction is feasible and Pb electrode grows larger with time.
- 2 Electrons flow from the Sn electrode to the Pb electrode.
- 3 Sn is the positive electrode while Pb is the negative electrode.
- 4 Concentrated KCl is suitable to be used as salt bridge.

A	1 and 2 only	В	2 and 3 only	С	1, 2 and 3 only	D	1, 2, 3 and 4
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#### **Answer: A**

**Concept: Electrochemical cell setup, predicting feasibility based on E**<sup>e</sup><sub>cell</sub> Answer: A (i and ii only)

 $Pb^{2+} + 2e \implies Pb -0.13 V = E_{\theta_{red}}$ 

 $Sn^{2+} + 2e \Longrightarrow Sn -0.14 V E_{\theta_{oxd}}$ 

 $E_{e_{cell}} = -0.13 - (-0.14) = + 0.01$ 

#### (reaction is feasible and Pb is formed)

Reduction:  $Pb^{2+} + 2e \rightarrow Pb$  .....Pb is the cathode (+)

Oxidation:  $Sn \rightarrow Sn^{2+} + 2e$  ......Sn is the anode (-)

Electrons flow from anode to cathode i.e. from Sn to Pb electrode.

KCl is unsuitable to be used as salt bridge as PbCl<sub>2</sub> will be precipitated instead.

**26** Electrolysis of aqueous copper(II) sulfate was carried out using copper electrodes and a steady current. Which graph shows the change in mass of the cathode with time?



Concept: Electrolysis, mass of substance liberated during electrolysis Answer: A

Reduction occurs at the cathode  $Cu^{2+} + 2e^- \rightarrow Cu$  (cathode mass increases) Since mass  $\alpha$  Q (Faraday's 1<sup>st</sup> Law Electrolysis) And Q = I t Therefore, mass  $\alpha$  time

**27** Aldol condensation is used in the manufacture of pharmaceuticals. One example of such a reaction is as shown below in the presence of a base.



Under similar conditions, what would be the product X?



Concept: Pattern recognition of novel reaction; predicting structure of product

**Answer: A** 



28 Which of the following reactions would yield the product shown?

0  $conc. \ H_2SO_4$ 1 HO(CH<sub>2</sub>)<sub>4</sub>COOH heat 2 C=C<sup>/I</sup> H C<sup>-O</sup> C=C H C<sup>-O</sup> H [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>/ OH<sup>-</sup> heat NaBr(aq) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH -► CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br 3 heat 1 only Α В 2 only 1 and 2 only С 1, 2 and 3 only D
### **Option 1 is correct:**

The alcohol and the carboxylic acid functional groups of  $HO(CH_2)_4COOH$  undergo condensation reaction to cyclic ester molecule.

#### **Option 2 is correct:**

The aromatic aldehyde undergoes mild oxidation with alkaline  $[Ag(NH_3)_2]^+$  (Tollen's reagent) to form a carboxylate ion.

#### **Option 3 is incorrect:**

Solid NaBr is needed to react with **conc**  $H_2SO_4$  while **heating under reflux** to produce hydrogen bromide, HBr.

NaBr(s) + conc.  $H_2SO_4 \rightarrow HBr(g) + NaHSO_4$ 

HBr undergoes nucleophilic substitution reaction with  $CH_3CH_2CH_2OH$  to form  $CH_3CH_2CH_2Br$ 

**29** Use of Data Booklet is relevant to this question.

The following diagram shows how the d-orbitals are split in an octahedral environment.



Some transition metal ions exhibit the ability to change their electronic configuration from a 'high spin' state to a 'low spin' state.

In a 'high spin' state, the electrons occupy all the d–orbitals singly first, before starting to pair up in the lower energy d–orbitals.

In a 'low spin' state, the lower energy d–orbitals are first filled, by pairing up if necessary, before the higher energy d–orbitals are used.

Which one of the following transition metal ions is likely to be able to exhibit both spin states?

1	Fe <sup>3+</sup>
2	Cu <sup>2+</sup>

- 3 Cr<sup>3+</sup>
- 4 Co<sup>3+</sup>

1 only **B** 1 and 4 only **C** 1, 2 and 4 only **D** 2 and 3 only

Answer: B

Α

Fe<sup>3+</sup>: [Ar] 3d<sup>5</sup>--The high spin and low spin configuration are different. Hence it can show a difference between the two spin states.

 $Cu^{2+}$ : [Ar]  $3d^9$  -- The high spin and low spin configuration are exactly the same. Hence it cannot show a difference between the two spin states.

Cr<sup>3+</sup>: [Ar] 3d<sup>3</sup> --The high spin and low spin configuration are exactly the same. Hence it cannot show a difference between the two spin states.

Co<sup>3+:</sup> [Ar] 3d<sup>6</sup> -- The high spin and low spin configuration are different. Hence it can show a difference between the two spin states.

**30** The absorbance graph below shows the visible spectra of two complexes of transition metal M, MX<sub>6</sub><sup>n+</sup> and MY<sub>6</sub><sup>n+</sup>.



What is the colour of each complex and which ligand causes a larger d-orbital splitting?

	Colour of MX <sub>6</sub> <sup>n+</sup>	Colour of MY <sub>6</sub> <sup>n+</sup>	ligand which causes a larger d-orbital splitting
Α	Violet	Orange-red	Х
В	Red	Green-blue	Х
С	Violet	Orange-red	Y
D	Red	Green-blue	Y

### Answer: B

For  $MX_6^{n+}$ , it absorbs wavelength at the 400-600 nm region, thus the colour observed will be red.

For  $MY_6^{n+}$ , it absorbs wavelength at the 550-650 nm region, thus the colour observed will be green-blue.

Shorter wavelength absorbed means a larger  $\Delta E \rightarrow$  Thus, X causes a larger d-orbital splitting.

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Catholic Junior College

JC2 Preliminary Examination Higher 2

CANDIDATE NAME

CLASS

2T

# CHEMISTRY

Paper 2 Structured Questions

Friday 23 August 2019

2 hours

9729/02

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

# READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

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

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

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

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

At the end of examination, fasten all your work securely together.

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

For Examiner's Use		
Paper 1		30
	Q 1	11
	Q 2	18
Paper 2	Q 3	18
	Q 4	10
	Q 5	10
	Q6	8 75
	Q 1	22
Paper 3	Q 2	19
	Q 3	19
	Q 4 / 5	20 80
Paper 4		55
Total		240
Total % and Grade		

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

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

- 1 The Taj Mahal is an ivory-white marble monument in the Indian city of Agra. The famous building is becoming brown and green from environmental pollution. Acid rain accelerates the erosion of marble monuments. Marble consists primarily of calcium carbonate.
  - (a) You should refer to the following solubility product data to help answer the following questions.

Substance	CaCO <sub>3</sub>	CaSO <sub>4</sub>	BaCO <sub>3</sub>	BaSO <sub>4</sub>
Solubility product / mol <sup>2</sup> dm <sup>-6</sup>	1.69 x 10 <sup>-8</sup>	2.03 x 10⁻³	8.28 x 10 <sup>−9</sup>	8.84 x 10 <sup>−11</sup>

The pollutant  $SO_2$  dissolves in rainwater to form sulfuric acid. The sulfuric acid slowly converts calcium carbonate into solid calcium sulfate.

(i) Write an equation for the reaction between calcium carbonate and sulfuric acid.

.....[1]

(ii) By calculating the solubilities of calcium carbonate and calcium sulfate, deduce why acid rain accelerates the erosion of marble.

[3]

The lifespan of Taj Mahal can be extended by treatment with an aqueous mixture of barium hydroxide,  $Ba(OH)_2$  and urea,  $CO(NH_2)_2$ . As this solution soaks into the porous marble, the urea slowly hydrolyses forming ammonia and carbon dioxide. The carbon dioxide released reacts with the barium hydroxide in the mixture forming barium carbonate.

(iii) Write an equation for the reaction between barium hydroxide and carbon dioxide.

.....[1]

(iv) By considering the reaction between surface barium carbonate and acid rain, explain how the erosion process can be slowed down.

- (b) Group 2 carbonates undergo decomposition in the same way at different temperatures.
  - (i) Predict and explain the order of decomposition temperatures for the three carbonates, MgCO<sub>3</sub>, CaCO<sub>3</sub> and BaCO<sub>3</sub>.

[3]

The graph given below shows the change in mass when 2.00 g of each CaCO<sub>3</sub> and BaCO<sub>3</sub> were heated separately at a temperature, T  $^{\circ}$ C.



(ii) From the shapes of the graphs, identify CaCO<sub>3</sub> and BaCO<sub>3</sub> in the spaces provided below.

Graph A:

- Graph B: .....
  - [1]
- (iii) Sketch on the same axes, a graph that would be obtained by heating 2.00 g of magnesium carbonate, MgCO<sub>3</sub>, at the same temperature, T °C.

[Total: 11]

[Turn over

2 Hydrogen peroxide is a common bleaching agent used to whiten wood pulp during the manufacture of paper. Transition metal ions such as Fe<sup>3+</sup>(aq), that are naturally present in wood pulp, would catalyse the decomposition of hydrogen peroxide, and hence reduce the bleaching efficiency. The wood pulp is therefore washed with a chelating agent such as EDTA to remove the transition metal ions before hydrogen peroxide is added.

 $[\mathsf{EDTA} = (^{-}\mathsf{O}_2\mathsf{CCH}_2)_2\mathsf{NCH}_2\mathsf{CH}_2\mathsf{N}(\mathsf{CH}_2\mathsf{CO}_2^{-})_2]$ 



(a) (i) Any Fe<sup>3+</sup>(aq) in the wood pulp would form a polydentate complex with EDTA. Give the formula of the complex formed. You may use the abbreviation 'EDTA' in your answer. .....[1] State the coordination number of the complex in (a)(i). (ii) .....[1] H<sub>2</sub>O and NH<sub>3</sub> are simple molecules. Explain why, at room temperature, H<sub>2</sub>O is a (b) (i) liquid while NH<sub>3</sub> is a gas. ..... ..... .....[2]

(ii) While EDTA is a polydentate *ligand*, H<sub>2</sub>O and NH<sub>3</sub> are examples of monodentate *ligands* in transition metal complexes. Explain what is meant by the term *ligand*.

(c) Consider the ion [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> present in an aqueous solution of copper(II) sulfate. When a central metal is surrounded by water ligands, it is known as an aqua complex. Addition of NH<sub>3</sub> to the copper(II) sulfate solution brings about a stepwise replacement of the water ligands by ammonia ligands such that the overall equation is shown below.

 $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$ 

The stability constant,  $K_{\text{stab}}$ , for the above equilibrium is given as:

$$K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2]^{2+}}{[Cu(H_2O)_6^{2+}][NH_3]^4} = 1 \times 10^{13} \,\text{mol}^{-4} \,\text{dm}^{12}$$

In the above expression, the square brackets imply concentrations in mol dm<sup>-3</sup>. Similar to the example shown above for  $[Cu(H_2O)_6]^{2+}$ , complexes of iron have values of  $K_{stab}$  which are measured against the relative stability of the aqua complex of iron.

The following table lists some iron complexes together with their colours and their stability constants.

aqueous complex	colour	<b>K</b> <sub>stab</sub>
[Fe(SCN)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	deep red	1 x 10 <sup>2</sup>
[FeF <sub>6</sub> ] <sup>3–</sup>	colourless	2 x 10 <sup>15</sup>
Fe <sup>3+</sup> (aq) complex with EDTA	yellow	x
[Fe(CN) <sub>6</sub> ] <sup>3–</sup>	pale yellow	1 x 10 <sup>31</sup>

- (i) Including equations where appropriate, use the data to explain
  - why an addition of KSCN(aq) to a solution of Fe<sup>3+</sup>(aq) produces a deep red solution.



	• what is observed when KF(aq) is added to the deep red solution mentioned above.
	[2]
(ii)	Deduce if the value of $x$ , the $K_{\text{stab}}$ of the Fe <sup>3+</sup> (aq) complex with EDTA, is expected to be higher or lower than the $K_{\text{stab}}$ value of $[\text{FeF}_6]^{3-}$ .
	[1]
(iii)	Give the electronic configuration of Fe in $[Fe(CN)_6]^{3-}(aq)$ .
	[1]
(iv)	$[Fe(CN)_6]^{3-}(aq)$ is a weaker oxidising agent than $Fe^{3+}(aq)$ . Explain this statement by quoting appropriate $E^e$ values from the <i>Data Booklet</i> .
	[2]
(i)	Carbon monoxide, CO, is a toxic gas. Draw the dot-and-cross structure of CO.

[1]

CO is also a ligand in iron pentacarbonyl, Fe(CO)<sub>5</sub>. CO binds to the central metal via the carbon atom.

(d)

(iii) Draw and name the shape of the complex, Fe(CO)<sub>5</sub>.

[2]

(iv) When iron pentacarbonyl reacts with iodine in hexane solution, iron is oxidised and an octahedral complex, Fe(CO)<sub>4</sub>I<sub>2</sub>, is formed.

Isomerism can occur in  $Fe(CO)_4I_2$  due to different positions of the ligands with respect to the central metal ion. Draw the two isomers of  $Fe(CO)_4I_2$ .

[1]

[Total: 18]

3 (a) Converting harmful greenhouse gases such as CO<sub>2</sub> into useful chemical commodities, such as methanol, CH<sub>3</sub>OH, is gaining traction in green chemistry as it is economically viable and environment–friendly.

A mixture containing 1.0 mol of  $CO_2$  and 3.0 mol of  $H_2$  is allowed to reach *dynamic equilibrium* at 200°C and 55 bar. Under these conditions, 32%  $CO_2$  is converted to methanol,  $CH_3OH$ .

 $CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$ 

Calculate the equilibrium pressure of each gas and hence calculate the  $K_p$  value, with the units for this reaction at 200°C.

[4]

(b) Methanol reacts with carbon monoxide with the help of catalyst to produce ethanoic acid.

Define the term *standard enthalpy change of formation* of liquid ethanoic acid,  $CH_3CO_2H$  (*l*).

.....[1]

(c) Using the enthalpy change values given below, complete the energy cycle and calculate the standard enthalpy change of formation for ethanoic acid, CH<sub>3</sub>CO<sub>2</sub>H (*l*).



(d) The ethanoic acid, CH<sub>3</sub>CO<sub>2</sub>H can undergo neutralisation with sodium hydroxide, NaOH. A thermochemical experiment was carried out to determine the enthalpy change of neutralisation using the experimental set–up below.



The following results were obtained:

Volume of NaOH added / cm <sup>3</sup>	50.0
Volume of CH <sub>3</sub> CO <sub>2</sub> H added / cm <sup>3</sup>	50.0
Concentration of NaOH used / mol dm-3	1.00
Concentration of CH <sub>3</sub> CO <sub>2</sub> H used / mol dm <sup>-3</sup>	0.65
Initial temperature of CH <sub>3</sub> CO <sub>2</sub> H / °C	25.0
Highest temperature reached / °C	28.5
Specific heat capacity of water / J g <sup>-1</sup> K <sup>-1</sup>	4.18
Density of water / g cm <sup>-3</sup>	1.00

(i) Use the results to determine the experimental enthalpy change of neutralisation.

[3]

(ii) The experiment described in (d)(i) was repeated using HCl instead of CH<sub>3</sub>CO<sub>2</sub>H, under the same conditions. The enthalpy change of neutralisation was found to be -57.9 kJ mol<sup>-1</sup>. Apart from heat loss, suggest another reason for the discrepancy between this value and that calculated in (d)(i).

.....[1]

(e) Like many acids, ethanoic acid reacts with basic carbonates such as magnesium carbonate, MgCO<sub>3</sub> to release carbon dioxide.

