NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY
Paper 1 Multiple Choice

9729/01
Thursday 14 Sept 2017
1 hour

Additional Materials: Multiple Choice Answer Sheet
                          Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, subject class and registration number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **30** 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.

This paper consists of **16** printed pages.

Instructions on how to fill in the Optical Mark Sheet

1. Enter your NAME (as in NRIC). TAN AH TECK
2. Enter the SUBJECT TITLE. CHEMISTRY
3. Enter the TEST NAME. SH2 Prelim
4. Enter the CLASS. cm2P

RUB OUT ERRORS THOROUGHLY
USE PENCIL ONLY FOR ALL ENTRIES ON THIS SHEET

Example:

Shade the index number in a 5 digit format on the optical mark sheet: 2nd digit and the last 4 digits of the Registration Number.

Student	Examples of Registration No.	Shade:
	1605648	65648

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 A mixture of two sulfur-containing gases, H_2S and CS_2, was burned in an excess of oxygen.

$$H_2S + \frac{3}{2}O_2 \rightarrow H_2O + SO_2$$

$$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$$
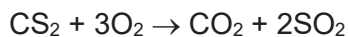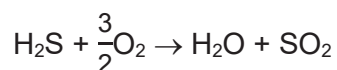
Upon complete combustion followed by cooling back to room temperature, the gaseous mixture was first passed through acidified $KMnO_4$. The volume contracted by 10.0 cm^3.

After which, the resulting gas was passed through aqueous sodium hydroxide, a further contraction of 2.0 cm^3 occurred. All volumes are measured under the same conditions.

What was the mole fraction of H_2S in the mixture?

A 0.333

B 0.500

C 0.750

D 0.833

2 Chromium has an oxidation state of +3 in its metal ore, chromite, $FeCr_2O_4$. Pure chromium is extracted from chromite in several steps show below.

$$FeCr_2O_4 \xrightarrow{\text{Step I}} Na_2CrO_4 \xrightarrow[H^+]{\text{Step II}} Na_2Cr_2O_7 \xrightarrow{\text{Step III}} Cr_2O_3 \xrightarrow{Al} Cr$$
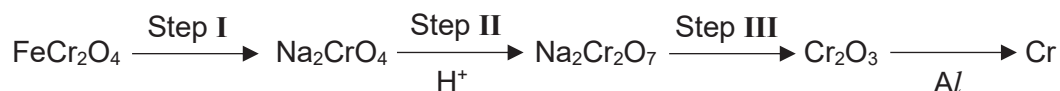
Which shows the correct type of reaction involving chromium in steps **I**, **II** and **III**?

	Step I	**Step II**	**Step III**
A	displacement	acid–base	displacement
B	oxidation	oxidation	reduction
C	displacement	oxidation	oxidation
D	oxidation	acid–base	reduction

3   *Use of the Data Booklet is relevant to this question.*

The amount of iron in a pill that contain iron(II) salts can be estimated by titration with $KMnO_4(aq)$.

When a pill is dissolved in 10 cm^3 of dilute sulfuric acid and titrated against 0.40 mol dm^{-3} $KMnO_4$, the E_{cell} was measured against a standard hydrogen electrode and plotted as shown:
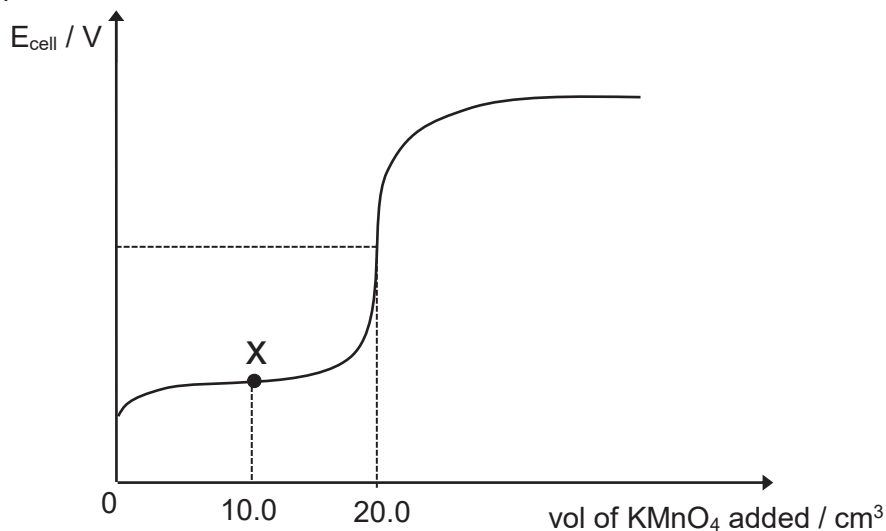
Which statements are correct?

1   The number of moles of Fe^{2+} in the pill is 4.0×10^{-2} mol.

2   The value of E_{cell} at point **X** is 0.77 V.

3   The colour change at end point is from pink to pale green.

A   **1** and **2** only

B   **1** and **3** only

C   **2** and **3** only

D   **1** only

4 The following graph represents the second ionisation energy trend of 9 consecutive elements in Periods 3 and 4.
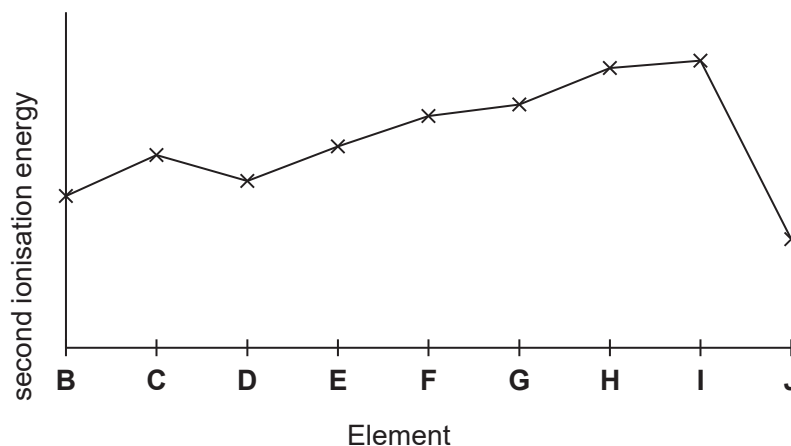
Which statement is correct?

A Element **C** is in Group 3.

B Element **F** has the lowest boiling point.

C The ionic radius of ion of **E** is greater than that of ion of **J**.

D The formula of the compound formed between elements **D** and **G** is **D$_2$G$_3$**.

5 Long-chain alkanes are converted on an industrial scale into alkylsulfates for use as detergents. One example is sodium lauryl sulfate shown below.

$$CH_3(CH_2)_{10}CH_2O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\displaystyle \|}{\underset{\displaystyle \|}{S}}}}-O^-Na^+$$
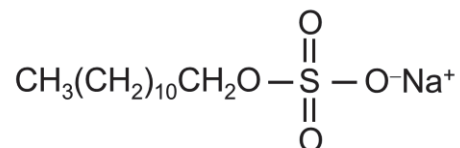
Which statements can be deduced from the structure given?

1 The compound can dissolve in both polar and non-polar solvents.

2 The shape about the sulfur atom is square planar.

3 All the C–C–C bond angles are 109.5°.

A **1**, **2** and **3**

B **1** and **2** only

C **1** and **3** only

D **2** and **3** only

6 Which statement is true for a fixed amount of an ideal gas when temperature increases at constant pressure?

(V = volume, p = pressure and T = temperature in K)

A V remains constant.

B $\dfrac{pV}{T}$ remains constant.

C Density of the gas remains constant.

D pV remains constant.

7 The reduction of iron ore, Fe_2O_3, by carbon monoxide is an exothermic reaction which occurs in the upper part of the furnace.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H = -27 \text{ kJ mol}^{-1}$$
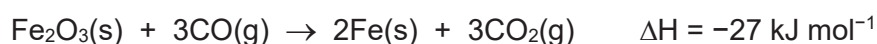
Given that ΔH_f^θ for CO_2 (g) = −394 kJ mol^{-1} and ΔH_f^θ for CO (g) = −110 kJ mol^{-1}, what is the standard enthalpy change of formation of Fe_2O_3(s)?

A +257 kJ mol^{-1}

B +825 kJ mol^{-1}

C −257 kJ mol^{-1}

D −825 kJ mol^{-1}

8 Which value would be required to calculate the lattice energy for the hypothetical ionic compound BaF_3 using Born-Haber cycle?

A Third electron affinity of fluorine

B Third ionisation energy of fluorine

C Ba–F bond energy

D F–F bond energy

9 A sample of X(g) with initial pressure of p atm is allowed to reach equilibrium at constant pressure.

$$X(g) \rightleftharpoons Y(g) + 2Z(g)$$
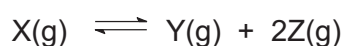
The equilibrium partial pressure of X is 0.25p atm.

What is the value of K_p?

A 0.5p **B** 4.5p **C** 0.25p^2 **D** 6.75p^2

10   Which indicator is suitable for use in a titration of 0.1 mol dm^{-3} H_2SO_4 with 0.1 mol dm^{-3} of NH_3?

   A   Methyl orange (pH range 3.3 – 4.4)

   B   Bromothymol blue (pH range 6.0 – 7.6)

   C   Phenolphthalein (pH range 8.3 – 10.0)

   D   None of the above

11   Magnesium hydroxide is extracted from the seawater as follows.

   Aqueous calcium hydroxide is added to seawater. Magnesium hydroxide is then filtered off.

$$Ca(OH)_2(aq) + MgCl_2(aq) \rightarrow Mg(OH)_2(s) + CaCl_2(aq)$$
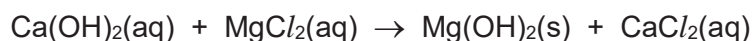
   Which statement best explains why magnesium hydroxide is formed in the above reaction?

   A   Magnesium is less electropositive than calcium.

   B   The solubility product for $Mg(OH)_2$ is lower than that for $Ca(OH)_2$.

   C   The enthalpy change of hydration for Mg^{2+} is less exothermic than for Ca^{2+}.

   D   The magnitude of the lattice energy of $Mg(OH)_2$ is less than that of $Ca(OH)_2$.

12 **P**, **Q** and **R** react in aqueous solution according to the following equation:

$$P + 3Q + 2R \rightarrow T + U$$

The kinetics of the above reaction was studied and the experimental results obtained are shown in the table below.

Expt	Volume of P /cm^3	Volume of Q /cm^3	Volume of R /cm^3	Volume of water /cm^3	Relative initial rate
1	10	10	10	20	16
2	10	5	20	15	32
3	5	5	10	30	4
4	10	5	10	25	8

What is the rate equation for the above reaction?

A   Rate = k[**P**][**Q**]

B   Rate = k[**P**][**Q**][**R**]

C   Rate = k[**P**][**Q**]^2[**R**]

D   Rate = k[**P**][**Q**][**R**]^2

13   *Use of the Data Booklet is relevant to this question.*

A cell is set up by connecting a Cu^{2+}/Cu half-cell and an acidified MnO_4^-/Mn^{2+} half-cell.

copper

platinum

voltmeter

salt bridge

$[Cu^{2+}(aq)]$ = 1.0 mol dm^{-3}

$[Mn^{2+}(aq)]$ = $[H^+(aq)]$ = $[MnO_4^-(aq)]$ = 1.0 mol dm^{-3}
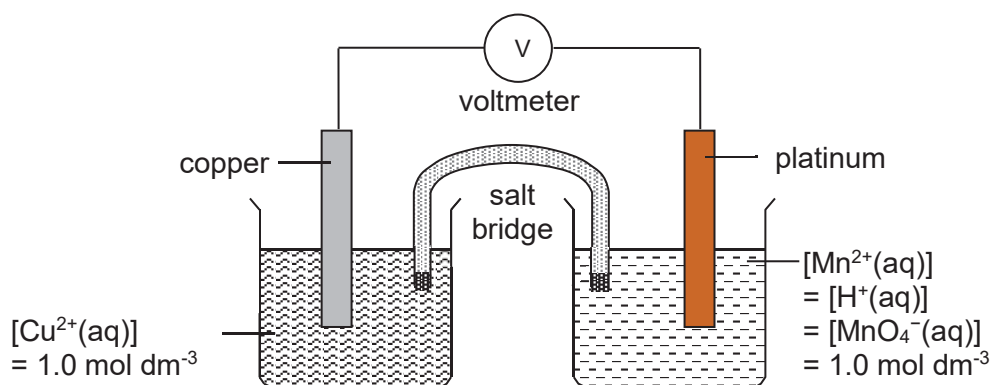
Which change in the set up will cause the corresponding effect on the e.m.f (potential difference) of the cell?

	Change	Effect on e.m.f of cell
A	Addition of excess NH_3 (aq) into oxidation half-cell	Increases
B	Addition of concentrated H_2SO_4 into reduction half-cell	Decreases
C	Increase the size of the copper electrode	Increases
D	Replace copper with an alloy of copper and zinc	Remains the same

14 *Use of the Data Booklet is relevant to this question.*

The AgCl / Ag reference electrode is based on the following reaction:

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

The reduction potential of the Fe^{2+} / Fe half−cell was found to be −0.64 V when measured using the AgCl / Ag reference electrode.

What is the reduction potential of the AgCl / Ag electrode with respect to the standard hydrogen electrode?

A   −1.10 V   **B**   −0.20 V   **C**   +0.20 V   **D**   +1.10 V

15 *Use of the Data Booklet is relevant to this question.*

A current is passed through a simple cell as shown below:
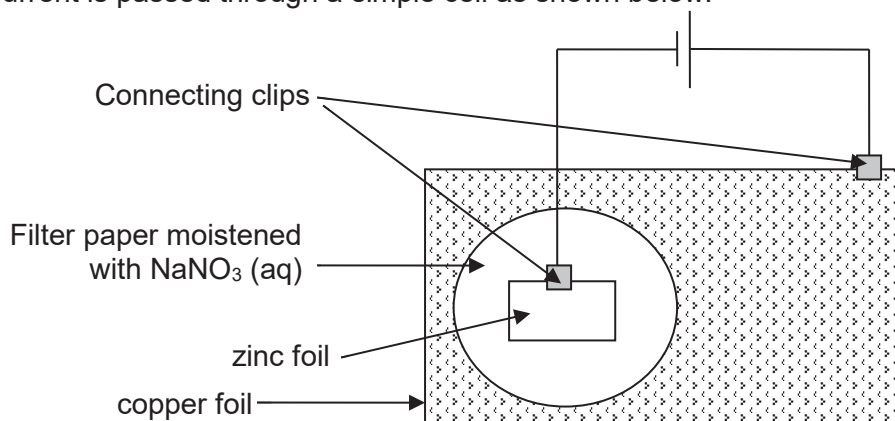
What could be an expected observation?

A   Sodium metal was deposited on the filter paper.

B   The size of the zinc foil reduced with time.

C   The filter paper turned blue.

D   A brown gas was observed.

16 Consider the sequence of oxides Na_2O, SiO_2, P_4O_{10}.

Which factor decreases in the order Na_2O, SiO_2, P_4O_{10}?

A   melting point

B   covalent character

C   pH when mixed with water

D   solubility with aqueous alkali

17 Anhydrous barium nitrate and anhydrous magnesium nitrate decompose on heating, nitrogen dioxide and oxygen are evolved and an oxide is formed.

Which statements concerning these decompositions are correct?

1 Nitrogen dioxide is evolved at a lower temperature from magnesium nitrate than from barium nitrate.

2 For both nitrates, the volume of nitrogen dioxide evolved is four times greater than the volume of oxygen.

3 The numerical value of the lattice energy of magnesium nitrate is smaller than that of barium nitrate.

A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **1** only

18 Element **Y** forms a chloride, **Y**Cl_n, which has a melting point of 3 °C. When treated with an excess of acidified silver nitrate, 0.50 g of the chloride produced 1.20 g of AgCl.