Using the following data and relevant data from the *Data Booklet*, complete the following energy level diagram and use it to determine the standard enthalpy change of formation of magnesium carbonate, MgCO<sub>3</sub>. [5]

lattice energy of MgCO3 (s) $= -3208 \text{ kJ mol}^{-1}$ standard enthalpy change of atomisation of Mg (s) $= +147 \text{ kJ mol}^{-1}$ sum of 1<sup>st</sup> and 2<sup>nd</sup> electron affinity of oxygen $= +702 \text{ kJ mol}^{-1}$ standard enthalpy change of formation of CO2 (g) $= -393 \text{ kJ mol}^{-1}$ standard enthalpy change of reaction below,  $\Delta H^{e}_{r}$  $= -778 \text{ kJ mol}^{-1}$ 

 $O^{2-}(g) + CO_2(g) \longrightarrow CO_3^{2-}(g)$ 

Energy

$$Mg^{2+}(g) + C(s) + O_{2}(g) + O^{2-}(g)$$

$$Mg^{2+}(g) + 2e^{-} + C(s) + \frac{3}{2}O_{2}(g)$$

$$1^{st} IE(Mg) + 2^{nd} IE(Mg)$$

$$Mg(g) + C(s) + \frac{3}{2}O_{2}(g)$$

$$\Delta H^{e}_{at}(Mg)$$

$$Mg(s) + C(s) + \frac{3}{2}O_{2}(g)$$

$$\Delta H^{e}_{f}(MgCO_{3}(s))$$

$$MgCO_{3}(s)$$

[Total: 18]

4 Dragons are able to breathe fire because the parasitic bacteria that live in their lungs produce flammable gases. If a dragon exhales sharply, the gas can ignite due to the friction against the rough walls of the larynx.

12

- (a) The gas exhaled by a dragon contains 20 mole % of hydrogen sulfide, H<sub>2</sub>S and 15 mole % of oxygen. The average volume of a dragon's lung is 5.1 m<sup>3</sup> and due to the high pressures experienced when a dragon exhales, the molar volume of the gas contained in their lungs is 15 dm<sup>3</sup> mol<sup>-1</sup>.
  - (i) Calculate the total amount of gas in moles contained in a dragon's lung.

[1]

(ii) Assuming the temperature of a dragon's lung is 40 °C and the gaseous mixture behaves ideally, use the ideal gas equation and your answer in (a)(i) to calculate the internal pressure in the lung experienced by a dragon.

(iii) The actual pressure in the dragon's lung is lower than the value calculated in (a)(ii). Account for the discrepancy observed.

......[1]

(iv) Write a balanced equation for the reaction that describes the burning of gas exhaled by the dragon. Hence, calculate the additional moles of oxygen required for the complete combustion of one exhalation of the dragon.

(b) The parasitic bacteria in the dragon's lung produces a protein molecule **A** which speeds up the formation of flammable gases.

In the study of the structure of **A**, it was digested using two different enzymes. The fragments obtained were separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

Digestion using the first enzyme:	Digestion using the second enzyme:
his-phe-gly ser-pro-glu asp-gly thr-phe-leu	gly-asp-gly-thr pro-glu phe-leu-ser his-phe

(i) Write out the amino acid sequence of the smallest polypeptide A.

......[2]

(ii) A tripeptide, his-phe-glu, obtained from A was further hydrolysed. The resulting solution was added to an excess of a buffer solution of pH 6.5 and placed at the centre of the plate. A potential difference was then applied across the plate.

Amino acids		H <sub>2</sub> N—CH—COOH CH <sub>2</sub>	H <sub>2</sub> N— CH—COOH   CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H
	his	phe	glu
Isoelectric point	7.58	5.48	3.10



Indicate the relative positions of the amino acids on the diagram below.

[2]



**5** Carvone is a chemical found naturally in essential oils extracted from the seeds of two common herbs, spearmint and dill.



Carvone

Two stereoisomers of carvone are responsible for the distinctively different flavor and smell of the two herbs.

(a) State the type of stereoisomerism carvone can exhibit.

.....[1]

(b) Draw the two stereoisomers of carvone.

[1]

(c) Carvone undergoes reduction with different reagents and conditions to form different products. One notable reduction method is the *Wolff-Kishner reduction* whereby the ketone functional group in carvone reacts with hydrazine, N<sub>2</sub>H<sub>4</sub>, in the presence of a strong base to form limonene, C<sub>10</sub>H<sub>16</sub>, a major component in the oil of citrus fruit peels.

The general reaction sequence of the *Wolff-Kishner reduction* is shown below.



.....[1]

The *Wolff-Kishner reduction* is unsuitable for base-sensitive reactants.

(i) Suggest the type of reaction in Step 1.

[Turn over

(ii) The following reaction scheme shows the various reduction reactions of carvone.
 Suggest the structural formulae of compounds A, B and C in the boxes below.



(iii) Suggest a simple chemical test that could distinguish between carvone and limonene. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: .....

	Observations:	Products:
Carvone		
Limonene		

- [3]
- (iv) Suggest a reason why the following compound is unlikely to undergo the *Wolff-Kishner reduction* despite the presence of a ketone functional group.



.....

......[1]

[Total: 10]

**6** When fuming sulfuric acid reacts with alkenes, electrophilic addition occurs to form alkyl hydrogensulfates. This is exemplified by the reaction involving ethene below.



When 1-methylcyclohexene reacts with fuming sulfuric acid, a mixture of two isomers **X** and **Y** are formed, with isomer **X** being the major product.

(a) Name and define the type of isomerism exhibited by isomers X and Y.

.....[2]

(b) Complete the following to suggest a mechanism for the reaction between 1-methylcyclohexene and sulfuric acid to form X. Show the structure of the intermediate, the movement of the electron pairs and the structure of X.



(c) Explain why benzene does not undergo addition reactions with fuming sulfuric acid.

[Total: 8]

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2 hours

Friday 23 August 2019

# CHEMISTRY

Paper 2 Structured Questions

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

# **WORKED SOLUTIONS**

Answer all the questions in the spaces provided.

- 1 The Taj Mahal is an ivory-white marble monument in the Indian city of Agra. The famous building is becoming brown and green from environmental pollution. Acid rain accelerates the erosion of marble monuments. Marble consists primarily of calcium carbonate.
  - (a) You should refer to the following solubility product data to help answer the following questions.

Substance	CaCO <sub>3</sub>	CaSO <sub>4</sub>	BaCO <sub>3</sub>	BaSO <sub>4</sub>
Solubility product / mol <sup>2</sup> dm <sup>-6</sup>	1.69 x 10 <sup>-8</sup>	2.03 x 10 <sup>−3</sup>	8.28 x 10 <sup>−9</sup>	8.84 x 10 <sup>−11</sup>

The pollutant SO<sub>2</sub> dissolves in rainwater to form sulfuric acid. The sulfuric acid slowly converts calcium carbonate into solid calcium sulfate.

(i) Write an equation for the reaction between calcium carbonate and sulfuric acid.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3$$
  
Or CaCO\_3 + H\_2SO\_4 \rightarrow CaSO\_4 + H\_2O + CO\_2 [1]

(ii) By calculating the solubilities of calcium carbonate and calcium sulfate, deduce why acid rain accelerates the erosion of marble.

Calculate the solubility of CaCO<sub>3</sub>, x:

CaCO<sub>3</sub>(s)  $\rightleftharpoons$  Ca<sup>2+</sup>(aq) + CO<sub>3</sub><sup>2-</sup>(aq) K<sub>sp</sub> (CaCO<sub>3</sub>) = [Ca<sup>2+</sup>][CO<sub>3</sub><sup>2-</sup>] 1.69 x 10<sup>-8</sup> = x<sup>2</sup> x = <u>1.30 x 10<sup>-4</sup></u> mol dm<sup>-3</sup>

Calculate the solubility of CaSO<sub>4</sub>, y:

 $\begin{array}{l} \mathsf{CaSO}_4(s) \rightleftarrows \quad \mathsf{Ca}^{2+}(\mathsf{aq}) + \mathsf{SO}_4^{2-}(\mathsf{aq}) \\ \mathsf{K}_{\mathsf{sp}}\left(\mathsf{CaSO}_4\right) = [\mathsf{Ca}^{2+}][\mathsf{SO}_4^{2^-}] \\ 2.03 \times 10^{-3} = y^2 \\ y = \underline{4.51 \times 10^{-2}} \text{ mol dm}^{-3} \\ \mathsf{Acid rain contains } \mathsf{H}_2\mathsf{SO}_4, \text{ which converts } \mathsf{CaCO}_3 \text{ into } \underline{\mathsf{CaSO}_4, \text{ which is}} \\ \underline{\mathsf{more soluble in water}}. \end{array}$ 

[3]

The lifespan of Taj Mahal can be extended by treatment with an aqueous mixture of barium hydroxide,  $Ba(OH)_2$  and urea,  $CO(NH_2)_2$ . As this solution soaks into the porous marble, the urea slowly hydrolyses forming ammonia and carbon dioxide. The carbon dioxide released reacts with the barium hydroxide in the mixture forming barium carbonate.

(iii) Write an equation for the reaction between barium hydroxide and carbon dioxide.

 $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$ 

[1]

(iv) By considering the reaction between surface barium carbonate and acid rain, explain how the erosion process can be slowed down.

BaCO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$  BaSO<sub>4</sub> + CO<sub>2</sub> + H<sub>2</sub>O or BaCO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$  BaSO<sub>4</sub> + H<sub>2</sub>CO<sub>3</sub> <u>BaCO<sub>3</sub> can react with SO<sub>2</sub> / H<sub>2</sub>SO<sub>4</sub> in the air to form a layer of barium</u> <u>sulfate, BaSO<sub>4</sub>. BaSO<sub>4</sub> is the least soluble</u> and hence, slow down the erosion process.

[1]

- (b) Group 2 carbonates undergo decomposition in the same way at different temperatures.
  - (i) Predict and explain the order of decomposition temperatures for the three carbonates, MgCO<sub>3</sub>, CaCO<sub>3</sub> and BaCO<sub>3</sub>.

Decomposition temperature:  $MgCO_3 < CaCO_3 < BaCO_3$ <u>Going down Group 2, size of cation increases from Mg<sup>2+</sup> to Ba<sup>2+</sup></u>. Hence, <u>charge density and polarising power of cation decreases from Mg<sup>2+</sup></u> <u>to Ba<sup>2+</sup></u>. Therefore, <u>the ability of cation to distort the CO<sub>3</sub><sup>2-</sup> electron cloud</u>, weakening and break the C-O bond <u>decreases from Mg<sup>2+</sup> to Ba<sup>2+</sup></u> Hence less energy is required to decompose MgCO<sub>3</sub> and the decomposition temperature is the lowest. [3]

The graph given below shows the change in mass when 2.00 g of each  $CaCO_3$  and  $BaCO_3$  were heated separately at a temperature T °C.



(ii) From the shapes of the graphs, identify CaCO<sub>3</sub> and BaCO<sub>3</sub> in the spaces provided below.

Graph A: BaCO<sub>3</sub> Graph B: <u>CaCO</u>3

[1]

CaCO<sub>3</sub> → CaO + CO<sub>2</sub> Amount of CaCO<sub>3</sub> = 2.00 / 100.1 = 2.00 x  $10^{-2}$  mol CaCO<sub>3</sub> ≡ CaO Mass of CaO = 2.00 x  $10^{-2}$  x 56.1 = 1.12 g

(iii) Sketch on the same axes, a graph that would be obtained by heating 2.00 g of magnesium carbonate, MgCO<sub>3</sub>, at the same temperature, T °C.



Shorter time to decompose + smaller residual mass

CaCO<sub>3</sub> → CaO + CO<sub>2</sub> Amount of CaCO<sub>3</sub> = 2.00 / 100.1 = 0.0200 mol CaCO<sub>3</sub> ≡ CaO Mass of CaO = 0.0200 x 56.1 = 1.12 g

Amount MgCO<sub>3</sub> = 2.00 / 84.3 = 0.0237 mol MgCO<sub>3</sub>  $\equiv$  MgO Mass of MgO = 0.0237 x 40.3 = 0.955 g MgCO<sub>3</sub> is less thermally stable than CaCO<sub>3</sub>. Hence, MgCO<sub>3</sub> decompose completely faster.

[Total: 11]

2 Hydrogen peroxide is a common bleaching agent used to whiten wood pulp during the manufacture of paper. Transition metal ions such as  $Fe^{3+}(aq)$ , that are naturally present in wood pulp, would catalyse the decomposition of hydrogen peroxide, and hence reduce the bleaching efficiency. The wood pulp is therefore washed with a chelating agent such as EDTA to remove the transition metal ions before hydrogen peroxide is added. [EDTA = ( $^{-}O_2CCH_2$ )\_2NCH\_2CH\_2N(CH\_2CO\_2^-)\_2]



 (a) (i) Any Fe<sup>3+</sup>(aq) in the wood pulp would form a polydentate complex with EDTA. Give the formula of the complex formed. You may use the abbreviation 'EDTA' in your answer.

	[Fe(EDTA)] <sup>-</sup> [1]
(ii)	State the coordination number of the complex in (a)(i).
	6 [1]
(i)	$H_2O$ and $NH_3$ are simple molecules. Explain why, at room temperature, $H_2O$ is a liquid while $NH_3$ is a gas.
	H <sub>2</sub> O is a liquid due to the presence of more extensive intermolecular
	• hydrogen bonding in H <sub>2</sub> O than •NH3:• On average, •H2O can form <u>two</u> ·······
	hydrogen bonds per molecule while NH <sub>3</sub> can only form one
	hydrogen bond per molecule. More energy is thus required to
	overcome the hydrogen bonds in H <sub>2</sub> O. [2]

## Alternative answer:

(b)

 $H_2O$  is a liquid due to the presence of <u>stronger</u> intermolecular hydrogen bonding in  $H_2O$  than  $NH_3$ . <u>O is more electronegative</u> than N hence <u>H-O bond is more polar</u> than H-N bond, thus a greater dipole moment of the H-O bond that makes the intermolecular hydrogen bonding stronger. More energy is thus required to overcome the hydrogen bonds in  $H_2O$ .

- (ii) While EDTA is a polydentate *ligand*, H<sub>2</sub>O and NH<sub>3</sub> are examples of monodentate *ligands* in transition metal complexes. Explain what is meant by the term *ligand*.
   A ligand is an ion or molecule that has at least one lone pair of electrons that can be donated into the vacant orbitals in the central metal atom or ion to form a dative covalent bond. [1]
- (c) Consider the ion [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> present in an aqueous solution of copper(II) sulfate. When a central metal is surrounded by water ligands, it is known as an aqua complex. Addition of NH<sub>3</sub> to the copper(II) sulfate solution brings about a stepwise replacement of the water ligands by ammonia ligands such that the overall equation is shown below.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

The stability constant,  $K_{stab}$ , for the above equilibrium is given as:

$$K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2]^{2+}}{[Cu(H_2O)_6^{2+}][NH_3]^4} = 1 \times 10^{13} \,\text{mol}^{-4} \,\text{dm}^{12}$$

In the above expression, the square brackets imply concentrations in mol dm<sup>-3</sup>. Similar to the example shown above for  $[Cu(H_2O)_6]^{2+}$ , complexes of iron have values of  $K_{stab}$  which are measured against the relative stability of the aqua complex of iron.

The following table lists some iron complexes together with their colours and their stability constants.

aqueous complex	colour	K <sub>stab</sub>
[Fe(SCN)(H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	deep red	1 x 10 <sup>2</sup>
[FeF <sub>6</sub> ] <sup>3–</sup>	colourless	2 x 10 <sup>15</sup>
Fe <sup>3+</sup> (aq) complex with edta	yellow	x
[Fe(CN) <sub>6</sub> ] <sup>3–</sup>	pale yellow	1 x 10 <sup>31</sup>

- (i) Including equations where appropriate, use the data to explain
  - why an addition of KSCN(aq) to a solution of Fe<sup>3+</sup>(aq) produces a deep red solution.

When KCSN is added, the deep red  $[Fe(SCN)(H_2O)_5]^{2+}$  is formed as <u>ligand exchange / displacement</u> takes place OR <u>as position of</u> <u>equilibrium shifts right as shown by the higher  $K_{stab}$  value</u>  $[Fe(H_2O)_6]^{3+} + SCN^- \Rightarrow [Fe(SCN)(H_2O)_5]^{2+} + H_2O$ [2] • what is observed when KF(aq) is added to the deep red solution mentioned above.

When KF is added, the <u>colourless [FeF<sub>6</sub>]<sup>3-</sup></u> is formed. (ligand exchange takes place. <u>[FeF<sub>6</sub>]<sup>3-</sup> is more stable</u> than [Fe(SCN)(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> as seen by the <u>larger  $K_{stab}$  value</u>.) [Fe(SCN)(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> + 6F<sup>-</sup>  $\Rightarrow$  [FeF<sub>6</sub>]<sup>3-</sup> + SCN<sup>-</sup> + 5H<sub>2</sub>O [2]

(ii) Deduce if the value of *x*, the  $K_{\text{stab}}$  of the Fe<sup>3+</sup>(aq) complex with EDTA, is expected to be higher or lower than the  $K_{\text{stab}}$  value of [FeF<sub>6</sub>]<sup>3-</sup>.

Higher because chelates tend to be more stable complexes, as the

polydentate ligands are able to hold the metal cation more securely. [1]

(Lecture notes)

(iii) Give the electronic configuration of Fe in  $[Fe(CN)_6]^{3-}(aq)$ .

1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>5</sup> or [Ar] 3d<sup>5</sup> [1]

(iv) [Fe(CN)<sub>6</sub>]<sup>3–</sup>(aq) is a weaker oxidising agent than Fe<sup>3+</sup>(aq). Explain this statement by quoting appropriate E<sup>9</sup> values from the *Data Booklet*.

 $[Fe(H_2O)_6]^{3+}(aq) + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}(aq) \qquad E^{\circ} = + 0.77 \text{ V}$   $[Fe(CN)_6]^{3-}(aq) + e^- \rightleftharpoons [Fe(CN)_6]^{4-}(aq) \qquad E^{\circ} = + 0.36 \text{ V}$ The less positive  $E^{\theta}$  value suggests that  $[Fe(CN)_6]^{3-}(aq)$  has a lower

tendency to be reduced to [Fe(CN)<sub>6</sub>]<sup>4-</sup>.

(This indicates that CN<sup>-</sup> ligand better stabilises Fe<sup>3+</sup> than H<sub>2</sub>O ligand) [2]

(d) (i) CO is a toxic gas. Draw the dot-and-cross structure of CO.

# $:C : \overset{\times}{\underset{\times}{}} O \overset{\times}{\underset{\times}{}} O \overset{\times}{\underset{\times}{}}$

[1]

CO is also a ligand in iron pentacarbonyl,  $Fe(CO)_5$ . CO binds to the central metal via the carbon atom.

(ii) What is the oxidation state of iron in  $Fe(CO)_5$ ?

)	41
	Ч.

(iii) Draw and name the shape of the complex, Fe(CO)<sub>5</sub>.



(iv) When iron pentacarbonyl reacts with iodine in hexane solution, iron is oxidised and an octahedral complex, Fe(CO)<sub>4</sub>I<sub>2</sub>, is formed.

Isomerism can occur in  $Fe(CO)_4I_2$  due to different positions of the ligands with respect to the central metal ion. Draw the two isomers of  $Fe(CO)_4I_2$ .



I<sup>-</sup> ligand can be either be <u>cis or trans position</u> / I<sup>-</sup> ligand can be in <u>opposite positions of the central metal or the same side</u> of the central metal.

[1]

[Total: 18]

**3** (a) Converting harmful greenhouse gases such as CO<sub>2</sub> into useful chemical commodities, such as methanol, CH<sub>3</sub>OH, is gaining traction in green chemistry as it is economically viable and environment–friendly.

A mixture containing 1.0 mol of  $CO_2$  and 3.0 mol of  $H_2$  is allowed to reach *dynamic equilibrium* at 200°C and 55 bar. Under these conditions, 32%  $CO_2$  is converted to methanol,  $CH_3OH$ .

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

Calculate the equilibrium pressure of each gas and hence calculate the  $K_{\rho}$  value, with the units for this reaction at 200°C. [4]

	CO <sub>2</sub> (g) +	3H₂ (g) 🗧	CH₃OH(g) ⊣	⊦ H₂O(g)
Initial amount / mol	1.0	3.0	0	0
Change / mol	$-\frac{32}{100}$ × 1.0 = -0.32	- 3(0.32) = -0.96	+0.32	+0.32
Equilibrium amount / mol	0.68	2.04	0.32	0.32

Total amount of gaseous particles = 0.68 + 2.04 + 0.32 + 0.32 = 3.36 mol

$$P_{CH_{3}OH} = P_{H_{2}O} = \frac{0.32}{3.36} \times 55 = 5.238 \text{ bar}$$

$$P_{CO_{2}} = \frac{0.68}{3.36} \times 55 = 11.13 \text{ bar}$$

$$P_{H_{2}} = \frac{2.04}{3.36} \times 55 = 33.39 \text{ bar}$$

$$K_{p} = \frac{(P_{CH_{3}OH}) (P_{H_{2}O})}{(P_{CO_{2}})(P_{H_{2}})^{3}}$$

$$=\frac{5.238 \times 5.238}{11.13 \times (33.39)^3} = \frac{6.62 \times 10^{-5} \text{ bar}^{-2}}{10.000}$$

(b) Methanol reacts with carbon monoxide with the help of catalyst to produce ethanoic acid.

Define the term standard enthalpy change of formation of liquid ethanoic acid,  $CH_3CO_2H(l)$ . [1]

Standard enthalpy change of formation of liquid ethanoic acid is the <u>energy change</u> when <u>one mole of  $CH_3CO_2H(l)$ </u> is <u>formed from its elements</u> (i.e. C (s), H<sub>2</sub> (g) and O<sub>2</sub>(g)) at <u>standard conditions</u> of 298K and 1 bar.

(c) Using the enthalpy change values given below, complete the energy cycle and calculate the standard enthalpy change of formation for ethanoic acid,  $CH_3CO_2H(l)$ .



 $\Delta H^{e}_{f} (CH_{3}CO_{2}H(l)) + \Delta H^{e}_{c} (CH_{3}CO_{2}H(l)) + \Delta H^{e}_{f} (H_{2}O(l)) = \Delta H^{e}_{f} (CH_{3}CH_{2}OH(l)) + \Delta H^{e}_{c} (CH_{3}CH_{2}OH(l)) + \Delta H^{e}_{c} (CH_{3}CH_{2}OH(l)) = (-278) + (-1371) - (-876) - (-286)$ 

= - 487 kJ mol<sup>-1</sup>

(d) The ethanoic acid, CH<sub>3</sub>CO<sub>2</sub>H can undergo neutralisation with sodium hydroxide, NaOH. A thermochemical experiment was carried out to determine the enthalpy change of neutralisation using the experimental set–up below.



The following results were obtained:

Volume of NaOH added / cm <sup>3</sup>	50.0
Volume of CH <sub>3</sub> CO <sub>2</sub> H added / cm <sup>3</sup>	50.0
Concentration of NaOH used / mol dm <sup>-3</sup>	1.00
Concentration of CH <sub>3</sub> CO <sub>2</sub> H used / mol dm <sup>-3</sup>	0.65
Initial temperature of CH <sub>3</sub> CO <sub>2</sub> H / °C	25.0
Highest temperature reached / °C	28.5
Specific heat capacity of water / J $g^{-1} K^{-1}$	4.18
Density of water / g cm <sup>-3</sup>	1.00

(i) Use the results to determine the experimental enthalpy change of neutralisation. [3]

Heat absorbed by the solution,  $Q = mc\Delta T = (100 \times 1.00) (4.18) (28.5 - 25.0)$ = **1463 J** 

Assuming no heat loss to surroundings, i.e. 100% efficiency,

$$\Delta H_{\rm n} = -\frac{Q'}{n_{\rm H_2O}}$$

No. of moles of CH<sub>3</sub>CO<sub>2</sub>H =  $0.65 \times \frac{50}{1000} = 0.0325$ No. of moles of NaOH =  $1 \times \frac{50}{1000} = 0.0500$ 

 $\Rightarrow$  CH<sub>3</sub>CO<sub>2</sub>H is the limiting reagent

Mole ratio:  $CH_3CO_2H \equiv H_2O$ 

No. of moles of  $H_2O$  formed = no. of moles of  $CH_3CO_2H = 0.0325$  mol

$$\Delta H_{\rm n} = -\frac{\rm Q'}{\rm n_{\rm H_2O}} = \frac{-1463}{0.0325} = -45.0 \text{ kJ mol}^{-1}$$

(ii) The experiment described in (d)(i) was repeated using HCl instead of CH<sub>3</sub>CO<sub>2</sub>H, under the same conditions. The enthalpy change of neutralisation was found to be -57.9 kJ mol<sup>-1</sup>. Apart from heat loss, suggest another reason for the discrepancy between this value and that calculated in (d)(i). [1]

The value calculated in (d)(i) is less exothermic, as  $CH_3CO_2H$ , as a weak acid, only *dissociates partially* in solution.

<u>Some of the heat released</u> from the neutralisation is used to <u>promote further</u> <u>dissociation of  $CH_3CO_2H$  molecules</u> (energy is used to break the O–H bonds in the remaining  $CH_3CO_2H$  molecules to form more  $H^+(aq)$  for neutralisation). Hence the overall enthalpy change is less exothermic.

(e) Like many acids, ethanoic acid reacts with basic carbonates such as magnesium carbonate, MgCO<sub>3</sub> to release carbon dioxide.

Using the following data and relevant data from the *Data Booklet*, complete the following energy level diagram and use it to determine the standard enthalpy change of formation of magnesium carbonate, MgCO<sub>3</sub>.

lattice energy of MgCO <sub>3</sub> (s)	= –3208 kJ mol <sup>-1</sup>
standard enthalpy change of atomisation of Mg (s)	= +147 kJ mol <sup>-1</sup>
sum of 1 <sup>st</sup> and 2 <sup>nd</sup> electron affinity of oxygen	= +702 kJ mol <sup>-1</sup>
standard enthalpy change of formation of CO <sub>2</sub> (g)	= -393 kJ mol <sup>-1</sup>
standard enthalpy change of reaction below, $\Delta H^{e}_{r}$	= -778 kJ mol <sup>-1</sup>
$O^{2-}(g) + CO_2(g) \longrightarrow CO_3^{2-}(g)$	

Energy

 $Mg^{2+}(g) + C(s) + O_2(g) + O^{2-}(g)$  $Mg^{2+}(g) + 2e^{-} + C(s) + \frac{3}{2}O_{2}(g)$ 1<sup>st</sup> IE (Mg) + 2<sup>nd</sup> IE (Mg) Mg (g) + C (s) +  $\frac{3}{2}$  O<sub>2</sub>(g)  $\Delta H^{e}_{at}$  (Mg) Mg (s) + C (s) +  $\frac{3}{2}O_2(g)$ 0  $\Delta H^{\Theta_f}(MgCO_3(s))$ MgCO₃(s)
Energy

 $Mg^{2+}(g) + C(s) + O_2(g) + O^{2-}(g)$  $\Delta H_{f}^{\circ}$  (CO<sub>2</sub> (g)) 1<sup>st</sup> EA (O) + 2<sup>nd</sup> EA (O)  $Mg^{2+}(g) + CO_2(g) + O^{2-}(g)$  $Mg^{2+}(g) + 2e + C(s) + O_2(g) + O(g)$ ∆**H**r<sup>⊕</sup>  $Mg^{2+}(g) + CO_3^{2-}(g)$ ∆**H**<sup>•</sup><sub>at</sub> (**O**) = ½ **BE**(**O**=**O**) Mg<sup>2+</sup> (g) + 2e<sup>-</sup> + C (s) +  $\frac{3}{2}$  O<sub>2</sub> (g)  $1^{st}$  IE (Mg) +  $2^{nd}$  IE (Mg) Mg (g) + C (s) +  $\frac{3}{2}$  O<sub>2</sub>(g)  $\Delta H_{latt}^{\theta}$  (MgCO<sub>3</sub>(s))  $\Delta H^{\Theta}_{at}$  (Mg) Mg (s) + C (s) +  $\frac{3}{2}O_2(g)$ 0  $\Delta H^{\Theta}_{f}(MgCO_{3}(s))$ MgCO<sub>3</sub> (s)

By Hess' Law,  $\Delta H_{f} (MgCO_{3} (s)) = \Delta H_{at}^{\theta} (Mg) + 1^{st} IE (Mg) + 2^{nd} IE (Mg) + \frac{1}{2} BE(O=O) + 1^{st} EA(O) + 2^{nd} EA (O) + \Delta H_{f}^{\theta} (CO_{2}) + \Delta H_{r}^{\theta} + \Delta H_{latt}^{\theta} (MgCO_{3})$   $\Delta H_{f} (MgCO_{3} (s)) = +147 + 736 + 1450 + \frac{1}{2}(496) + 702 + (-393) + (-778) + (-3208) = -1096 \text{ kJ mol}^{-1}$ [Total: 18]

- 4 Dragons are able to breathe fire because the parasitic bacteria that live in their lungs produce flammable gases. If a dragon exhales sharply, the gas can ignite due to the friction against the rough walls of the larynx.
  - (a) The gas exhaled by a dragon contains 20 mole % of hydrogen sulfide, H<sub>2</sub>S and 15 mole % of oxygen.

The average volume of a dragon's lung is  $5.1 \text{ m}^3$  and due to the high pressures experienced when a dragon exhales, the molar volume of the gas contained in their lungs is  $15 \text{ dm}^3 \text{ mol}^{-1}$ .

(i) Calculate the total amount of gas in moles contained in a dragon's lung.

Total amount of gas =  $5.1 \times 10^3 / 15$ = <u>340</u> mol

[1]

(ii) Assuming the temperature of a dragon's lung is 40 °C and the gaseous mixture behaves ideally, use the ideal gas equation and your answer in (a)(i) to calculate the internal pressure in the lung experienced by a dragon.

Let p to be the internal pressure in the dragon's lung pV = nRT p x 5.1 = 340 x 8.314 x (40 + 273) $p = \frac{173 x 10^3 Pa}{1000}$ 

[1]

(iii) The actual pressure in the dragon's lung is lower than the value calculated in(a)(ii). Account for the discrepancy observed.

The calculated value in part (a)(ii) is based on the assumption gases in the dragon's lung are ideal gases. However, they behave as real gases.

There are <u>significant intermolecular forces of attractions between these gas</u> <u>molecules</u>. Hence, these gases exert smaller amount of force on the walls of the lung.

The actual pressure is expected to be smaller than that calculated by ideal gas equation.

[1]

(iv) Write a balanced equation for the reaction that describes the burning of gas exhaled by the dragon. Hence, calculate the additional moles of oxygen required for the complete combustion of one exhalation of the dragon.

 $H_2S + (3/2)O_2 \rightarrow SO_2 + H_2O$ 

Amount of H<sub>2</sub>S gas =  $340 \times 0.2 = 68$  mol Amount of O<sub>2</sub> gas contained in the dragon's lung =  $340 \times 0.15$  = 51 mol H<sub>2</sub>S  $\equiv (3/2)O_2$ The amount of O<sub>2</sub> gas required for complete combustion  $= 68 \times 3/2 = 102$  mol The additional moles of O<sub>2</sub> required = 102 - 51 = 51 mol

[3]

(b) The parasitic bacteria in the dragon's lung produces a protein molecule A which speeds up the formation of flammable gases.
 In the study of the structure of A, it was digested using two different enzymes. The fragments obtained were separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

Digestion using the first enzyme:	Digestion using the second enzyme:
his-phe-gly	gly-asp-gly-thr
ser-pro-glu	pro-glu
asp-gly	phe-leu-ser
thr-phe-leu	his-phe

(i) Write out the amino acid sequence of the smallest polypeptide A.

```
From 2nd enzyme:gly-asp-gly-thrFrom 1st enzyme:his-phe-gly asp-gly thr-phe-leuFrom 2nd enzyme:his-phephe-leu-serser-pro-gluhis-phe-gly-asp-gly-thr-phe-leu-ser-pro-glu
```

[2]

(ii) A tripeptide, his-phe-glu, obtained from **A** was further hydrolysed. The resulting solution was added to an excess of a buffer solution of pH 6.5 and placed at the centre of the plate. A potential difference was then applied across the plate.

Amino acids		H <sub>2</sub> N—CH—COOH CH <sub>2</sub>	H <sub>2</sub> N— CH—COOH   CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H
	his	phe	glu
Isoelectric point	7.58	5.48	3.10

Indicate the relative positions of the amino acids on the diagram below.



Positively charged species will migrate to the cathode (negative electrode) Negatively charged species will migrate to the anode (positive electrode)

17

[Total: 10]

**5** Carvone is a chemical found naturally in essential oils extracted from the seeds of two common herbs, spearmint and dill.



Carvone

Two stereoisomers of carvone are responsible for the distinctively different flavor and smell of the two herbs.