Another 0.50 g sample of the chloride was heated strongly. Chlorine gas was evolved and the residue gave 0.72 g of AgCl when treated with an excess of acidified silver nitrate.

What is the value of **n** and the identity of element **Y**?

	value of n	identity of element Y
A	5	Sb
B	5	P
C	4	Ge
D	4	Si

19 Which statements are correct for the compounds in the following sequence?

hydrogen chloride, hydrogen bromide, hydrogen iodide

1 The thermal stability increases.

2 The enthalpy change of formation becomes less exothermic.

3 The ease of oxidation increases.

A **1**, **2** and **3**

B **1** and **2** only

C **1** and **3** only

D **2** and **3** only

20 Fehling's solution is a common reagent used to identify aldehyde functional group in organic compound. It can be prepared by mixing aqueous copper(II) sulfate with tartrate ions in presence of strong alkalis.

The formation of copper tartrate complex is shown in the following equation.
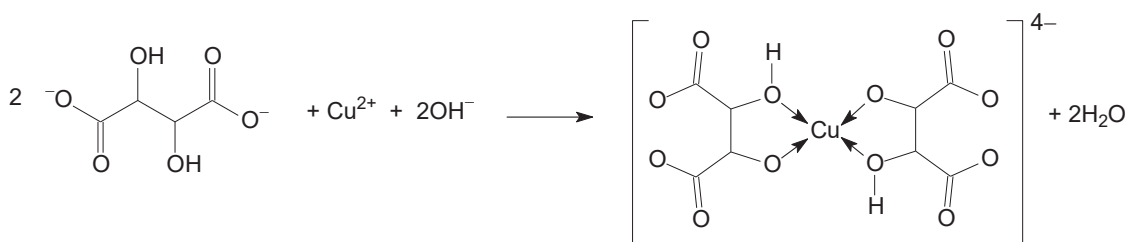
tartrate ion   copper tartrate complex

Which statement is correct for the above reaction?

A The tartrate ion acts as a Lewis acid.

B The tartrate ion can exist as 3 stereoisomers.

C The coordination number of the complex ion is 2.

D The oxidation number of Cu in the complex ion is 0.

21 Hybridisation of orbitals can be observed for central atoms such as C, N and O.

How many atoms in the following molecule are sp^3 hybridised?

HO
O
NH
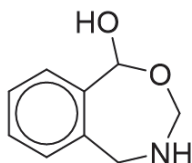
A 3 **B** 4 **C** 5 **D** 6

22 An alkyne, a hydrocarbon with C≡C bond, undergoes hydration in a similar mechanism as an alkene. However, the formation of an enol is unstable and would undergo rearrangement to form a carbonyl compound.

One example of the reaction is shown below.

$$R-C{\equiv}C-H \xrightarrow{\text{hydration}} \underset{\text{enol}}{R-\overset{\overset{\displaystyle OH}{|}}{C}{=}\overset{\overset{\displaystyle H}{|}}{C}-H} \xrightarrow{\text{rearrangement}} R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

alkyne   enol
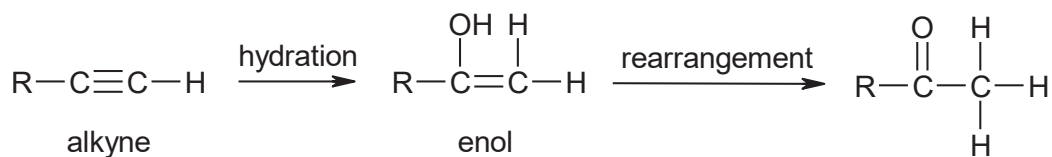
Which product is **not** the major product when the corresponding alkyne undergoes hydration?

	alkyne	product
A	H—C≡C—H	H—C(=O)—CH$_3$
B	H—C≡C—CH$_3$	H—C(=O)—CH$_2$CH$_3$
C	CH$_3$—C≡C—H	CH$_3$—C(=O)—CH$_3$
D	CH$_3$—C≡C—CH$_3$	CH$_3$—C(=O)—CH$_2$CH$_3$

23 When compound **A** was heated with excess acidified $KMnO_4$, carbon dioxide gas was produced.
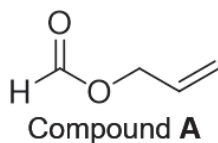
Compound **A**

Carbon dioxide gas reacts with excess calcium hydroxide according to the following equation.

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$
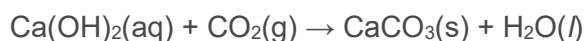
What is the mass of calcium carbonate ($M_r = 100.1$) that can be obtained when 1 mole of compound **A** is treated with hot excess acidified $KMnO_4$?

A   100.1 g   **B**   200.2 g   **C**   300.3 g   **D**   400.4 g

24 Compound **X** has the following structure.
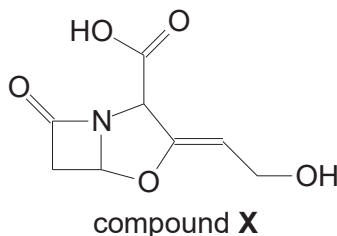
compound **X**

Which statements regarding compound **X** are correct?

1   Its molecular formula is $C_8H_8NO_5$.

2   It has 2^3 stereoisomers.

3   2 mol of Br atoms are added when 1 mol of compound **X** reacts with excess HBr(g).

4   6 mol of H atoms are added when 1 mol of compound **X** reacts with $LiAlH_4$ in dry ether.

A   **1** and **2** only

B   **1** and **3** only

C   **2** and **3** only

D   **2** and **4** only

25 The energy profile diagram for the nucleophilic substitution reaction between hydroxide ions and 2–chloro–2–methylpropane is shown below.

Which statements can be inferred from the information given above?

1 The intermediate **Z** is

2 This reaction has an overall order of reaction of 1.

3 Removal of 2−methylpropan−2−ol product does not affect the yield of the reaction.

4 Increasing the concentration of hydroxide ions reduces the time taken for reaction to complete.

A **1** and **2** only

B **1** and **4** only

C **2** and **3** only

D **3** and **4** only

26 Which compound will **not** react with NaBH₄, but react with H₂ when heated with nickel catalyst?

    1 CH_3CH_2COOH

    2 CH_3CH_2CHO

    3 CH_3CH_2CN

    4 $CH_3CH=CH_2$
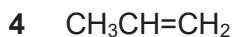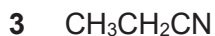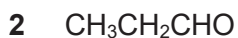
    A   **1** and **3** only

    B   **1** and **4** only

    C   **2** and **3** only

    D   **3** and **4** only

27
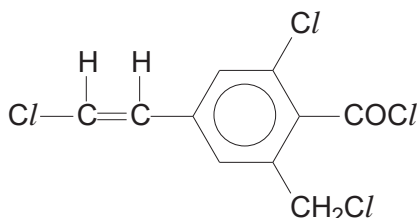
1 mole of the above molecule is treated with NaOH(aq) and warmed, followed by adding excess dilute nitric acid.

How many moles of silver chloride will be formed when excess aqueous silver nitrate is added?

A   1   **B**   2   **C**   3   **D**   4

28 3-bromophenol is a versatile starting material for the synthesis of medicinal compounds. Which compound is likely to be the major product of the reaction between dilute nitric acid and 3-bromophenol?
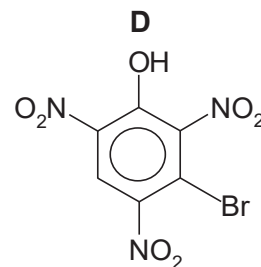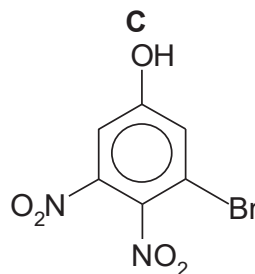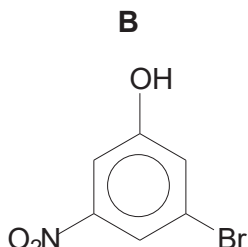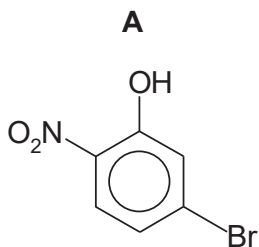
29 Cyanohydrins are useful intermediates in organic syntheses. They can be made by reacting carbonyl compounds with hydrogen cyanide.