(a) State the type of stereoisomerism carvone can exhibit.

Optical isomerism / enantiomerism [1]

(b) Draw the two stereoisomers of carvone.



[1]

(c) Carvone undergoes reduction with different reagents and conditions to form different products. One notable reduction method is the *Wolff-Kishner reduction* whereby the ketone functional group in carvone reacts with hydrazine, N<sub>2</sub>H<sub>4</sub>, in the presence of a strong base to form limonene, C<sub>10</sub>H<sub>16</sub>, a major component in the oil of citrus fruit peels.

The general reaction sequence of the Wolff-Kishner reduction is shown below.



The Wolff-Kishner reduction is unsuitable for base-sensitive reactants.

(i) Suggest the type of reaction in **Step 1**.

Condensation / Addition-Elimination [1]

(ii) The following reaction scheme shows the various reduction reactions of carvone. Suggest the structural formulae of compounds A, B and C in the boxes below.



(iii) Suggest a simple chemical test that could distinguish between carvone and limonene. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: 2, 4-dinitrophenylhydrazine, heat

	Observations:	Products:
Carvone	Orange ppt formed	
Limonene	No orange ppt formed	N.A.
		[3]

(iv) Suggest a reason why the following compound is unlikely to undergo the *Wolff-Kishner reduction* despite the presence of a ketone functional group.



Presence of <u>acidic</u> phenolic group which would react with the base
used in step 1 [1]

[Total: 10]

20

**6** When fuming sulfuric acid reacts with alkenes, electrophilic addition occurs to form alkyl hydrogensulfates. This is exemplified by the reaction involving ethene below.



When 1-methylcyclohexene reacts with fuming sulfuric acid, a mixture of two isomers X and Y are formed, with isomer X being the major product.

(a) Name and define the type of isomerism exhibited by isomers X and Y.

Positional/Constitutional isomerism Constitutional isomers have the <u>same molecular formula</u> but <u>different</u> <u>structural formula</u>. In addition, positional isomers have the same substituents / functional groups, but at different positions (-OSO<sub>3</sub>H).

(b) Complete the following to suggest a mechanism for the reaction between 1-methylcyclohexene and sulfuric acid to form X. Show the displayed structure of H<sub>2</sub>SO<sub>4</sub>, the structure of the intermediate, the movement of the electron pairs and the structure of X. [4]



(c) Explain why benzene does not undergo addition reactions with fuming sulfuric acid.

Benzene contains a <u>ring of delocalised  $\pi$  electrons</u> which leads <u>to extra</u> <u>stability (resonance stability)</u>, hence to <u>maintain the stability of benzene</u>, it would not undergo <u>addition</u> <u>reaction which will lead to breaking the ring of delocalised  $\pi$  electrons and giving less stable products due to loss of resonance stability. [2]</u>

[Total: 8]



# **Catholic Junior College**

JC2 Preliminary Examinations Higher 2

CANDIDATE	
NAME	

CLASS

# **CHEMISTRY**

Paper 3 Free Response

Friday 30 August 2019 2 hours

9729/03

Candidates answer on separate paper.

**2T** 

Additional Materials: Answer Paper Data Booklet

### **READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the work you hand in. Write in dark blue or black pen. You may use an HB pencil for any diagrams or graphs. Do not use staples, paper clips, glue or correction fluid.

#### Section A Answer all questions.

Section B

Answer **one** question.

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

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

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

#### Section A Answer all the questions in this section.

 (a) Chemical energy can be directly converted to electrical energy in batteries and fuel cells. Fuel cells require a continuous source of fuel and oxygen to sustain the chemical reaction, whereas in batteries, the chemical energy is usually derived from reactions of metals or metal oxides present in the battery.

> The nickel-cadmium (NiCd) battery is a rechargeable battery used in many devices such as handphones and laptops. A simplified diagram of the NiCd electrochemical cell is as shown:



Electrode **X** is made of a solid nickel compound, NiO(OH), and electrode **Y** is made of solid cadmium. The electrolyte is aqueous potassium hydroxide. During discharge,  $Ni(OH)_2(s)$  and  $Cd(OH)_2(s)$  are formed at the respective electrodes.

- (i) Construct the half-equations at the electrodes of this alkaline NiCd electrochemical cell. Hence, give the balanced overall equation for the reaction that occurs during discharge.
- (ii) Write a cell representation for the NiCd electrochemical cell, indicating clearly the direction of electron flow in the external circuit.
   [2]
- (iii) NiCd batteries can be recharged by applying a current across the two electrodes. How long would it take to recharge a NiCd battery at a current of 2.0 A, if 5.6 g of cadmium was converted to Cd(OH)<sub>2</sub>?
- (b) Methane gas, CH<sub>4</sub>, is the simplest alkane used to power a fuel cell. The methane-oxygen fuel cell has recently been shown to be an efficient source of electrical energy. In the simplest version of this fuel cell, an acid is used as the electrolyte and methane undergoes reaction at one of the electrodes while oxygen undergoes reaction at the other electrode.

$$CO_2 + 8H^+ + 8e^- \stackrel{\Rightarrow}{\Rightarrow} CH_4 + 2H_2O$$
  $E^{\theta} = +0.17 V$   
 $O_2 + 4H^+ + 4e^- \stackrel{\Rightarrow}{\Rightarrow} 2H_2O$ 

(i) By using the half-equations above and relevant data from the *Data Booklet*, calculate the  $E^{\theta}_{cell}$  of this fuel cell. [1]

- (ii) Draw a fully labelled diagram of the electrochemical cell you could use to measure this  $E_{cell}^{\theta}$ . [3]
- (c) An alternative fuel used in fuel cells is dimethyl oxalate,  $(CH_3)_2C_2O_4$ , which is obtained by the esterification of ethanedioic acid,  $H_2C_2O_4$ , with methanol,  $CH_3OH$ . The ethanedioate ion,  $C_2O_4^{2^-}$ , is commonly found in ionic salts such as  $\mathbf{X}C_2O_4$ . When these ethanedioate salts,  $\mathbf{X}C_2O_4$ , are oxidised by acidified potassium manganate(VII), KMnO\_4, both the  $\mathbf{X}^{2^+}$  and  $C_2O_4^{2^-}$  ions are oxidised. Carbon dioxide gas is formed as one of the products in the reaction.
  - (i) Write a balanced equation for the reaction between MnO<sub>4</sub><sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> under acidic conditions.
  - (ii) 25.0 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> XC<sub>2</sub>O<sub>4</sub> solution was titrated with 0.1 mol dm<sup>-3</sup> of acidified KMnO<sub>4</sub>. Determine the volume of KMnO<sub>4</sub> needed to oxidise C<sub>2</sub>O<sub>4</sub><sup>2-</sup> only. [2]
  - (iii) Given that 15.00 cm<sup>3</sup> of acidified KMnO<sub>4</sub> was required to completely oxidise 25.0 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> XC<sub>2</sub>O<sub>4</sub> solution, and using your answer in (c)(ii), find the oxidation state of X in the product. [3]
- (d) Potassium manganate(VII), KMnO<sub>4</sub>, can be used to oxidise alkenes in different ways. Alkene P, C<sub>8</sub>H<sub>16</sub>, reacts with hot acidified KMnO<sub>4</sub> to form one organic product only, which gives a yellow precipitate with hot aqueous alkaline iodine. P also reacts with cold alkaline KMnO<sub>4</sub> to form an optically inactive diol, Q. When P is treated with chlorine in ultraviolet light, it produces a mixture of chlorinated compounds, including R, C<sub>8</sub>H<sub>14</sub>Cl<sub>2</sub>, which does not have any chiral carbon. When R is reacted with ethanolic NaOH, compound S, C<sub>8</sub>H<sub>12</sub>, is the only product formed. S produces two compounds, CO<sub>2</sub> and CH<sub>3</sub>COCO<sub>2</sub>H in equimolar amounts when it is oxidised by hot acidified KMnO<sub>4</sub>.
  - (i) Suggest the structural formulae for compounds P, Q, R and S. [4]
  - (ii) Draw the structural formula of an isomer of R, C<sub>8</sub>H<sub>14</sub>Cl<sub>2</sub>, that could give S on dehydrochlorination.
  - (iii) Suggest, with a reason, the number of stereoisomers for compound **S**. [1]

- 2 With the prospect that fossil fuels will become increasingly scarce in the future, many compounds are being considered for use in internal combustion engines. One of these is DME or dimethyl ether, CH<sub>3</sub>OCH<sub>3</sub>. DME is a gas which can be synthesised from methanol. Methanol can be obtained from biomass, such as plant waste from agriculture.
  - (a) Write a balanced equation to define the term *standard enthalpy change of combustion*,  $\Delta H_c^{-\circ}$ , of DME. [1]
  - (b) A 0.31 g sample of DME was completely burnt in air. The heat produced raised the temperature of 200 g of water by 11.7 °C. Assume no heat losses occurred during this experiment.
    - (i) Use relevant data from the *Data Booklet* to calculate the amount of heat released in this experiment. [1]
    - (ii) Hence calculate the enthalpy change of combustion,  $\Delta H_c^{-\circ}$ , of DME. [1]
  - (c) (i) Use the bond energies given in the *Data Booklet* to calculate another value for the *enthalpy change of combustion*,  $\Delta H_c^{-\Phi}$ , of DME. [2]
    - (ii) Suggest a reason for the discrepancy, if any, between this  $\Delta H_c^{-\bullet}$  value and that calculated in (b)(ii). [1]
  - (d) DME may be synthesised from methanol according to the following equation.

$$2CH_3OH(l) \rightarrow CH_3OCH_3(g) + H_2O(l)$$
  $\Delta H^{--} = +7.10 \text{ kJ mol}^{-1}$ 

- (i) The entropy change for this reaction,  $\Delta S^{\bullet}$ , is +83.62 J K<sup>-1</sup> mol<sup>-1</sup>. Explain the significance of the sign of  $\Delta S^{\bullet}$ .
- (ii) Use the value of  $\Delta S^{\bullet}$  and  $\Delta H^{\bullet}$  given above to calculate a value for the standard Gibbs Free energy,  $\Delta G^{\bullet}$ , for this reaction. [1]

[1]

- (iii) By considering the effect of temperature on the spontaneity of this reaction, suggest and explain whether high or low temperature should be used to produce DME. [2]
- (iv) Explain, in molecular terms, how the rate of the above reaction is affected by changing the concentration of methanol. [2]
- (e) Methanol is also a reagent to synthesise vanillin. Vanillin is an important raw material for the production of L-DOPA used in the treatment of Parkinson's disease.



A student carried out some reactions with samples of L-DOPA and vanillin using reagents X, Y and Z.

- Reagent **X** reacted with L-DOPA **and** with vanillin.
- Reagent Y reacted with L-DOPA but not with vanillin.
- Reagent **Z** reacted with vanillin but **not** with L-DOPA.

Assume that the CH<sub>3</sub>O– group in vanillin is inert and does not react.

Suggest possible identities of reagents **X**, **Y** and **Z** and give the structures of the organic products formed in each case. [7]

[Total: 19]

**3** (a) The hydroformylation reaction is an industrial process for the production of aldehydes from alkenes. For example, butanal can be synthesised from propene, C<sub>3</sub>H<sub>6</sub>, as follows:



- (i) Write an expression for  $K_p$  of the reaction, including units.
- (ii) Given that the magnitude of  $K_p$  for the above reaction is 775, deduce what the  $K_p$  value indicates about the position of equilibrium. Hence, state the sign of  $\Delta G^{-\sigma}$  for the reaction. [2]

[2]

- (iii) Given that the above reaction is exothermic, suggest, with a reason, the effect of an increased temperature on the amount of butanal formed at equilibrium. [1]
- (iv) The mechanism of hydroformylation of propene resembles the electrophilic addition of alkenes and can result in the formation of two isomeric products. Apart from butanal, suggest the structure of the other isomer that can be formed.
  [1]
- (b) In the Leuckart-Wallach reaction, a carbonyl compound reacts with a primary amine to form a secondary amine.



(i) Stage 1 occurs in 2 steps. The first step involves a nucleophilic attack while in the second step, a proton transfer occurs within the intermediate to form the alcohol group.

Name and outline the 2-step mechanism for Stage 1, to form Compound **A**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [3]

- (ii) Compound **B** undergoes reduction in Stage 3. Describe the change in oxidation state of carbon which occurs in this stage. [1]
- (iii) Unlike primary amines, amides cannot be used in the Leuckart-Wallach reaction. Explain why this is so. [1]
- (iv) 2-bromopyrrolidine, a cyclic amine, can be synthesised via the Leuckart-Wallach reaction.



2-bromopyrrolidine

Draw the displayed formula of the starting compound used in the synthesis of 2-bromopyrrolidine. [1]

- (v) State and explain the relative basicities of 2-bromopyrrolidine and compound **C**. [2]
- (c) Carbon also forms compounds with other Group 16 elements like sulfur and selenium. The properties of some of these compounds are given in the table below.

Compound	Structure	Dipole moment	Boiling point / °C
CS <sub>2</sub>	S=C=S	0	46
COS	S=C=O	0.71	-50
COSe	Se=C=O	X	-22

- (i) Explain, in terms of structure and bonding, the difference in the boiling point of CS<sub>2</sub> and COS. [2]
- (ii) Predict a value for the dipole moment of COSe, *x*, and explain. [1]
- (iii) Aside from the common oxides, carbon forms a series of straight-chained reactive oxocarbons. One such compound is tricarbon monoxide, C<sub>3</sub>O, a reactive molecule found in space. Suggest a displayed structure of tricarbon monoxide. Indicate clearly any lone pairs of electrons present in your structure.
- (iv) Tricarbon monoxide is isoelectronic to cyanogen, (CN)<sub>2</sub>. The molecule of cyanogen contains a C–C single bond.
   Draw the dot-and-cross diagram of cyanogen. In your diagram, you should distinguish the electrons originating from each of the two carbon atoms and those from the two nitrogen atoms.

#### Section B

Answer **one** question from this section.

**4** (a) Benzene is a widely used starting organic compound to synthesize other chemicals, such as benzenesulfonic acid and 2-methylphenol.

Benzenesulfonic acid can be produced by heating benzene under reflux with concentrated sulfuric acid for several hours. This process is similar to the nitration of benzene.



The first step of the mechanism involves the protonation of one molecule of sulfuric acid by another and the loss of a molecule of water.

- (i) Describe the mechanism for the above reaction. Show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons. [4]
- (ii) Similarly, methylbenzene also reacts with concentrated sulfuric acid to form a mixture of the three isomers, in equilibrium.



Suggest why there is a lower concentration of 1,2-isomer than that of 1,4-isomer in the equilibrium mixture. [1]

(iii) The chlorinated compound MCPA, widely used as a weed killer, can be synthesized from 2-methylphenol.



Using **not** more than 3 steps, draw a reaction scheme to show how MCPA can be synthesised from 2–methylphenol. [5]

- (b) The chemical reactions of benzene sometimes require iron as a catalyst. Iron is a hard grey transition metal which is resistant to corrosion at ordinary temperatures. In contrast, calcium is a fairly soft, silvery-grey Group 2 metal which quickly tarnishes in air.
  - (i) By considering relevant electronic configurations, explain why the atomic radius of iron is smaller than that of calcium, even though iron has more electrons. [2]
  - (ii) Iron can exist in different oxidation states whereas calcium does not. Explain why.

[2]

- (iii) Explain why iron(II) complexes are green in colour. [3]
- (iv) Iron(III) ions catalyse the reaction between I<sup>-</sup> ions and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions through homogeneous catalysis.
   Explain why iron(III) ions can be described as a homogeneous catalyst. By considering relevant E<sup>e</sup> values from the *Data Booklet*, show by means of balanced equations, how the iron(III) ions carry out its role in this reaction. [3]

[Total: 20]

- **5** (a) Aluminium oxide, Al<sub>2</sub>O<sub>3</sub>, and aluminium chloride, AlCl<sub>3</sub>, are widely used in various industrial and commercial applications.
  - (i) Aluminium oxide has a melting point of 2072 °C while aluminium chloride sublimes at 180 °C. Explain the difference in melting points in terms of structure and bonding in each compound.
  - (ii) Describe the reactions, if any, of aluminium oxide and aluminium chloride with water, suggesting the pH of the resulting solutions and writing equations, where appropriate. [4]
  - (b) The reaction between chlorine gas and hot sodium hydroxide is as follows.

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

- (i) State the type of reaction occuring.
- (ii) State the change in oxidation numbers of chlorine that occur during this reaction. [2]
- (c) Ethers are a class of organic compounds that has two organic groups bonded to the same oxygen atom, R-O-R'. The organic groups could be alkyl and aryl groups. Williamson synthesis could be used to synthesis ethers by a reaction between primary alkyl halides and metal alkoxides.

A typical example of the Williamson synthesis is a two-step reaction to synthesize *tert*-butyl methyl ether.

The first step of the reaction involved the preparation of sodium alkoxide in the presence of sodium hydride, NaH.



sodium alkoxide

[1]

The second step of the reaction involved the reaction between the alkoxide ion and the primary alkyl halide.



- (i) Suggest the role of sodium hydride in step 1. [1]
- (ii) Suggest the type of reaction which occurs in step 2. [1]
- (iii) Suggest why primary alkyl halide is used in Williamson synthesis instead of secondary or tertiary alkyl halide.
- (iv) The following scheme shows a three-step synthesis of compound L from 1-chloropropane. Given that step 3 involves Williamson synthesis, suggest the reagents and conditions you would use for each step and identify the intermediates J and K.



- (d) (i) Using monohalogenethanes, C<sub>2</sub>H<sub>5</sub>X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds with respect to hydrolysis. [1]
  - (ii) There are other methods to synthesise ethers. A cyclic ether N could be formed as shown below. Predict the outcomes of the following transformations, drawing the structures of the intermediate M and the product N.



[2]

[Total: 20]

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# **Catholic Junior College**

JC2 Preliminary Examinations Higher 2

CANDIDATE	
NAME	

CLASS

# CHEMISTRY

Paper 3 Free Response

**9729/03** Friday 30 August 2019

2 hours

Candidates answer on separate paper.

**2T** 

Additional Materials: Answer Paper Data Booklet

## READ THESE INSTRUCTIONS FIRST

# **WORKED SOLUTIONS**

#### Section A Answer all the questions in this section.

 (a) Chemical energy can be directly converted to electrical energy in batteries and fuel cells. Fuel cells require a continuous source of fuel and oxygen to sustain the chemical reaction, whereas in batteries, the chemical energy is usually derived from reactions of metals or metal oxides present in the battery.

> The nickel-cadmium (NiCd) battery is a rechargeable battery used in many devices such as handphones and laptops. A simplified diagram of the NiCd electrochemical cell is as shown:



Electrode **X** is made of a solid nickel compound, NiO(OH), and electrode **Y** is made of solid cadmium. The electrolyte is aqueous potassium hydroxide. During discharge,  $Ni(OH)_2(s)$  and  $Cd(OH)_2(s)$  are formed at the respective electrodes.

(i) Construct the half-equations at the electrodes of this alkaline NiCd electrochemical cell. Hence, give the balanced overall equation for the reaction that occurs during discharge.

Electrode X: NiO(OH) + H<sub>2</sub>O +  $e^- \rightarrow Ni(OH)_2 + OH^-$ 

Electrode Y: Cd + 2OH<sup>-</sup>  $\rightarrow$  Cd(OH)<sub>2</sub> + 2e<sup>-</sup>

Overall equation: Cd +  $2NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$ 

(ii) Write a cell representation for the NiCd electrochemical cell, indicating clearly the direction of electron flow in the external circuit.
 [2]

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e<sup>−</sup> flow

↓

Cd(s), Cd(OH)<sub>2</sub>(s) // NiO(OH)(s), Ni(OH)<sub>2</sub>(s)
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 (iii) NiCd batteries can be recharged by applying a current across the two electrodes. How long would it take to recharge a NiCd battery at a current of 2.0 A, if 5.6 g of cadmium was converted to Cd(OH)<sub>2</sub>?

Moles of Cd converted = 5.6 / 112.4 = 0.0498 mol Moles of electrons required =  $0.0498 \times 2 = 0.0996$  mol

Total charge required = 
$$0.0996 \times 96500 = 9615 \text{ C}$$
  
Time required =  $9615 / 2.0 = 4807 \text{ s}$  (or 80.1 min)

(b) Methane gas, CH<sub>4</sub>, is the simplest alkane used to power a fuel cell. The methane-oxygen fuel cell has recently been shown to be an efficient source of electrical energy. In the simplest version of this fuel cell, an acid is used as the electrolyte and methane undergoes reaction at one of the electrodes while oxygen undergoes reaction at the other electrode.

 $CO_2 + 8H^+ + 8e^- \stackrel{<}{=} CH_4 + 2H_2O$   $E^{\theta} = +0.17 V$  $O_2 + 4H^+ + 4e^- \stackrel{<}{=} 2H_2O$ 

(i) By using the half–equations above and relevant data from the *Data Booklet*, calculate the  $E^{\theta}_{cell}$  of this fuel cell. [1]

 $O_2 + 4H^+ + 4e^- ≈ 2H_2O$   $E^θ = +1.23 V$  $E^θ_{cell} = 1.23 - (0.17) = +1.06 V$ 

(ii) Draw a fully labelled diagram of the electrochemical cell you could use to measure this  $E_{cell}^{\theta}$ . [3]



- (c) An alternative fuel used in fuel cells is dimethyl oxalate,  $(CH_3)_2C_2O_4$ , which is obtained by the esterification of ethanedioic acid,  $H_2C_2O_4$ , with methanol,  $CH_3OH$ . The ethanedioate ion,  $C_2O_4^{2-}$ , is commonly found in ionic salts such as  $XC_2O_4$ . When these ethanedioate salts,  $XC_2O_4$ , are oxidised by acidified potassium manganate(VII), KMnO\_4, both the  $X^{2+}$  and  $C_2O_4^{2-}$  ions are oxidised. Carbon dioxide gas is formed as one of the products in the reaction.
  - (i) Write a balanced equation for the reaction between MnO<sub>4</sub><sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> under acidic conditions.
     [1]

 $5C_2O_4^{2-} + 2MnO_4^{-} + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$ 

(ii) 25.0 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> XC<sub>2</sub>O<sub>4</sub> solution was titrated with 0.1 mol dm<sup>-3</sup> of acidified KMnO<sub>4</sub>. Determine the volume of KMnO<sub>4</sub> needed to oxidise C<sub>2</sub>O<sub>4</sub><sup>2-</sup> only. [2]

Moles of  $C_2O_4^{2-}$  ions = 0.025 x 0.1 = 0.0025 mol Since  $C_2O_4^{2-}$ : MnO<sub>4</sub><sup>-</sup> is 5 : 2, Moles of MnO<sub>4</sub><sup>-</sup> needed to oxidise  $C_2O_4^{2-}$  = 0.0025 x 2/5 = 0.001 mol Volume of MnO<sub>4</sub><sup>-</sup> needed = (0.001 / 0.1) x 1000 = 10 cm<sup>3</sup> (iii) Given that 15.00 cm<sup>3</sup> of acidified KMnO<sub>4</sub> was required to completely oxidise 25.0 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> XC<sub>2</sub>O<sub>4</sub> solution, and using your answer in (c)(ii), find the oxidation state of X in the product. [3]

Volume of  $MnO_4^-$  ions needed to oxidise  $X^{2+}$  ions =  $15 - 10 = 5 \text{ cm}^3$ Moles of  $MnO_4^-$  ions =  $(5 / 1000) \times 0.1 = 0.0005 \text{ mol}$ From Data Booklet,  $MnO_4^- + 8H^+ + 5e^- \implies Mn^{2+} + 4H_2O$ Moles of electrons gained by  $MnO_4^- = 0.0005 \times 5 = 0.0025$  mol Moles of  $X^{2+}$ ions =  $0.025 \times 0.1 = 0.0025$  mol Therefore, mole ratio of  $X^{2+}$  : e = 1 : 1Since 1 mole of  $X^{2+}$  loses 1 mole of electrons, Oxidation state of X in the product = +3

(d) Potassium manganate(VII), KMnO<sub>4</sub>, can be used to oxidise alkenes in different ways. Alkene P, C<sub>8</sub>H<sub>16</sub>, reacts with hot acidified KMnO<sub>4</sub> to form one organic product only, which gives a yellow precipitate with hot aqueous alkaline iodine. P also reacts with cold alkaline KMnO<sub>4</sub> to form an optically inactive diol, Q. When P is treated with chlorine in ultraviolet light, it produces a mixture of chlorinated compounds, including R, C<sub>8</sub>H<sub>14</sub>Cl<sub>2</sub>, which does not have any chiral carbon. When R is reacted with ethanolic NaOH, compound S, C<sub>8</sub>H<sub>12</sub>, is the only product formed. S produces two compounds, CO<sub>2</sub> and CH<sub>3</sub>COCO<sub>2</sub>H in equimolar amounts when it is oxidised by hot acidified KMnO<sub>4</sub>.



(i) Suggest the structural formulae for compounds P, Q, R and S.

[4]



(ii) Draw the structural formula of an isomer of R, C<sub>8</sub>H<sub>14</sub>Cl<sub>2</sub>, that could give S on dehydrochlorination.



(iii) Suggest, with a reason, the number of stereoisomers for compound **S**. [1]

There is 1 alkene double bond that is capable of exhibiting cis-trans isomerism as there are 2 different groups attached to each C atom across C=C double bond; no of stereoisomers=  $\underline{2}$ .

[Total:22]

- 2 With the prospect that fossil fuels will become increasingly scarce in the future, many compounds are being considered for use in internal combustion engines. One of these is DME or dimethyl ether, CH<sub>3</sub>OCH<sub>3</sub>. DME is a gas which can be synthesised from methanol. Methanol can be obtained from biomass, such as plant waste from agriculture.
  - (a) Write a balanced equation to define the term *standard enthalpy change of combustion*,  $\Delta H_c^{-\phi}$ , of DME. [1]

 $CH_3OCH_3(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ 

- (b) A 0.31 g sample of DME was completely burnt in air. The heat produced raised the temperature of 200 g of water by 11.7 °C. Assume no heat losses occurred during this experiment.
  - (i) Use relevant data from the *Data Booklet* to calculate the amount of heat released in this experiment. [1]

heat released = mc  $\Delta T$ = 200 × 4.18 × 11.7 = 9781 J (or 9.78 kJ)

(ii) Hence calculate the enthalpy change of combustion,  $\Delta H_c^{\bullet}$ , of DME. [1]

*M*<sub>r</sub> of DME, CH<sub>3</sub>OCH<sub>3</sub> = 2(12.0) + 6(1.0) + 16.0 = 46.0 0.31 g of DME produce 9.78 kJ ∴  $\Delta H_c^{-\Theta}$  of DME =  $-\frac{9.78 \times 46.0}{0.31}$  = -1451 kJ mol<sup>-1</sup>

(c) (i) Use the bond energies given in the *Data Booklet* to calculate another value for the *enthalpy change of combustion*,  $\Delta H_c^{\bullet}$ , of DME. [2]

 $CH_3OCH_3(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ 

Bonds broken ( $\Delta H_1$ / kJ mol <sup>-1</sup> )		<u>Bonds formed</u> ( $\Delta H_2$ / kJ mol <sup>-1</sup> )	
2 <b>C</b> –O	2(+360)	4 C=O	4(-805)
6 C–H	6(+410)	6 O–H	6(-460)
3 O=O	3(+496)		

 $\therefore \Delta H_c^{-+} = 2(+360) + 6(+410) + 3(+496) + 4(-805) + 6(-460)$  $= -1312 \text{ kJ mol}^{-1}$ 

(ii) Suggest a reason for the discrepancy, if any, between this  $\Delta H_c^{-\bullet}$  value and that calculated in (b)(ii). [1]

This  $\Delta H_c^{\bullet}$  value is <u>less exothermic</u> than that calculated in (b)(ii) because <u>bond</u> energies given in <u>Data Booklet</u> are <u>average</u> values and do not relate to any specific compound.

(d) DME may be synthesised from methanol according to the following equation.

$$2CH_3OH(l) \rightarrow CH_3OCH_3(g) + H_2O(l)$$
  $\Delta H^{\oplus} = +7.10 \text{ kJ mol}^{-1}$ 

(i) The entropy change for this reaction,  $\Delta S^{-\Phi}$ , is +83.62 J K<sup>-1</sup> mol<sup>-1</sup>. Explain the significance of the sign of  $\Delta S^{-\Phi}$ .

 $\Delta S^{\bullet}$  is <u>positive</u>, which shows that the reaction proceeds with an <u>increase in</u> <u>disorderliness</u> due to the <u>increase in number of moles of gas</u> from <u>0 mol to 1 mol</u>.

(ii) Use the value of  $\Delta S^{-\bullet}$  and  $\Delta H^{-\bullet}$  given above to calculate a value for the standard Gibbs Free energy,  $\Delta G^{-\bullet}$ , for this reaction. [1]

 $\Delta G^{-\bullet} = \Delta H^{-\bullet} - T \Delta S^{-\bullet}$ = +7.10 - (298)(+83.62 × 10<sup>-3</sup>) = -17.82 kJ mol<sup>-1</sup>

(iii) By considering the effect of temperature on the spontaneity of this reaction, suggest and explain whether high or low temperature should be used to produce DME.

As temperature <u>decreases</u>, the term  $(-T\Delta S^{\bullet})$  becomes <u>less negative</u> and so,  $\Delta G^{\bullet}$  will become <u>less negative</u>; and the reaction is <u>less spontaneous</u>. OR

As temperature <u>increases</u>, the term  $(-T\Delta S^{\bullet})$  becomes <u>more negative</u> and so,  $\Delta G^{\bullet}$  will become <u>more negative</u>; and the reaction is <u>more spontaneous</u>.

- To ensure that the reaction remains spontaneous (△G → < 0), the production of DME should be carried out at <u>high temperature</u>.
- (iv) Explain, in molecular terms, how the rate of the above reaction is affected by changing the concentration of methanol. [2]
  - rate of reaction <u>increases</u> when concentration of methanol is <u>increased</u> due to increase in frequency of collisions between methanol molecules which are now closer together, and this <u>increases the number of</u> <u>successful/effective collisions</u>.
  - OR rate of reaction <u>decreases</u> when concentration of methanol is <u>decreased</u> due to <u>decrease in frequency of collisions</u> between methanol molecules which are now <u>further apart</u>, and this <u>reduces</u> the <u>number of successful</u> <u>collisions</u>.

[1]

(e) Methanol is also a reagent to synthesise vanillin. Vanillin is an important raw material for the production of L-DOPA used in the treatment of Parkinson's disease.



A student carried out some reactions with samples of L-DOPA and vanillin using reagents **X**, **Y** and **Z**.

- Reagent X reacted with L-DOPA and with vanillin.
- Reagent **Y** reacted with L-DOPA but **not** with vanillin.
- Reagent Z reacted with vanillin but not with L-DOPA.

Assume that the CH<sub>3</sub>O– group in vanillin is inert and does not react.

Suggest possible identities of reagents **X**, **Y** and **Z** and give the structures of the organic products formed in each case. [7]

•Reagent X: for <u>phenol</u> - any one of aq. Br<sub>2</sub>; NaOH, Na, RCOC*l*; OR

LiA/H<sub>4</sub> for reduction of carboxylic acid & aldehyde

- Reagent Y: for <u>carboxylic acid</u> any one of Na<sub>2</sub>CO<sub>3</sub>; NaHCO<sub>3</sub>, SOCl<sub>2</sub>, PCl<sub>5</sub>, ROH + H<sub>2</sub>SO<sub>4</sub>; OR for <u>amines</u> - any one of HCl, CH<sub>3</sub>Cl
- Reagent Z: for <u>aldehyde</u> any one of Tollens' reagent, 2,4-dinitrophenylhydrazine; acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, HCN + trace NaCN/NaOH, NaBH<sub>4</sub>

[Total: 19]

3 (a) The hydroformylation reaction is an industrial process for the production of aldehydes from alkenes. For example, butanal can be synthesised from propene,  $C_3H_6$ , as follows:



(i) Write an expression for  $K_{\rm p}$  of the reaction, including units. [2]

 $\mathcal{K}_{p} = \frac{p_{CH_{3}CH_{2}CH_{2}CH0}}{(p_{CH_{3}CH=CH_{2}})(p_{CO})(p_{H_{2}})} \operatorname{atm^{-2} or Pa^{-2}}$ 

(ii) Given that the magnitude of  $K_p$  for the above reaction is 775, deduce what the  $K_p$  value indicates about the position of equilibrium. Hence, state the sign of  $\Delta G^{\bullet}$  for the reaction. [2]

As  $\underline{K_p}$  is large, and thus position of equilibrium lies very much to the right.  $\Delta G^{e}$  is negative.