Which statements are correct about the reaction of propanone and hydrogen cyanide?

1 Propanone reacts with HCN to give a racemic mixture.

2 Propanal reacts with HCN at a faster rate than propanone.

3 The cyanohydrin obtained from the reaction can be distinguished from propanone by warming with NaOH(aq).

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

30 Deuterium, D, is an isotope of hydrogen, ^2_1H.

Which reaction will **not** yield an organic compound containing deuterium, D?
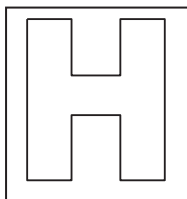
A CH_3CH_2CN $\xrightarrow[\text{D}Cl,\text{ heat}]{\text{D}_2\text{O}}$

B CH_3COCHI_2 $\xrightarrow[\text{D}_2\text{O, warm}]{\text{I}_2,\text{ NaOD}}$

C —$COCl$ $\xrightarrow[\text{KOD}]{\text{D}_2\text{O}}$

D $CH_3CH_2CONHCH_3$ $\xrightarrow{\text{LiA}l\text{D}_4}$

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

Paper 2 Structured Questions

Candidates answer on Question Paper.
Additional Materials: Data Booklet

9729/02
Thursday
24 August 2017
2 hours

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid/tape.

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

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

Appropriate significant figures and units are expected for final numerical answers.

For Examiner's Use	
1	/14
2	/16
3	/11
4	/16
5	/18
Paper 2 Total	/75

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

1 Nitrous oxide, N_2O and nitrogen dioxide, NO_2, are atmospheric pollutants. Nitrous oxide has an atmospheric residence time as long as 20 to 30 years but nitrogen dioxide has a residence time of only approximately 4 days.

(a) Suggest how NO_2 is formed in a car engine and how it may be removed from car exhaust gases.

....

....

....

.... [2]

(b) **(i)** Draw the dot-and-cross diagrams of N_2O and NO_2, given that nitrogen is the central atom in both species.

[2]

(ii) Hence, explain for the difference in residence times between N_2O and NO_2.

....

[1]

(c) In the gaseous state, NO_2 can dimerise as follows.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

The following data are for $NO_2(g)$ and $N_2O_4(g)$ at 298 K.

	$\Delta H_f^\ominus$ / kJ mol^{-1}	$\Delta S_f^\ominus$ / J mol^{-1}K^{-1}
$NO_2(g)$	+33.2	+240
$N_2O_4(g)$	+9.2	+304

(i) Calculate $\Delta H^\ominus$ and $\Delta S^\ominus$ for the above reaction.

[2]

(ii) Explain the signs of your calculated $\Delta H^\ominus$ and $\Delta S^\ominus$.

....

....

....

.... [2]

(iii) The two gases in the above reaction can co-exist in an equilibrium. Calculate the temperature at which a dynamic equilibrium is established.

[2]

(iv) At 294 K, N_2O_4 liquefies. Given that the molar entropy change of vaporisation of N_2O_4 is +88 J mol^{-1}K^{-1}, calculate the molar enthalpy change of vaporisation of N_2O_4.

[1]

(v) With reference to your answers in **(c)(i)** and **(iv)**, calculate ΔH and ΔS for the reaction below.

$$2NO_2(g) \rightarrow N_2O_4(l)$$
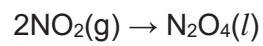
[2]

[Total: 14]

2 This question is about the reactions of iodine and its compounds.

(a) In the 18th and 19th centuries, iodine was industrially produced from kelp, a large seaweed. Combustion of kelp converts the organic substances to ash, and sodium halides (mainly sodium iodide) are obtained.

In the laboratory, a similar process can be done according to the following procedure.

1. Fill a large crucible on a tripod with the seaweed. Heat with a strong Bunsen flame until all the seaweed has been turned to ash.

2. Boil the ash with about 20 cm^3 of purified water in a beaker, and filter while hot. Collect the filtrate in a second beaker and allow to cool.

3. Add about 2 cm^3 of dilute sulfuric acid to the filtrate, followed by hydrogen peroxide solution.

4. Transfer the mixture to a separating funnel and add 10−20 cm^3 of a suitable *organic solvent*. Stopper the separating funnel and shake vigorously for about 30 s. With the separating funnel inverted, release any pressure that has built by opening the tap briefly.

5. Clamp the funnel and allow the layers to separate.

6. Run off the aqueous layer into a 250 cm^3 conical flask.

7. Run the organic layer into an evaporating basin, and set aside to evaporate in the fume cupboard to obtain the iodine crystals.

(i) State and explain, with the aid of a relevant equation, what you would observe during procedure **3**.

....

....

.... [2]

(ii) With reference to the *Data Booklet*, explain why hydrochloric acid is **not** used in the acidification process in procedure **3**.

....

....

....

[2]

(iii)   Suggest a suitable organic solvent for the extraction of iodine in procedure **4** and state what you would observe.

....

....

.... [2]

(iv)   Suggest a reason why in procedure **7**, evaporation is employed instead of direct heating over a strong Bunsen flame.

....

.... [1]

(v)   In order to check if the kelp contained significant amount of chloride anions, a student transferred 1 cm^3 of the filtrate obtained in procedure **2** into a test tube and added acidified silver nitrate solution. A cream precipitate was obtained.

State and explain what reagent should be added to verify if there was a significant amount of chloride mixed with iodide.

....

....

.... [2]

(b) Sodium iodate, NaIO$_4$ (M_r = 214.0), is a powerful oxidising agent that can be used to oxidise thioethers into sulfoxides.

Thioanisole (M_r = 124.1), C$_6$H$_5$SCH$_3$, is a thioether. In a reaction between thioanisole and sodium iodate, it was found that 0.9 cm^3 of thioanisole (density = 1.06 g cm^{-3}) reacts completely with 15.40 cm^3 of 107 g dm^{-3} solution of sodium iodate to give methyl phenyl sulfoxide, C$_6$H$_5$SOCH$_3$.

thioanisole → methyl phenyl sulfoxide
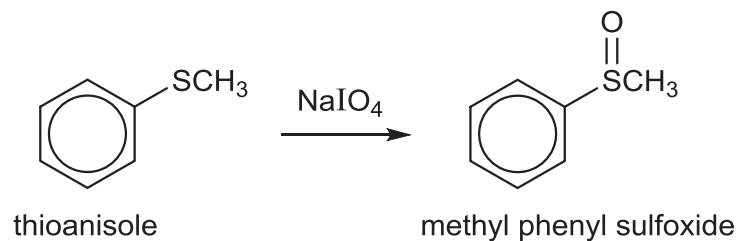
(i) Deduce the stoichiometry ratio for the reaction between thioanisole and sodium iodate.

[2]

(ii) Hence, write the balanced chemical equation for the reaction.

.... [1]

(iii) Thiophenol, C$_6$H$_5$SH, has similar reactions as phenol. Suggest how thioanisole can be synthesized from thiophenol in two steps.

[2]

(c) Hydrogen peroxide, H_2O_2, is another common redox reagent which can act as either an oxidising agent or reducing agent. H_2O_2 is a weak acid that dissociates according to the following equilibrium.

$$H_2O_2 \rightleftharpoons HO_2^- + H^+$$

With reference to the *Data Booklet*, deduce whether H_2O_2 is a better reducing agent in acidic or alkaline condition.

....

....