(iii) Given that the above reaction is exothermic, suggest, with a reason, the effect of an increased temperature on the amount of butanal formed at equilibrium. [1]

When the temperature is increased, the <u>position of equilibrium shifts to the left</u> as the <u>reverse reaction</u> is <u>endothermic</u> and absorbs heat. Thus, the amount of butanal at equilibrium <u>decreases</u>.

(iv) The mechanism of hydroformylation of propene resembles the electrophilic addition of alkenes and can result in the formation of two isomeric products. Apart from butanal, suggest the structure of the other isomer that can be formed. [1]



(b) In the Leuckart-Wallach reaction, a carbonyl compound reacts with a primary amine to form a secondary amine.



(i) Stage 1 occurs in 2 steps. The first step involves a nucleophilic attack while in the second step, a proton transfer occurs within the intermediate to form the alcohol group.

Name and outline the 2-step mechanism for Stage 1, to form Compound **A**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [3]

Nucleophilic Addition



- (ii) Compound B undergoes reduction in Stage 3. Describe the change in oxidation state of carbon which occurs in this stage.
   [1] There is a decrease in oxidation number of the C (of the C=N) from +1 to -1
- (iii) Unlike primary amines, amides cannot be used in the Leuckart-Wallach reaction. Explain why this is so. [1]

In amides, the lone pair of electrons on the nitrogen atom can delocalise into the  $\pi$  electron cloud of the adjacent C=O bond/electron-withdrawing C=O group. Hence, the lone pair of electrons is not available for donation/less available to accept a proton and unable to act as a nucleophile in Stage 1.

(iv) 2-bromopyrrolidine, a cyclic amine, can be synthesised via the Leuckart-Wallach reaction.

2-bromopyrrolidine

Draw the displayed formula of the starting compound used in the synthesis of 2-bromopyrrolidine. [1]



(v) State and explain the relative basicities of 2-bromopyrrolidine and compound **C**. [2]

2-bromopyrrolidine is a <u>weaker base</u> than compound C. 2-bromopyrrolidine has an <u>electron-withdrawing Br atom</u>, and thus the <u>lone pair of electrons on</u> <u>nitrogen is less available for donation to a proton</u>.

(c) Carbon also forms compounds with other Group 16 elements like sulfur and selenium. The properties of some of these compounds are given in the table below.

Compound	Structure	Dipole moment	Boiling point / °C
CS <sub>2</sub>	S=C=S	0	46
COS	S=C=O	0.71	-50
COSe	Se=C=O	x	-22

- (i) Explain, in terms of structure and bonding, the difference in the boiling point of CS<sub>2</sub> and COS.
   Both CS<sub>2</sub> and COS have simple molecular structures. CS<sub>2</sub> has a larger number of electrons (or larger electron cloud) than COS. More energy is required to overcome the stronger instantaneous dipole-induced dipole attractions between CS<sub>2</sub> molecules than the permanent dipole-permanent dipole attractions between COS molecules. Hence, CS<sub>2</sub> has a higher boiling point.
- (ii) Predict a value for the dipole moment of COSe, *x*, and explain. [1]

0.73 (> 0.71)

<u>C=S bond is more polar than C=Se</u> (since S is more electronegative than Se). There is smaller difference in the dipole moment of C=O and C=S as compared to that between C=O and C=Se.

(iii) Aside from the common oxides, carbon forms a series of straight-chained reactive oxocarbons. One such compound is tricarbon monoxide, C<sub>3</sub>O, a reactive molecule found in space. Suggest a displayed structure of tricarbon monoxide. Indicate clearly any lone pairs of electrons present in your structure.

[1]

(iv) Tricarbon monoxide is isoelectronic to cyanogen, (CN)<sub>2</sub>. The molecule of cyanogen contains a C–C single bond.
 Draw the dot-and-cross diagram of cyanogen. In your diagram, you should distinguish the electrons originating from each of the two carbon atoms and those from the two nitrogen atoms.

[Total: 19]

### Section B

Answer **one** question from this section.

**4** (a) Benzene is a widely used starting organic compound to synthesize other chemicals, such as benzenesulfonic acid and 2-methylphenol.

Benzenesulfonic acid can be produced by heating benzene under reflux with concentrated sulfuric acid for several hours. This process is similar to the nitration of benzene.



benzenesulfonic acid

The first step of the mechanism involves the protonation of one molecule of sulfuric acid by another and the loss of a molecule of water.

(i) Describe the mechanism for the above reaction. Show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons. [4]
 Electrophilic substitution

 $H_2SO_4 + H_2SO_4 \rightarrow HSO_3^+ + H_2O + HSO_4^-$ 



(ii) Similarly, methylbenzene also reacts with concentrated sulfuric acid to form a mixture of the three isomers, in equilibrium.



Suggest why there is a lower concentration of 1,2-isomer than that of 1,4isomer in the equilibrium mixture. [1]

This may be due to <u>steric hindrance of  $-CH_3$  group</u>, as the  $-CH_3$  group may have electrostatic repulsion with the large incoming SO<sub>3</sub>H<sup>+</sup> group.

(iii) The chlorinated compound MCPA, widely used as a weed killer, can be synthesized from 2-methylphenol.



Using **not** more than 3 steps, draw a reaction scheme to show how MCPA can be synthesised from 2–methylphenol. [5]



(b) The chemical reactions of benzene sometimes require iron as a catalyst. Iron is a hard grey transition metal which is resistant to corrosion at ordinary temperatures. In contrast, calcium is a fairly soft, silvery-grey Group 2 metal which quickly tarnishes in air.

(i) By considering relevant electronic configurations, explain why the atomic radius of iron is smaller than that of calcium, even though iron has more electrons. [2]

Ca: [Ar] 4s<sup>2</sup> Fe: [Ar] 3d<sup>6</sup>4s<sup>2</sup> The atomic radius of iron is smaller (0.126nm) than that of Ca (0.197 nm). Iron has a <u>higher nuclear charge</u> (due to greater no. of protons) and <u>relatively</u> <u>poor shielding effect by the 3d electrons</u>, the outermost 4s electrons are <u>more</u> <u>strongly attracted by the nucleus</u>.

(ii) Iron can exist in different oxidation states whereas calcium does not. Explain why. [2]

The <u>3d and 4s electrons are of similar energy</u> so <u>different number of 3d and 4s</u> <u>electrons can be removed</u> to form ions of similar stability, giving rise to variable oxidation states.

However, for s-block elements, <u>only the valence s electrons can be removed. A</u> <u>lot of energy is required to remove the inner shell p electrons</u> as they are more closely bound by the nucleus. Thus, s-block elements have fixed oxidation states.

(iii) Explain why iron(II) complexes are green in colour.

[3]

In the <u>presence of ligands</u>, the <u>partially-filled degenerate d orbitals in Fe<sup>2+</sup></u> <u>become non-degenerate</u> and split into <u>two groups of non-degenerate d</u> <u>orbitals with a small energy gap.</u> When exposed to visible light, d electron in a d orbital of lower energy absorbs

energy in the <u>red region</u> and is <u>promoted</u> to a higher energy d\* orbital. This is called <u>*d*-*d*\* electronic transition</u>, where d\* is the higher energy orbital. The <u>complementary colour</u> of red, i.e. green, is <u>not absorbed</u> and thus green is seen as the colour of the complex.

(iv) Iron(III) ions catalyse the reaction between I<sup>-</sup> ions and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions through homogeneous catalysis.
 Explain why iron(III) ions can be described as a homogeneous catalyst. By considering relevant E<sup>e</sup> values from the *Data Booklet*, show by means of balanced equations, how the iron(III) ions carry out its role in this reaction. [3] Fe<sup>3+</sup> operates in the same phase as the reactants (iodide and peroxodisulfate) and is regenerated.

 $\begin{array}{rll} 2Fe^{3+}(aq) &+& 2I^{-}(aq) &\longrightarrow & 2Fe^{2+}(aq) &+& I_{2}(aq) \\ E^{e} &=& +0.77 - (+0.54) = +0.23V \\ 2Fe^{2+}(aq) &+& S_{2}O_{8}^{2-}(aq) &\longrightarrow & 2Fe^{3+}(aq) &+& 2SO_{4}^{2-}(aq) \\ E^{e} &=& +2.01 - (+0.77) = +1.24V \end{array}$ 

[Total: 20]
- **5** (a) Aluminium oxide, Al<sub>2</sub>O<sub>3</sub>, and aluminium chloride, AlCl<sub>3</sub>, are widely used in various industrial and commercial applications.
  - (i) Aluminium oxide has a melting point of 2072 °C while aluminium chloride sublimes at 180 °C. Explain the difference in melting points in terms of structure and bonding in each compound.

Aluminium oxide has a <u>giant ionic structure</u> while aluminium chloride has a <u>simple</u> <u>molecular structure</u>. A larger amount of energy is needed to overcome the <u>stronger ionic bonds</u> (electrostatic force of attraction) between  $Al^{3+}$  ions and  $O^{2-}$  ions than the <u>weaker</u> instantaneous dipole-induced dipole attractions between aluminium chloride <u>molecules</u>.

 (ii) Describe the reactions, if any, of aluminium oxide and aluminium chloride with water, suggesting the pH of the resulting solutions and writing equations, where appropriate.

For Al<sub>2</sub>O<sub>3</sub>: Does not dissolve in water, pH of resultant solution= 7

 $\begin{array}{l} \underline{\text{For } AlCl_3:} \\ AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^{-}(aq) \\ [Al(H_2O)_6]^{3+}(aq) + H_2O(l) & \qquad [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^{+}(aq) \end{array}$ 

The  $Al^{3+}$  ion has a <u>high charge density</u> (higher charge and smaller radius compared to Na<sup>+</sup>) The small, <u>highly polarizing  $Al^{3+}$  cation then weakens the O-H bonds of the water molecules</u> in its sphere of coordination and results in the <u>release of H<sup>+</sup> ions</u> in the solution. **pH of solution of AlCl<sub>3</sub> ≈ 3** 

(b) The reaction between chlorine gas and hot sodium hydroxide is as follows.

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

(i) State the type of reaction occuring.

[1]

[2]

Disproportionation

(ii) State the change in oxidation numbers of chlorine that occur during this reaction.

The oxidation number of Cl is decreased from <u>0</u> in Cl<sub>2</sub> to <u>-1</u> in Cl<sup>-</sup> (reduction) and increased from <u>0</u> in Cl<sub>2</sub> to <u>+5</u> in ClO<sub>3</sub><sup>-</sup> (oxidation).

(c) Ethers are a class of organic compounds that has two organic groups bonded to the same oxygen atom, R-O-R'. The organic groups could be alkyl and aryl groups. Williamson synthesis could be used to synthesis ethers by a reaction between primary alkyl halides and metal alkoxides.

A typical example of the Williamson synthesis is a two-step reaction to synthesize *tert*-butyl methyl ether.

The first step of the reaction involved the preparation of sodium alkoxide in the presence of sodium hydride, NaH.



The second step of the reaction involved the reaction between the alkoxide ion and the primary alkyl halide.



- (i) Suggest the role of sodium hydride in step 1. [1] Base
- (ii) Suggest the type of reaction which occurs in step 2. [1] <u>S<sub>N</sub>2 nucleophilic substitution</u>
- (iii) Suggest why primary alkyl halide is used in Williamson synthesis instead of secondary or tertiary alkyl halide.
   [1] The alkoxide, which acts as a nucleophile has 3 bulky substituents. Only a primary alkyl halide that has smaller hydrogen atoms compared to bulky alkyl groups in secondary or tertiary alkyl halide will cause less steric hindrance and allow the bulky nucleophile to attack the carbon centre easily from the rear.
- (iv) The following scheme shows a three-step synthesis of compound L from 1-chloropropane. Given that step 3 involves Williamson synthesis, suggest the reagents and conditions you would use for each step and identify the intermediates J and K.



- (d) (i) Using monohalogenethanes, C<sub>2</sub>H<sub>5</sub>X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds with respect to hydrolysis. [1] Bromoethane is more reactive towards hydrolysis (nucleophilic substitution) as <u>C-Br bond is weaker</u> and thus requires less energy to break the bond.
  - (ii) There are other methods to synthesise ethers. A cyclic ether N could be formed as shown below. Predict the outcomes of the following transformations, drawing the structures of the intermediate M and the product N.



[2]





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Paper 4 Practical

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2 hours 30 minutes

Candidates answer on the Question Paper.

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Write your name and class in the boxes above.

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Write in dark blue or black pen.

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

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

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

The use of an approved scientific calculator is expected, where appropriate. 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 14 and 15.

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



For Examiner's Use		
1	16	
2	14	
3	13	
4	12	
Total	55	

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

[Turn over

#### 1 Determination of the percentage by mass of iron(II) sulfate in an iron tablet

Iron tablets, taken for the prevention and treatment of iron deficiency, are health supplements readily available in pharmacies. These iron tablets contain iron(II) sulfate, which is a soluble form of iron. Assuming that all the iron in the tablets is in the form of Fe<sup>2+</sup>, it is possible to estimate the iron content by titration against potassium manganate(VII).

The equation for this reaction is

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

You are provided with the following.

FA 1 contains 5 iron tablets, crushed to a powder. FA 2 is 0.00500 mol dm<sup>-3</sup> potassium manganate(VII), KMnO<sub>4</sub>. 1.0 mol dm<sup>-3</sup> sulfuric acid, H<sub>2</sub>SO<sub>4</sub>. deionised water

In this experiment, you will determine the percentage of iron(II) sulfate heptahydrate, FeSO<sub>4</sub>.7H<sub>2</sub>O, present in the iron tablets **FA 1**.

#### (a) Preparation of FA 3, a solution of $FeSO_4.7H_2O$ .

- Use a measuring cylinder to transfer about 100 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> sulfuric acid into a conical flask.
- Determine accurately the mass of the crushed iron tablets used, **FA1**, and record your readings in the space below.

mass of the crushed iron tablets used = ...... g

- Add all the crushed tablets, **FA 1**, to the sulfuric acid.
- Warm the mixture gently, do not overheat, and stir for about two minutes.
- Allow the flask to cool for around five minutes.
- Filter the mixture into a 250 cm<sup>3</sup> volumetric flask. Ensure that no solution is lost. <u>Note</u>: The filtration takes time. **Proceed to Question 2 whilst the mixture is filtering.**
- Wash out the conical flask with deionised water and add the washings through the filter into the volumetric flask.
- Make up the contents of the flask to the 250 cm<sup>3</sup> mark with deionised water. Stopper and mix the contents thoroughly to obtain a homogeneous solution.
- Label this solution **FA 3**.

#### (b) Titration of FA 3 with FA 2

- Fill the burette with **FA 2**.
- Pipette 25.0 cm<sup>3</sup> of **FA 3** into a conical flask.
- Use a measuring cylinder to add about 25.0 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> sulfuric acid to the conical flask.
- Titrate with FA 2 until the appearance of a first permanent pale-pink colour.
- Record your titration results in the space below. Make certain that the recorded results show the precision of your practical work.
- Repeat the titration as many times as necessary to obtain reliable results.

#### **Titration Results**

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

volume of **FA 2** = ......[1]

(c) (i) Calculate the amount of  $MnO_4^-$  ions contained in the mean titre.

amount of  $MnO_4^-$  ions =..... [1]

(iii) Calculate the amount of  $Fe^{2+}$  ions in the five crushed tablets, **FA 1**.

(iv) Calculate the mass of FeSO<sub>4</sub>.7H<sub>2</sub>O in **one** tablet. [*A*<sub>r</sub>: Fe, 55.8; S, 32.1; O, 16.0; H, 1.0]

(v) Hence calculate the percentage by mass of  $FeSO_4.7H_2O$  in **one** tablet.

percentage by mass of FeSO<sub>4</sub>.7H<sub>2</sub>O in one tablet =.....[2]

(d) Explain why in the procedure described in (a), the volume of sulfuric acid was measured using a measuring cylinder rather than a burette.

......[1]

(e) To confirm the formula of iron(II) sulfate heptahydrate in the tablet, a student dissolved one of the tablets in nitric acid and added a few drops of barium nitrate to the filtrate.
 State the observation expected from this chemical test. Give your reasoning.

.....[1]

[Total: 16]

#### 2 Determination of the enthalpy change for the reaction of citric acid with NaHCO<sub>3</sub>(aq)

Antacid, taken for quick relieve of occasional heartburn, is also readily available in pharmacies. Antacid contains mainly citric acid and sodium hydrogencarbonate, which react when in contact with water to give carbon dioxide.

In this experiment, you will determine the enthalpy change when citric acid reacts with sodium hydrogencarbonate.

You are provided with the following.

**FA 4** is  $0.8 \text{ mol } \text{dm}^{-3}$  citric acid.

FA 5 is solid sodium hydrogencarbonate, NaHCO<sub>3</sub>.

#### (a) Method

You will carry out the following experiment twice.

- Weigh between 6.5 g and 7.0 g of **FA 5** in a dry weighing bottle.
- Use a pipette to transfer 50.0 cm<sup>3</sup> of FA 4 into the plastic cup supported in a 250 cm<sup>3</sup> beaker.
- Place the thermometer in the acid in the plastic cup and record its initial temperature.
- Carefully add the weighed sample of **FA 5**, in *small portions*, into the acid in the plastic cup. Stir the mixture carefully with the thermometer.
- Record the lowest temperature reached.
- Reweigh the weighing bottle and any residual **FA 5**.

Record in a single table, in the space given on page 7,

- all measurements of mass and temperature, and
- the temperature fall,  $\Delta T$ .

Empty and rinse the plastic cup.

Repeat the experiment and calculate the mean value of

- $\Delta T$ , and
- mass of **FA 5** added.

Results

mean value of  $\Delta T$  =..... mean mass of FA 5 added =.....[4]

- (b) Citric acid is a tribasic acid; i.e. one mole of the acid reacts with three moles of sodium hydrogencarbonate.
  - (i) Write a balanced equation, with state symbols, to show how citric acid reacts with sodium hydrogencarbonate in the experiment. You may use H<sub>3</sub>A to represent citric acid.

......[1]

(ii) Calculate the heat energy when **FA 5** was added to the acid.

[Assume that 4.3 J are required to raise the temperature of 1.0 cm<sup>3</sup> of any solution by 1.0  $^{\circ}$ C.]

heat energy =..... J [1]

(iii) In the experiment carried out in **2(a)**, excess citric acid was used. Using your answer to **2(b)(i)**, calculate the amount of citric acid that has reacted with the mean mass of **FA 5** added. [*A*<sub>r</sub>: Na, 23.0; O, 16.0; C, 12.0; H, 1.0]

amount of citric acid = ..... mol [2]

(iv) Calculate the enthalpy change, in kJ mol<sup>-1</sup>, when 1 mol of citric acid reacts with sodium hydrogencarbonate. Your answer should include the appropriate sign.

enthalpy change,  $\Delta H = \dots kJ \text{ mol}^{-1}$  [2]

(v) Explain the significance of the sign you have given in 2(b)(iv) and how it is related to your experimental results.
 [1]
 (c) Explain why FA 5 is added in *small portions* in the procedure described in 2(a).

(d) A student repeated the experiment described in 2(a) on another day when the room temperature was much higher. Suggest how this higher room temperature would affect the value of  $\Delta T$ . Give your reasoning.

#### 3 Planning

The reaction between an acid and a metal hydroxide is exothermic. By using this fact, it is possible to determine the equivalence point of a neutralisation reaction without the use of an indicator. This process is known as *thermometric titration*.

In the experiment, the temperature is monitored as portions of acid are progressively added to a fixed volume of the alkali until the equivalence point is reached and passed. The data obtained is plotted and two best-fit graph lines are drawn. One line is drawn using data before the equivalence point and the second line using the remaining data. These lines are then extrapolated until they intersect.

(a) In a thermometric titration where an acid is run into an alkali, state and explain how you would recognise that the equivalence point has been passed.

 (b) In this question, you are required to write a plan for a thermometric titration in which citric acid is added to 25.0 cm<sup>3</sup> of aqueous sodium hydroxide.

You are provided with the following materials.

- 2.00 mol dm<sup>-3</sup> sodium hydroxide, NaOH
- 0.8 mol dm<sup>-3</sup> citric acid
- equipment normally found in a school laboratory
- Using the information given above, show that the volume of citric acid required to reach the equivalence point is 20.90 cm<sup>3</sup>.
   You may use H<sub>3</sub>A to represent citric acid, which is a tribasic acid.

[1]

(ii) Outline how you would carry out the proposed thermometric titration using only the materials provided.

In your plan, you should include

- brief, but specific, details of the apparatus you would use, considering the levels of precision they offer;
- measurements you would make to allow for a suitable graph to be drawn in **3(b)(iii)**, in order to determine the value of  $\Delta H_n^{\bullet}$  for this reaction; and
- how you would recognise that the equivalence point had been passed.

Outline your plan as a series of numbered steps.

- (iii) Sketch, on the axes provided, the graph you would expect to obtain using information in 3(b)(i) and the measurements you planned to make in 3(b)(ii). Label clearly the axes. You should also indicate on your graph,
  - the equivalence point, and
  - the maximum temperature rise,  $\Delta T_1$ .



[3]

(iv) Write an ionic equation to represent the enthalpy change of neutralisation,  $\Delta H_n$ .

......[1]

(v) Given that  $\Delta T_1$  is 11.0 °C and using the information in **3(b)(i)**, determine the value of  $\Delta H_n^{-\Phi}$  for this reaction.

 $\Delta H_{n^{-\Phi}} = \dots kJ mol^{-1}$  [2]

[Total: 13]

#### 4 Inorganic Analysis

You are provided with three solutions, **FA 6**, **FA 7** and **FA 8**, each containing one cation and one anion.

#### Identification of the anions in FA 6, FA 7 and FA 8.

One or more of the solutions contains a halide ion.

- (a) From the Qualitative Analysis Notes on page 15, you are to select and use
  - (i) one reagent to precipitate any halide ion that is present,
  - (ii) a second reagent to confirm the identity of any halide ion present.

# Since the solutions are coloured, you will need to remove traces of solution from the precipitate.

Record the tests performed, the practical procedures used and the observations made for each of the solutions.

Present this information as clearly as possible in a single table in the space below.

(b) Use your observations to identify any halide ions present in the solutions, FA 6, FA 7 and FA 8, and state which ion is present in which solution.

[1]

#### Identification of the cations in FA 6, FA 7 and FA 8.

(c) Using aqueous NaOH and aqueous NH<sub>3</sub>, it is possible to identify two of the cations present and to draw conclusions about the nature of the remaining cation.

Carry out tests with these reagents and record the observations made for each of the solutions.

Test	FA 6	FA 7	FA 8
<ol> <li>Add aqueous NaOH dropwise until no further change is seen.</li> </ol>			
<ol> <li>Add aqueous NH₃ dropwise until no further change is seen.</li> </ol>			

- [4]
- (d) Use your observations in 4(c) to identify two of the cations present and state which of the solutions contain those cations.

The cation contained in **FA** ..... is .....

Evidence:

.....

The cation contained in FA ..... is .....

Evidence:

-----

[2]

(e) From your observations in **4(c)**, what conclusion can you draw about the general nature of the third cation? Explain your answer.

......[1] [Total: 12]

# **Qualitative Analysis Notes**

[ppt. = precipitate]

# (a) Reactions of aqueous cations

action	reaction with		
cation	NaOH(aq)	NH₃(aq)	
aluminium, A <i>l</i> <sup>3+</sup> (aq)	white ppt. soluble in excess	white ppt. insoluble in excess	
ammonium, NH₄⁺(aq)	ammonia produced on heating	_	
barium, Ba <sup>2+</sup> (aq)	no ppt. (if reagents are pure)	no ppt.	
calcium, Ca <sup>2+</sup> (aq)	white ppt. with high [Ca <sup>2+</sup> (aq)]	no ppt.	
chromium(III), Cr <sup>3+</sup> (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess	
copper(II), Cu²+(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution	
iron(II), Fe <sup>2+</sup> (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 <sup>3+</sup> (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess	
magnesium, Mg <sup>2+</sup> (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess	
manganese(II), Mn <sup>2+</sup> (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 <sup>2+</sup> (aq)	white ppt. soluble in excess	white ppt. soluble in excess	

# (b) Reactions of anions

anion	reaction
carbonate, CO <sub>3</sub> <sup>2-</sup>	CO <sub>2</sub> liberated by dilute acids
chloride, C <i>l⁻</i> (aq)	gives white ppt. with Ag⁺(aq) (soluble in NH₃(aq))
bromide, Br⁻(aq)	gives pale cream ppt. with Ag <sup>+</sup> (aq) (partially soluble in NH <sub>3</sub> (aq))
iodide, I⁻(aq)	gives yellow ppt. with Ag <sup>+</sup> (aq) (insoluble in $NH_3(aq)$ )
nitrate, NO₃⁻(aq)	NH <sub>3</sub> liberated on heating with OH <sup>-</sup> (aq) and A <i>l</i> foil
nitrite, NO₂⁻(aq)	NH <sub>3</sub> liberated on heating with OH <sup>-</sup> (aq) and A <i>l</i> foil; NO liberated by dilute acids (colourless NO $\rightarrow$ (pale) brown NO <sub>2</sub> in air)
sulfate, SO₄²⁻(aq)	gives white ppt. with Ba <sup>2+</sup> (aq) (insoluble in excess dilute strong acids)
sulfite, SO <sub>3</sub> ²⁻(aq)	SO <sub>2</sub> liberated with dilute acids; gives white ppt. with Ba <sup>2+</sup> (aq) (soluble in dilute strong acids)

### (c) Tests for gases

gas	test and test result
ammonia, NH₃	turns damp red litmus paper blue
carbon dioxide, CO <sub>2</sub>	gives a white ppt. with limewater (ppt. dissolves with excess CO <sub>2</sub> )
chlorine, Cl <sub>2</sub>	bleaches damp litmus paper
hydrogen, H <sub>2</sub>	"pops" with a lighted splint
oxygen, O <sub>2</sub>	relights a glowing splint
sulfur dioxide, SO <sub>2</sub>	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 <sub>2</sub>	greenish yellow gas	pale yellow	pale yellow
bromine, Br <sub>2</sub>	reddish brown gas / liquid	orange	orange-red
iodine, I2	black solid / purple gas	brown	purple

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CANDIDATE NAME	
CLASS	2T

# CHEMISTRY

Paper 4 Practical

9729/04 19 August 2019

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidential Instructions

#### READ THESE INSTRUCTIONS FIRST

Write your name and class in the boxes above.

Give details of 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, 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 14 and 15.

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1	16	
2	14	
3	13	
4	12	
Total	55	

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

[Turn over

#### 1 Determination of the percentage by mass of iron(II) sulfate in an iron tablet

Iron tablets, taken for the prevention and treatment of iron deficiency, are health supplements readily available in pharmacies. These iron tablets contain iron(II) sulfate, which is a soluble form of iron. Assuming that all the iron in the tablets is in the form of Fe<sup>2+</sup>, it is possible to estimate the iron content by titration against potassium manganate(VII).

The equation for this reaction is

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

You are provided with the following.

FA 1 contains 5 iron tablets, crushed to a powder. FA 2 is 0.00500 mol dm<sup>-3</sup> potassium manganate(VII), KMnO<sub>4</sub>. 1.0 mol dm<sup>-3</sup> sulfuric acid, H<sub>2</sub>SO<sub>4</sub>. deionised water

In this experiment, you will determine the percentage of iron(II) sulfate heptahydrate,  $FeSO_{4.7}H_2O$ , present in the iron tablets **FA 1**.

#### (a) Preparation of FA 3, a solution of $FeSO_4.7H_2O$ .

- Use a measuring cylinder to transfer about 100 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> sulfuric acid into a conical flask.
- Determine accurately the mass of the crushed iron tablets used, **FA1**, and record your readings in the space below.

mass of container + FA1 / g	m <sub>2</sub>
mass of container + residual FA1 / g	m <sub>1</sub>
mass of <b>FA1</b> used / g	<b>m</b> <sub>2</sub> – <b>m</b> <sub>1</sub>

mass of the crushed iron tablets used = ...... g

- Add all the crushed tablets, **FA 1**, to the sulfuric acid.
- Warm the mixture gently, do not overheat, and stir for about two minutes.
- Allow the flask to cool for around five minutes.
- Filter the mixture into a 250 cm<sup>3</sup> volumetric flask. Ensure that no solution is lost. <u>Note</u>: The filtration takes time. Proceed to Question 2 whilst the mixture is filtering.
- Wash out the conical flask with deionised water and add the washings through the filter into the volumetric flask.
- Make up the contents of the flask to the 250 cm<sup>3</sup> mark with deionised water. Stopper and mix the contents thoroughly to obtain a homogeneous solution.
- Label this solution **FA 3**.

#### (b) Titration of FA 3 with FA 2

- Fill the burette with FA 2.
- Pipette 25.0 cm<sup>3</sup> of **FA 3** into a conical flask.
- Use a measuring cylinder to add about 25.0 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> sulfuric acid to the conical flask.
- Titrate with FA 2 until the appearance of a first permanent pale-pink colour.
- Record your titration results in the space below. Make certain that the recorded results show the precision of your practical work.
- Repeat the titration as many times as necessary to obtain reliable results.

#### **Titration Results**

	1	2
final burette reading / cm <sup>3</sup>		
initial burette reading / cm <sup>3</sup>		
volume of FA 2 used / cm <sup>3</sup>	<b>V</b> 1	<b>V</b> <sub>2</sub>
	<ul> <li>✓</li> </ul>	<ul> <li>✓</li> </ul>

[6]

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

average titre = 
$$\frac{v_1 + v_2}{2}$$
  
= ...... cm<sup>3</sup>

(c) (i) Calculate the amount of  $MnO_4^-$  ions contained in the mean titre.

mol of MnO<sub>4</sub><sup>-</sup> = 
$$cV = 0.00500 \times \frac{\text{average titre}}{1000}$$
  
= ..... mol

amount of  $MnO_4^-$  ions =..... [1]

(ii) Calculate the amount of  $Fe^{2+}$  ions that reacted with the  $MnO_4^-$  ions calculated in (c)(i).

```
mol of Fe<sup>2+</sup> reacted = 5 × mol of MnO<sub>4</sub><sup>-</sup>
= 5 × ans to (b)(i)
= ..... mol
```

amount of  $Fe^{2+}$  ions =.....[1]

(iii) Calculate the amount of  $Fe^{2+}$  ions in the five crushed tablets, **FA 1**.

```
mol of Fe<sup>2+</sup> in 5 crushed tablets = mol of Fe<sup>2+</sup> in 250 cm<sup>3</sup> solution
= \frac{250}{25.0} × ans to (b)(ii)
= ..... mol
```

(iv) Calculate the mass of FeSO<sub>4</sub>.7H<sub>2</sub>O in one tablet.
 [A<sub>r</sub>: Fe, 55.8; S, 32.1; O, 16.0; H, 1.0]

 $M_r$  of FeSO<sub>4</sub>.7H<sub>2</sub>O = 55.8 + 32.1 + 4(16.0) + 7[2(1.0) + 16.0] = 277.9 mass of FeSO<sub>4</sub>.7H<sub>2</sub>O in 5 tablets =  $nM_r$  = ans to (b)(iii) x 277.9 = ..... g ∴ mass of FeSO<sub>4</sub>.7H<sub>2</sub>O in 1 tablet =  $\frac{1}{5}$  x above ans = ..... g

- 5
- (v) Hence calculate the percentage by mass of FeSO<sub>4</sub>.7H<sub>2</sub>O in **one** tablet.

```
% by mass of FeSO<sub>4</sub>.7H<sub>2</sub>O in 1 tablet = \frac{5 \times \text{ans to (b)(iv)}}{\text{mass of FA1}} \times 100
= ......%
```

percentage by mass of FeSO<sub>4</sub>.7H<sub>2</sub>O in one tablet =.....[2]

- (d) Explain why in the procedure described in (a), the volume of sulfuric acid was measured using a measuring cylinder rather than a burette.
  - sulfuric acid is in <u>excess</u> and so, its volume need not be measured precisely.
    [1]
- (e) To confirm the formula of iron(II) sulfate heptahydrate in the tablet, a student dissolved one of the tablets in nitric acid and added a few drops of barium nitrate to the filtrate.
   State the observation expected from this chemical test. Give your reasoning.

white ppt of BaSO₄ formed confirmed the presence of SO₄<sup>2−</sup> ion.
 [1]
 [1]

#### 2 Determination of the enthalpy change for the reaction of citric acid with NaHCO<sub>3</sub>(aq)

Antacid, taken for quick relieve of occasional heartburn, is also readily available in pharmacies. Antacid contains mainly citric acid and sodium hydrogencarbonate, which react when in contact with water to give carbon dioxide.