.... [2]
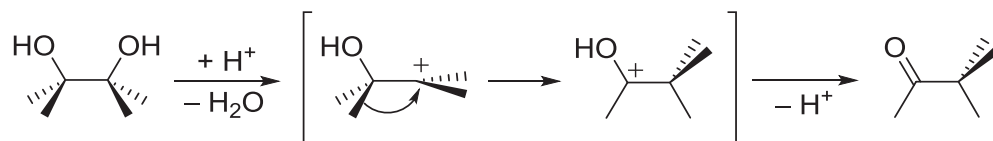
[Total: 16]

3 The pinacol rearrangement is a 1,2–rearrangement procedure which converts 1,2–diol to a carbonyl compound. This rearrangement process occurs under acidic condition (e.g. H_2SO_4). The diagram below shows the key steps in the mechanism, with movement of electrons pairs represented by curly arrows, needed to generate the carbonyl from 1,2–diol.

In a particular synthetic route, an alkene **U**, of molecular formula of C_8H_{14}, was first converted into a diol **W**. Compound **W** then reacted with H_2SO_4 to form two carbonyls **X** and **Y** as major products, in a reaction similar to pinacol rearrangement.
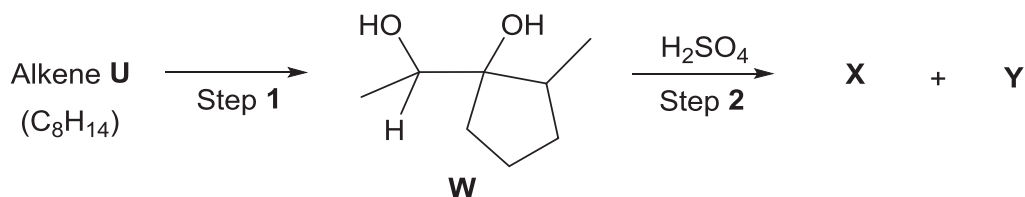
Compound **X** produces a yellow precipitate when heated with alkaline I_2 solution but not for compound **Y**. Compound **Y** gives a silver mirror when warmed with ammonical solution of silver nitrate.

(a) Suggest the structure of alkene **U**.

[1]

(b) State the reagents and conditions required for Step **1**.

Reagents : ....

Conditions : .... [1]
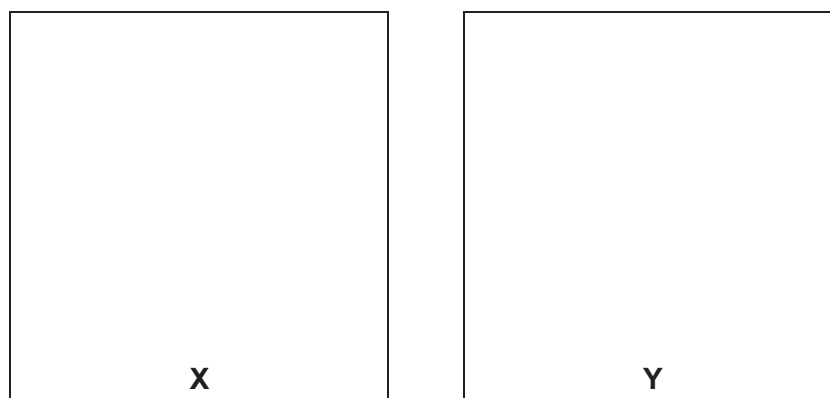
(c) Draw the structure of the most stable carbocation intermediate involved in Step **2** which resulted in the formation of the major products **X** and **Y**. Explain your answer.
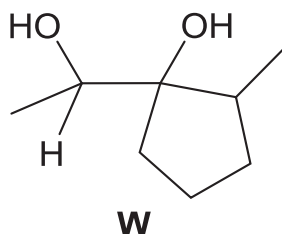
Structure of carbocation intermediate

....

....

.... [2]

(d) Deduce the structures of compounds **X** and **Y**.

X	**Y**

[2]

(e) Compound **W** exhibits optical isomerism.

(i) Indicate each chiral atom(s) of compound **W** on the structure given below with an asterisk (*).
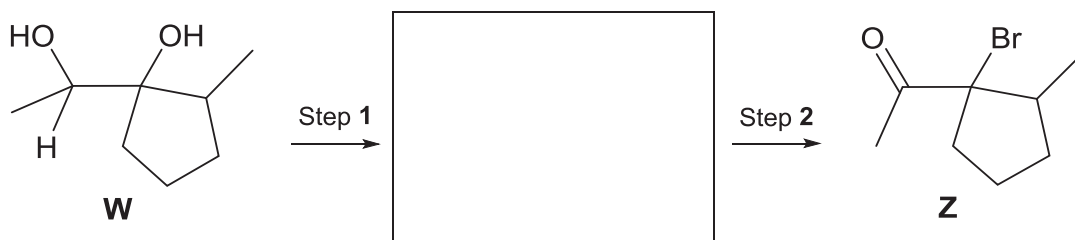
HO   OH

H

W

[1]

(ii) State the number of possible stereoisomers of compound **W**.

[1]

(f) State the reagents and conditions needed to convert diol **W** into compound **Z** shown below in 2 steps. Show the structure of the intermediate organic compound.

Reagents and Conditions

Step **1** ....

Step **2** ....
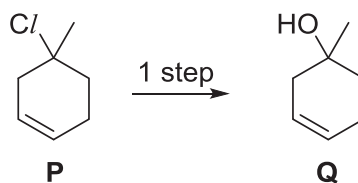
[3]

[Total: 11]

4   Chlorine, bromine and iodine are group 17 elements which are commonly found in organic material and used extensively in organic synthesis.

(a)   Halogenoalkane is an example of such organic compounds and it can be converted into alcohol. For instance, 4–chloro–4–methylcyclohexene can be converted into an alcohol as shown below.

(i)   State the reagents and conditions for the formation of compound **Q** from compound **P**.

    ....   [1]

(ii)   Two experiments with different initial concentrations of **P** were used to study the kinetics of the reaction. A [nucleophile]–time graph was plotted using the results obtained from the experiments.
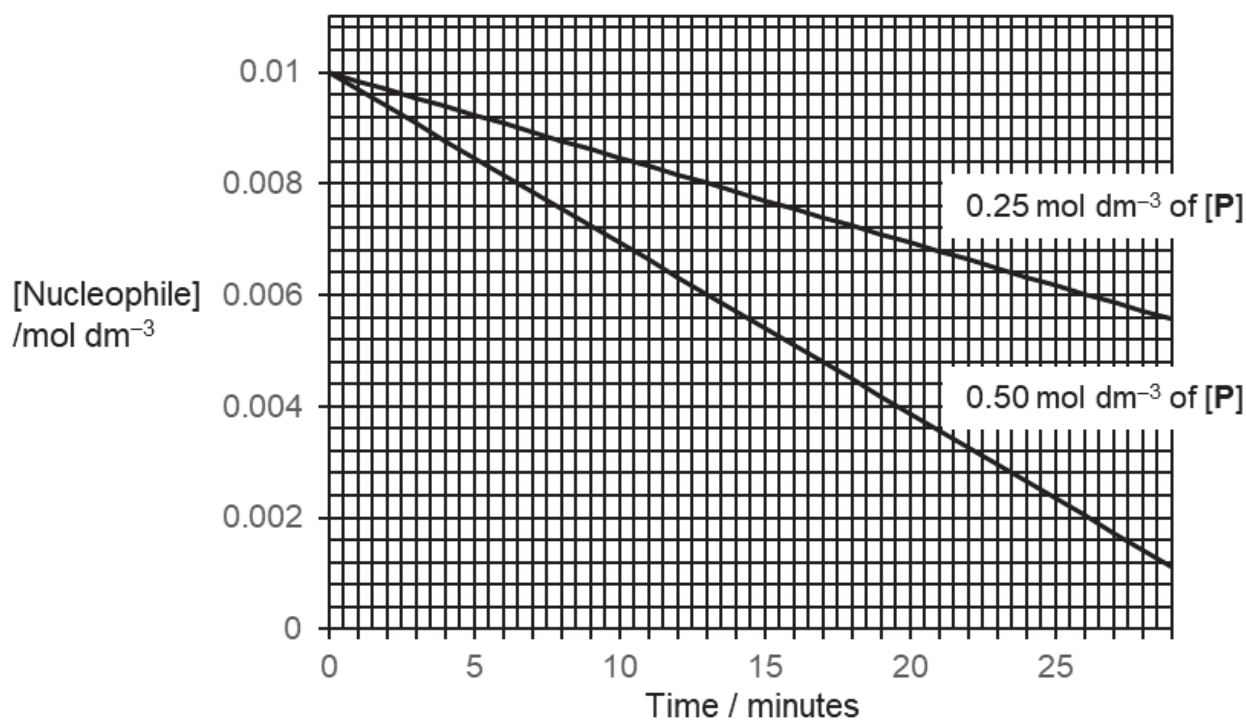
Deduce the order of reaction with respect to compound **P** and the nucleophile. Hence, state the rate equation.

....

....

....

....

....

Rate Equation : .... [3]

(iii) Using the nucleophile you have suggested in **(i)**, suggest the mechanism for this reaction.

Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[3]

(iv) Suggest if any optical activity is present in the products of this reaction. Explain your answer.

....

....

....

....

.... [3]

(v) Bromoalkane and iodoalkane can undergo the same substitution reaction as chloroalkane to give alcohols but with different rates of reaction.

Rank the compounds, in increasing order of the time taken to undergo complete reaction with a nucleophile. Explain your answer, with reference to the *Data Booklet*.

You may use R to represent the hydrocarbon chain.

....

....

....

[2]

(b) Acyl chloride is an alternative for carboxylic acid in making esters.

Diphenylethandioate (M_r = 242.0), is an ester which produces the light in glow sticks when oxidised. It can be made from phenol (M_r = 94.0) and ethanedioyl dichloride (M_r =127.0).

Diphenylethandioate
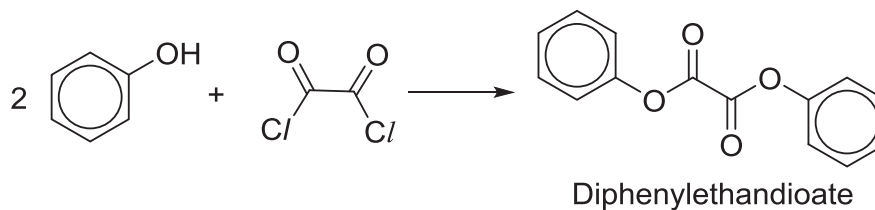
(i) Given that this reaction has an average experimental yield of 75% and ethanedioyl dichloride is used in excess, calculate the mass of phenol needed to obtain 20 g of diphenylethandioate.

[2]

(ii) With reference to **(b)(i)**, suggest a simple chemical test that could be carried out to check if the reaction is completed.

....

....

.... [2]

[Total: 16]

5 Haemoglobin reacts with oxygen to form oxyhaemoglobin as follows.

$$Hb + O_2 \rightleftharpoons HbO_2$$
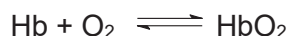
In order for haemoglobin to absorb oxygen, iron must be present. The structure of the iron containing haem group is shown below.
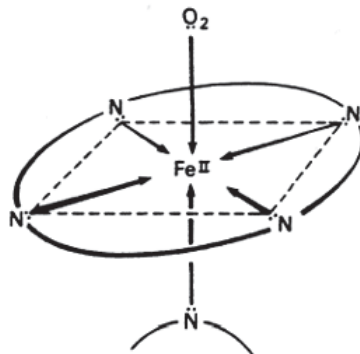
In the presence of vitamin C, iron taken into the body in the diet as Fe^{3+} is converted into Fe^{2+} and incorporated in the haemoglobin structure. Vitamin C itself is oxidized in the process as follows.

Vitamin C
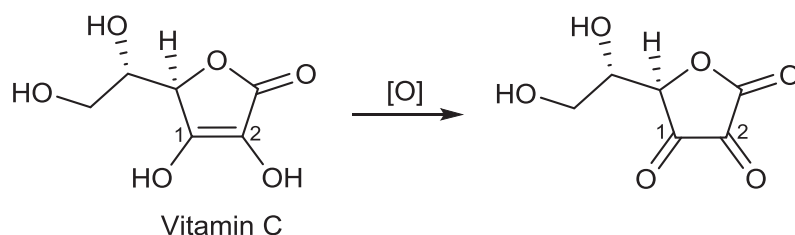
Approximately 10,000 million new blood cells are formed in the bone marrow daily. Red blood cells have a lifespan of 120 days. Each person should have about 150 mg of haemoglobin per cm^3 of their blood and a blood count of 5 million red blood cells per cm^3. Iron makes up 4% by mass of the haemoglobin molecule.

(a) **(i)** State the oxidation state of C_1 of vitamin C before and after oxidation.

Oxidation state of C_1 in vitamin C   : ....

Oxidation state of C_1 after oxidation : .... [1]

(ii) Hence or otherwise, complete the half equation for the oxidation of vitamin C below.

.... [1]
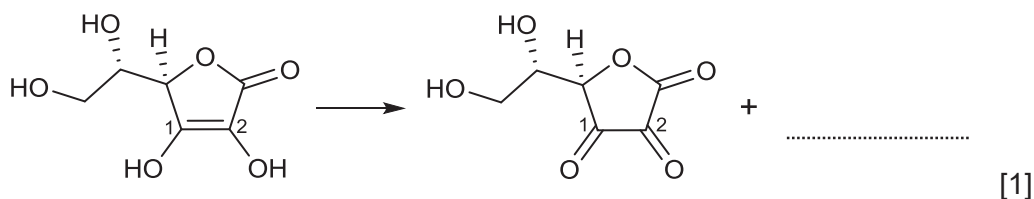
(b) (i) Calculate the amount of iron, in moles, that needs to be available each day within the bone marrow for the production of new red blood cells.

[3]

(ii) The recommended dietary allowance of iron is 20 mg per day which is lower than the value calculated in **(b)(i)**. Suggest a reason for this.

....

.... [1]

(c) (i) In the space provided below, draw the shapes of all the 3d orbitals. Label the axes clearly.

d_{z^2}	$d_{x^2-y^2}$

d_{xy}	d_{xz}	d_{yz}

[2]

[Turn over
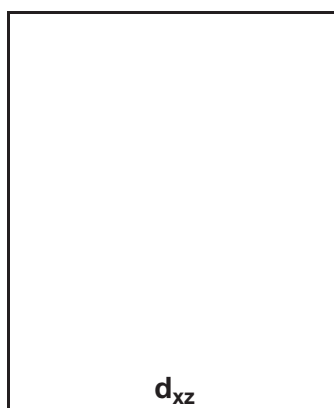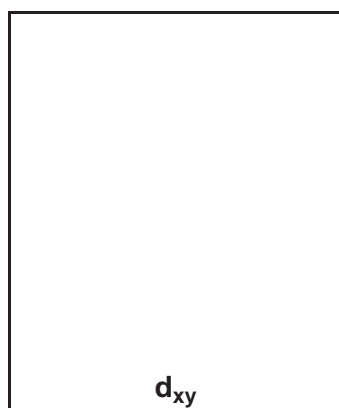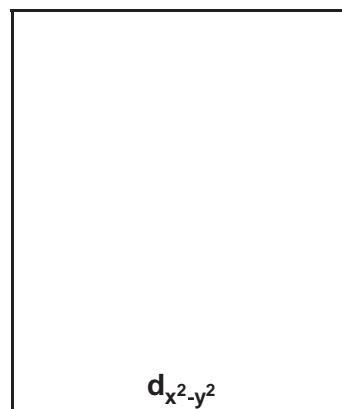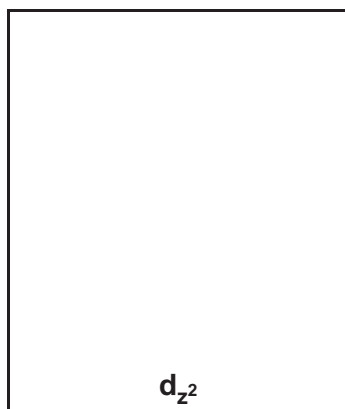
(ii) Account for the red colouration of blood.