In this experiment, you will determine the enthalpy change when citric acid reacts with sodium hydrogencarbonate.

You are provided with the following.

**FA 4** is  $0.8 \text{ mol } \text{dm}^{-3}$  citric acid.

FA 5 is solid sodium hydrogencarbonate, NaHCO<sub>3</sub>.

#### (a) Method

You will carry out the following experiment twice.

- Weigh between 6.5 g and 7.0 g of **FA 5** in a dry weighing bottle.
- Use a pipette to transfer 50.0 cm<sup>3</sup> of FA 4 into the plastic cup supported in a 250 cm<sup>3</sup> beaker.
- Place the thermometer in the acid in the plastic cup and record its initial temperature.
- Carefully add the weighed sample of **FA 5**, in *small portions*, into the acid in the plastic cup. Stir the mixture carefully with the thermometer.
- Record the lowest temperature reached.
- Reweigh the weighing bottle and any residual **FA 5**.

Record in a single table, in the space given on page 7,

- all measurements of mass and temperature, and
- the temperature fall,  $\Delta T$ .

Empty and rinse the plastic cup.

Repeat the experiment and calculate the mean value of

- $\Delta T$ , and
- mass of **FA 5** added.

#### Results

	Expt 1	Expt 2
mass of weighing bottle + FA 5 / g	<b>m</b> 1	m <sub>3</sub>
mass of weighing bottle + residual FA 5 / g	m <sub>2</sub>	m4
mass of <b>FA 5</b> used / g	m <sub>1</sub> – m <sub>2</sub>	m <sub>3</sub> – m <sub>4</sub>
initial temperature / °C	<b>T</b> 1	T <sub>3</sub>
lowest temperature / °C	T <sub>2</sub>	T <sub>4</sub>
temperature fall, $\Delta T / °C$	$T_1 - T_2$	$T_3 - T_4$

- mean value of  $\Delta T = \frac{(T_1 T_2) + (T_3 T_4)}{2} = \dots ^{\circ}C$
- mean mass of FA 5 added =  $\frac{(m_1 m_2) + (m_3 m_4)}{2}$  = ...... g

mean value of  $\Delta T$  =..... mean mass of FA 5 added =.....[4]

- (b) Citric acid is a tribasic acid; i.e. one mole of the acid reacts with three moles of sodium hydrogencarbonate.
  - (i) Write a balanced equation, with state symbols, to show how citric acid reacts with sodium hydrogencarbonate in the experiment. You may use H<sub>3</sub>A to represent citric acid.

 $H_{3}A(aq) + 3NaHCO_{3}(s) \rightarrow Na_{3}A(aq) + 3H_{2}O(l) + 3CO_{2}(g)$ [1]

(ii) Calculate the heat energy when **FA 5** was added to the acid.

[Assume that 4.3 J are required to raise the temperature of 1.0 cm<sup>3</sup> of any solution by 1.0  $^{\circ}$ C.]

heat absorbed = mc  $\Delta T$ = 50 × 4.3 × mean  $\Delta T$ = ......J

heat energy =..... J [1]

(iii) In the experiment carried out in **2(a)**, excess citric acid was used. Using your answer to **2(b)(i)**, calculate the amount of citric acid that has reacted with the mean mass of **FA 5** added. [*A*<sub>r</sub>: Na, 23.0; O, 16.0; C, 12.0; H, 1.0]

```
M_{\rm r} \text{ of NaHCO}_3 = 23.0 + 1.0 + 12.0 + 3(16.0) = 84.0
mol of NaHCO<sub>3</sub> used = \frac{\text{mean mass of FA5}}{84.0}
= ..... mol
mol of citric acid reacted = \frac{1}{3} \times \text{mol of NaHCO}_3
= \frac{1}{3} \times \text{above answer}
= ..... mol
```

amount of citric acid = ..... mol [2]

(iv) Calculate the enthalpy change, in kJ mol<sup>-1</sup>, when 1 mol of citric acid reacts with sodium hydrogencarbonate. Your answer should include the appropriate sign.

 $\Delta H = + \frac{\text{ans to (b)(ii)}}{\text{ans to (b)(iii)}}$  $= + \dots \text{ kJ mol}^{-1}$ 

enthalpy change,  $\Delta H = \dots kJ \text{ mol}^{-1}$  [2]

- (v) Explain the significance of the sign you have given in **2(b)(iv)** and how it is related to your experimental results.
  - <u>+ sign because the reaction is endothermic (or heat is absorbed in the</u> reaction or <u>temperature falls</u> during the reaction)
    [1]
- (c) Explain why **FA 5** is added in *small portions* in the procedure described in **2(a)**.
  - to <u>prevent excessive effervescence / acid spray</u> which results in loss of solution.
    [1]

(d) A student repeated the experiment described in 2(a) on another day when the room temperature was much higher. Suggest how this higher room temperature would affect the value of  $\Delta T$ . Give your reasoning.

#### 3 Planning

The reaction between an acid and a metal hydroxide is exothermic. By using this fact, it is possible to determine the equivalence point of a neutralisation reaction without the use of an indicator. This process is known as *thermometric titration*.

In the experiment, the temperature is monitored as portions of acid are progressively added to a fixed volume of the alkali until the equivalence point is reached and passed. The data obtained is plotted and two best-fit graph lines are drawn. One line is drawn using data before the equivalence point and the second line using the remaining data. These lines are then extrapolated until they intersect.

- (a) In a thermometric titration where an acid is run into an alkali, state and explain how you would recognise that the equivalence point has been passed.
  - Since reaction is exothermic, temperature of the mixture <u>increases</u> until the equivalence point is reached.
  - Beyond the equivalence point; temperature of the mixture decreases
     as no further reaction takes place and the acid added is at a lower
     temperature than the mixture.

......[2]

(b) In this question, you are required to write a plan for a thermometric titration in which citric acid is added to 25.0 cm<sup>3</sup> of aqueous sodium hydroxide.

You are provided with the following materials.

- 2.00 mol dm<sup>-3</sup> sodium hydroxide, NaOH
- 0.8 mol dm<sup>-3</sup> citric acid
- equipment normally found in a school laboratory
- Using the information given above, show that the volume of citric acid required to reach the equivalence point is 20.90 cm<sup>3</sup>.
   You may use H<sub>3</sub>A to represent citric acid, which is a tribasic acid.

Since citric acid is tribasic,  $H_3A = 3NaOH$  [OR  $H_3A + 3NaOH \rightarrow Na_3A + 3H_2O$ ] mol of  $H_3A = \frac{1}{3} \times mol$  of NaOH

$$= \frac{1}{3} \times 2.00 \times \frac{25.0}{1000} = 0.0167 \text{ mol}$$

: approx. vol of H<sub>3</sub>A at equivalence point =  $\frac{0.0167}{0.8} \times 1000 = 20.90 \text{ cm}^3$ 

[1]

(ii) Outline how you would carry out the proposed thermometric titration using only the materials provided.

In your plan, you should include

- brief, but specific, details of the apparatus you would use, considering the levels of precision they offer;
- measurements you would make to allow for a suitable graph to be drawn in 3(b)(iii), in order to determine the value of ΔH<sub>n</sub><sup>-Φ</sup> for this reaction; and
- how you would recognise that the equivalence point had been passed.

Outline your plan as a series of numbered steps.

- 1. <u>Pipette 25.0 cm<sup>3</sup> of aq. NaOH into a plastic cup supported in a 250 cm<sup>3</sup></u> <u>beaker</u>. Record the initial temperature of aq. NaOH (using a thermometer calibrated to 0.2°C)
- 2. Fill a 50 cm<sup>3</sup> burette with the citric acid.
- 3. Add 5.00 cm<sup>3</sup> of citric acid from the burette to the plastic cup. Stir the mixture with the thermometer and record the highest temperature reached.
- 4. Add a further 5.00 cm<sup>3</sup> of citric acid to the plastic cup, and again record
  - the highest temperature reached.
- 5. Repeat step 4 until the <u>temperature recorded starts to decrease</u>, showing that equivalence point has been passed. Then add <u>three further</u> 5.00 cm<sup>3</sup>
  - portions of citric acid and record the steady temperature reached after each addition.

- (iii) Sketch, on the axes provided, the graph you would expect to obtain using information in 3(b)(i) and the measurements you planned to make in 3(b)(ii). Label clearly the axes. You should also indicate on your graph,
  - the equivalence point, and
  - the maximum temperature rise,  $\Delta T_1$ .



[3]

(iv) Write an ionic equation to represent the enthalpy change of neutralisation,  $\Delta H_n$ .

 $H^{+}(aq) + OH^{-}(aq) \rightarrow H_{2}O(I)$ [1]

(v) Given that  $\Delta T_1$  is 11.0 °C and using the information in **3(b)(i)**, determine the value of  $\Delta H_n^{-\Phi}$  for this reaction.

heat evolved = mc $\Delta T_1$  = (25.0 + 20.90) × 4.3 × 11.0 = 2171 J mol of H<sub>2</sub>O = mol of NaOH = 2.00 ×  $\frac{25.0}{1000}$  = 0.0500 mol  $\therefore \Delta H_n^{-6-} = -\frac{2171}{0.0500}$  = -4340 J mol<sup>-1</sup> = -43.4 kJ mol<sup>-1</sup>

 $\Delta H_{n^{-\Phi}} = \dots -43.4 \dots kJ mol^{-1}$  [2]

[Total: 13]

#### 4 Inorganic Analysis

You are provided with three solutions, **FA 6**, **FA 7** and **FA 8**, each containing one cation and one anion.

#### Identification of the anions in FA 6, FA 7 and FA 8.

One or more of the solutions contains a halide ion.

- (a) From the Qualitative Analysis Notes on page 15, you are to select and use
  - (i) one reagent to precipitate any halide ion that is present,
  - (ii) a second reagent to confirm the identity of any halide ion present.

# Since the solutions are coloured, you will need to remove traces of solution from the precipitate.

Record the tests performed, the practical procedures used and the observations made for each of the solutions.

Present this information as clearly as possible in a single table in the space below.

	Test	<b>FA 6</b>	FA 7	<b>FA 8</b>
1.	Add aq <u>AgNO<sub>3</sub></u> to each solution.	<u>white</u> ppt.	<u>yellow</u> ppt	no ppt
	Decant / filter to remove the coloured solution.			
2.	Add aq <u>NH<sub>3</sub> to the</u> <u>precipitate</u> obtained in the above test.	ppt <u>dissolves</u> to give a colourless solution	ppt <u>insoluble</u> in aq. NH₃	-

[4]

- (b) Use your observations to identify any halide ions present in the solutions, FA 6, FA 7 and FA 8, and state which ion is present in which solution.
  - $Cl^-$  present in FA 6, I<sup>-</sup> present in FA 7, and no halide ions present in FA 8

[1]

#### Identification of the cations in FA 6, FA 7 and FA 8.

(c) Using aqueous NaOH and aqueous NH<sub>3</sub>, it is possible to identify two of the cations present and to draw conclusions about the nature of the remaining cation.

Carry out tests with these reagents and record details of the observations made for each of the solutions.

Test	FA 6	FA 7	FA 8
<ol> <li>Add aqueous NaOH dropwise until no further change is seen.</li> </ol>	<u>red-brown</u> ppt. <u>insoluble</u> in excess NaOH	<u>grey-green</u> ppt <u>soluble</u> in excess NaOH giving a dark green solution	blue ppt turns brown with excess NaOH; insoluble in excess NaOH
<ol> <li>Add aqueous NH₃ dropwise until no further change is seen.</li> </ol>	<u>red-brown</u> ppt. <u>insoluble</u> in excess NH₃	<u>grey-green</u> ppt <u>insoluble</u> in excess NH <sub>3</sub>	<u>blue</u> ppt; <u>insoluble</u> in excess NH₃

[4]

(d) Use your observations in 4(c) to identify two of the cations present and state which of the solutions contain those cations.

The cation contained in **FA**...**6**..... is .....**Fe**<sup>3+</sup>.....

Evidence:

FA 6 gives red-brown ppt with NaOH and with NH<sub>3</sub>

The cation contained in **FA**...**7**..... is .....**C**r<sup>3+</sup>.....

Evidence:

FA 7 gives grey-green ppt with NaOH and with NH<sub>3</sub> OR grey-green ppt with NaOH, soluble in excess to give a green solution [2]

(e) From your observations in **4(c)**, what conclusion can you draw about the general nature of the third cation? Explain your answer.

•	FA 8 contains a transition metal cation deduced from the coloured
	solution and ppt.
	[1] [Total: 12]

# **Qualitative Analysis Notes**

[ppt. = precipitate]

# (a) Reactions of aqueous cations

action	reaction with			
cation	NaOH(aq)	NH₃(aq)		
aluminium, A <i>l</i> <sup>3+</sup> (aq)	white ppt. soluble in excess	white ppt. insoluble in excess		
ammonium, NH₄⁺(aq)	ammonia produced on heating	_		
barium, Ba <sup>2+</sup> (aq)	no ppt. (if reagents are pure)	no ppt.		
calcium, Ca <sup>2+</sup> (aq)	white ppt. with high [Ca <sup>2+</sup> (aq)]	no ppt.		
chromium(III), Cr <sup>3+</sup> (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess		
copper(II), Cu²+(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution		
iron(II), Fe <sup>2+</sup> (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 <sup>3+</sup> (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess		
magnesium, Mg <sup>2+</sup> (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess		
manganese(II), Mn <sup>2+</sup> (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 <sup>2+</sup> (aq)	white ppt. soluble in excess	white ppt. soluble in excess		

# (b) Reactions of anions

anion	reaction	
carbonate, CO <sub>3</sub> <sup>2-</sup>	CO <sub>2</sub> liberated by dilute acids	
chloride, C <i>l</i> <sup>-</sup> (aq)	gives white ppt. with Ag⁺(aq) (soluble in NH₃(aq))	
bromide, Br⁻(aq)	gives pale cream ppt. with Ag⁺(aq) (partially soluble in NH₃(aq))	
iodide, I⁻(aq)	gives yellow ppt. with Ag <sup>+</sup> (aq) (insoluble in $NH_3(aq)$ )	
nitrate, NO₃⁻(aq)	NH <sub>3</sub> liberated on heating with OH <sup>-</sup> (aq) and A <i>l</i> foil	
nitrite, NO₂⁻(aq)	NH <sub>3</sub> liberated on heating with OH <sup>-</sup> (aq) and A <i>l</i> foil; NO liberated by dilute acids (colourless NO $\rightarrow$ (pale) brown NO <sub>2</sub> in air)	
sulfate, SO <sub>4</sub> ²-(aq)	gives white ppt. with Ba <sup>2+</sup> (aq) (insoluble in excess dilute strong acids)	
sulfite, SO <sub>3</sub> ²⁻(aq)	SO <sub>2</sub> liberated with dilute acids; gives white ppt. with Ba <sup>2+</sup> (aq) (soluble in dilute strong acids)	

### (c) Tests for gases

gas	test and test result
ammonia, NH₃	turns damp red litmus paper blue
carbon dioxide, CO <sub>2</sub>	gives a white ppt. with limewater (ppt. dissolves with excess CO <sub>2</sub> )
chlorine, Cl <sub>2</sub>	bleaches damp litmus paper
hydrogen, H <sub>2</sub>	"pops" with a lighted splint
oxygen, O <sub>2</sub>	relights a glowing splint
sulfur dioxide, SO <sub>2</sub>	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 <sub>2</sub>	greenish yellow gas	pale yellow	pale yellow
bromine, Br <sub>2</sub>	reddish brown gas / liquid	orange	orange-red
iodine, I2	black solid / purple gas	brown	purple

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