....

....

....

....

.... [3]

(d) Complexes of Ni^{2+} are commonly found to have coordination number of 4, and exist either as tetrahedral or square planar complexes.

The splitting of the energy levels of d orbitals for tetrahedral and square planar complexes are different from that of an octahedral complex.

Tetrahedral complex
complex

Isolated gaseous Ni^{2+}

Square planar
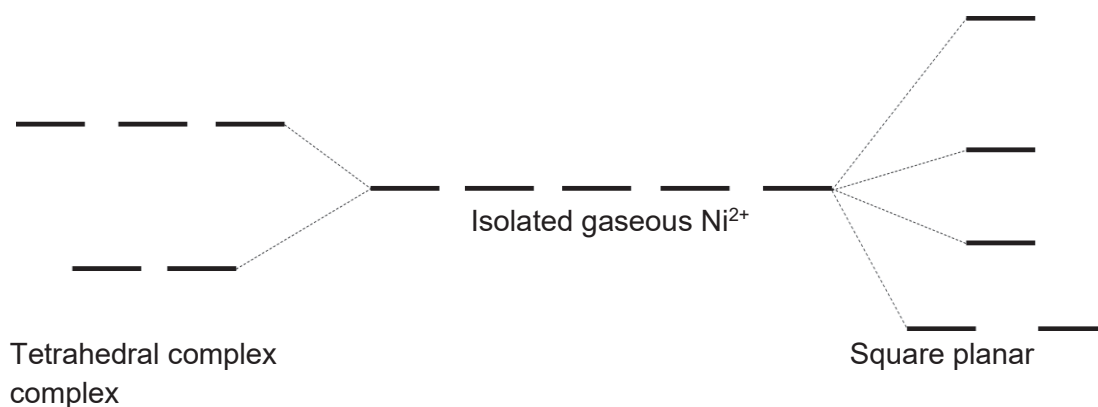
(i) Complete the electronic configuration for Ni^{2+}.

$1s^2\ 2s^2\ 2p^6$ .... [1]

(ii) The Aufbau principle states that in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels.

On the energy levels provided in **(d)**, show the electronic arrangement of the 3d electrons of Ni^{2+} in the tetrahedral and square planar complex.

[1]

(iii) Complex ions with only paired electrons are considered to be diamagnetic while those with at least one unpaired electron are considered to be paramagnetic.

A Ni^{2+} complex $[NiX_4]^{2-}$ is found to be diamagnetic, with reference to your answer in **(ii)**, state the shape of this complex ion.

.... [1]

(e) Forensic investigators use luminol to detect traces of blood at crime scenes, as it reacts with the iron in haemoglobin. Luminol can be synthesized using the following route.
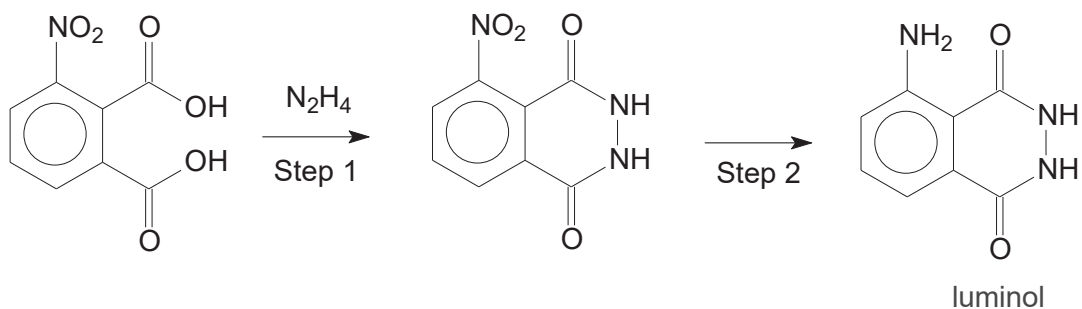
(i) State the type of reaction for Step 1.

.... [1]

(ii) A research student used the following reagent for Step 2.

Sn, conc HCl, heat under reflux, followed by excess NaOH(aq)

Suggest a reason why his method will not give luminol as the product.

....

.... [1]

(iii) Suggest and explain the relative basicity of N_2H_4 as compared to luminol.

....

....

....

.... [2]

[Total: 18]

End of Paper
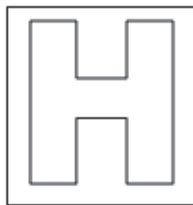
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NATIONAL JUNIOR COLLEGE

SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY   **9729/03**

Paper 3 Free Response   **Monday 11 Sep 2017**
                                                              2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
                                     Answer Paper

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.

You may use a soft pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid/tape.

Section A
Answers **all** questions.

Section B
Answers **one** question.

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

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

_____

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

Section A

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

1 **(a)** **(i)** Write an equation for the thermal decomposition of barium carbonate. [1]

(ii) Describe and explain the trend observed in the ease of thermal decomposition of the carbonates of the Group 2 elements. [2]

(b) Monuments made of marble or limestone, such as the Taj Mahal in India and the Mayan temples in Mexico, are eroded by acid rain containing sulfuric acid. The carbonate stone is converted into sulfate by acid rain.

$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

The life of such monuments is now being extended by treating them with a mixture of urea, $(NH_2)_2CO$, and barium hydroxide solutions.

reaction 1: After soaking in the pores of the carbonate stone containing water, urea reacts gradually to give ammonia and carbon dioxide.

reaction 2: Carbon dioxide produced then reacts with barium hydroxide to form barium carbonate.

(i) State the shape and bond angle around the C atom of $(NH_2)_2CO$. [2]

(ii) Write balanced equations for **reactions 1** and **2**. [2]

(c) When carbon dioxide gas dissolves in water, carbonic acid, H_2CO_3, is formed.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
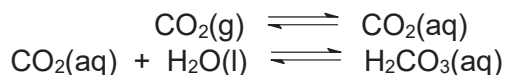
In a school laboratory, a student was instructed to titrate 25.0 cm^3 of 0.100 mol dm^{-3} carbonic acid with 0.125 mol dm^{-3} NaOH using phenolphthalein indicator. (K_{a1} of H_2CO_3 = 4.3 × 10^{-7} mol dm^{-3})

(i) Calculate the pH of 0.100 mol dm^{-3} H_2CO_3. [1]

(ii) Calculate the volume of NaOH needed to completely react with 25.0 cm^3 of 0.100 mol dm^{-3} H_2CO_3. [1]

(iii) Calculate the pH of the solution when H_2CO_3 and HCO_3^- are in equal concentrations. [1]

(iv) Calculate the pH of the resulting solution when 20.0 cm^3 of NaOH is added to 25.0 cm^3 of H_2CO_3. [2]

(v) Using your answers in **(i)** to **(iv)**, sketch the shape of the pH curve during the titration. [2]

(d) Barium compounds also have other uses and soluble barium salts are highly poisonous. For example, barium sulfate is used as a 'barium meal' in X-ray diagnostic work for patients with digestive tract problems. On the other hand, barium carbonate is used in rat poison.

The solubility products of $BaCO_3$ and $BaSO_4$ at 25 °C are given in the table below.

	Numerical value of K_{sp}
$BaCO_3$	5.5×10^{-10}
$BaSO_4$	1.3×10^{-10}

(i) Calculate the solubility of barium carbonate in mol dm^{-3} at 25 °C.

[1]

(ii) When the concentration of Ba^{2+} ions exceeds 0.100 mol dm^{-3}, it is lethal. Suggest a reason why barium carbonate is poisonous when ingested by mouth whereas barium sulfate is safe. [2]

(e) The values of lattice energy of $CaSO_4$ and $BaSO_4$ are −2374 kJ mol^{-1} and −2480 kJ mol^{-1} respectively.

Some standard enthalpy changes of hydration are listed below.

$$\Delta H_{hyd}^{\ominus} / kJ\ mol^{-1}$$

Ca^{2+} −1577
Ba^{2+} −1305
SO_4^{2-} −1099

Determine the enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, for these two salts. Hence, comment on the difference in the solubilities of the two salts. [3]

[Total: 20 marks]

2 This question is about the chemistry of aluminium, iron and ruthenium, Ru.

(a) Anodising is a process used to increase the thickness of the natural oxide on the surface of metal parts. Aluminium is a common metal which can be anodised as aluminium is a reactive metal that is readily oxidised by oxygen. This forms a layer of aluminium oxide, Al_2O_3, making it resistant to corrosion.

   (i) Using $H_2SO_4(aq)$ as the electrolyte and an inert electrode, draw an electrolysis set-up to show how an iPhone 7®, which is made of Al, can be anodised. [2]

   (ii) Write chemical equations to show the reactions at the anode during anodising. [2]

   (iii) The iPhone 7® has a surface area of 93.0 cm² to be anodised. Calculate the time needed to form a 0.2 mm protective layer of Al_2O_3 on the iPhone 7® if a current of 2.0 A is passed through the set-up. [2]
   (Density of Al_2O_3 is 3.95 g cm^{-3})

(b) Iron metal is dissolved in limited amounts of dilute and concentrated sulfuric acid solutions and the resultant solutions undergo a series of reactions as shown below.
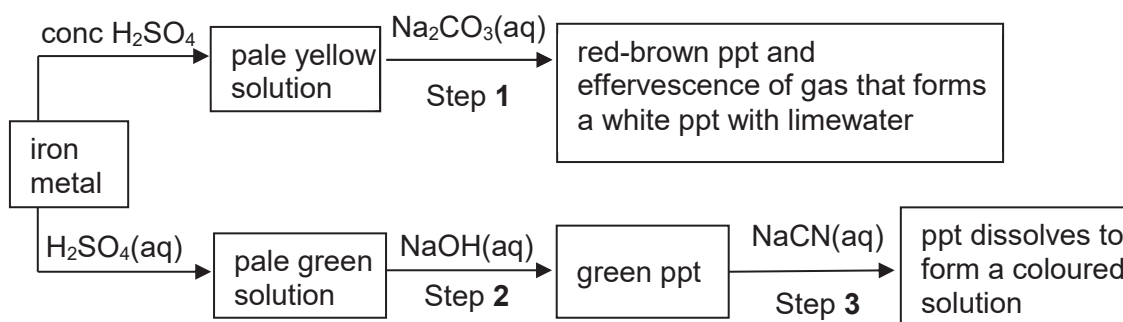
   (i) Account for the observations seen in step **1**. [2]

   (ii) Write equations with state symbols to account for the observations in steps **2** and **3**. [2]

(c) When aqueous ruthenium(III) chloride is treated with zinc and aqueous ammonia, an orange compound is formed. The orange compound contains 36.9% ruthenium, 30.7% nitrogen, 25.8% chlorine and a certain percentage of hydrogen by mass. When aqueous silver nitrate is added, 1 mol of the orange compound forms 2 mol of $AgCl$ precipitate.

   Given that 1 mol of the orange compound contains only 1 mol of Ru, determine the molecular formula of the orange compound. Draw a diagram of the structure of the complex ion in the orange compound. [3]

(d) Robert H. Grubbs used catalysts containing ruthenium for ring-closing reactions involving dienes.

An example of such reactions is as shown.
(Note: =Ru represents CH_2=Ru)

Step 1: [structure] + =Ru ⟶ [structure with Ru]

Step 2: [structure with Ru] ⟶ [structure with Ru] + **Q**

Step 3: [structure with Ru] ⟶ [structure with Ru]

Step 4: [structure with Ru] ⟶ [structure] + =Ru
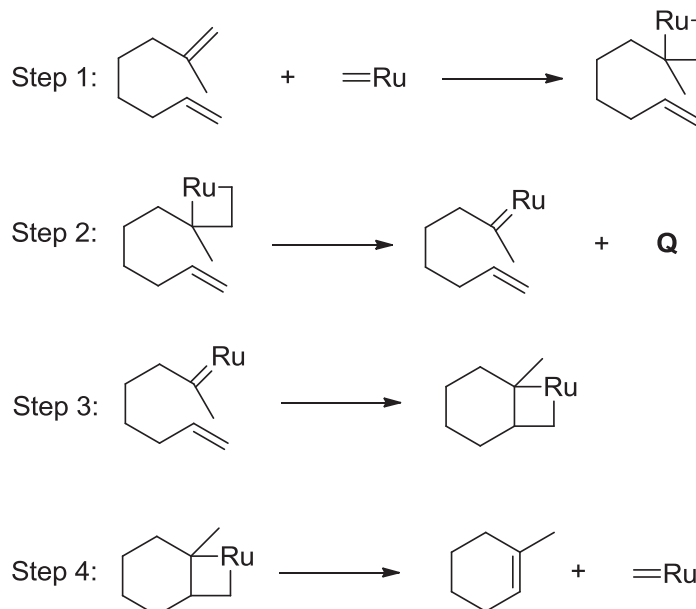
(i) Formation of **Q** thermodynamically drives this reaction forward.
State the identity of **Q**. [1]

(ii) Copy step **4** onto your writing paper. Draw 2 full-headed curly arrows showing the movement of electrons to form the products. [1]

(iii) Suggest suitable reactants to synthesize **S** using the above method.

S [2]

(e)

[structure] **S** $\xrightarrow{\text{hot acidified KMnO}_4}$ **T** $\xrightarrow[\text{trace amount of KCN}]{\text{HCN}}$ **U** $\xrightarrow{\text{H}_2, \text{Pt}}$ **V**
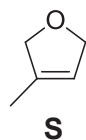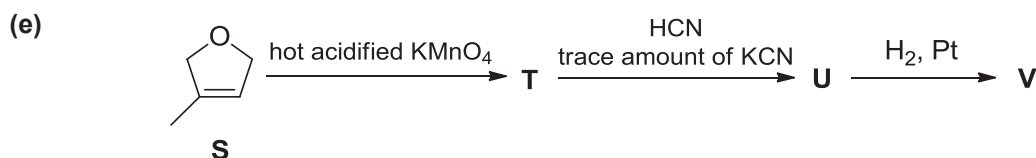
The ether functional group, $-CH_2-O-CH_2-$, in compound **S** is inert.
V exists as a crystalline solid at 300 °C.
Draw the structures of **T**, **U** and **V**. [3]

[Total: 20]

[Turn over

3 **(a)** The colour of blackberries is due to a compound known as cyanidin. At certain pH, cyanidin (Cy) exist as CyH^+, which is red, and at higher pH as Cy, which is purple.
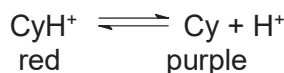
$$CyH^+ \rightleftharpoons Cy + H^+$$
$$\text{red} \qquad \text{purple}$$

(i) Write an expression for the acid dissociation constant, K_a of CyH^+. [1]

(ii) Given the K_a value of CyH^+ is 5×10^{-5}, calculate the ratio of $\dfrac{[CyH^+]}{[Cy]}$ in the blackberries fruit juice buffered at pH = 5.3 and hence predict the colour of the solution at pH = 5.3. [2]

(b) Fruit juices are often preserved by adding small quantities of sulfur dioxide, but SO_2 also reacts with both forms of cyanidin to give colourless compounds. For the red form, the reaction can be represented as follows:

$$CyH^+(aq) + SO_2(aq) + H_2O(l) \rightleftharpoons CySO_3H_2(aq) + H^+(aq) \quad \text{Equilibrium (1)}$$

When sufficient sulfur dioxide is added to a fruit juice buffered at pH = 3.0 to reach an equilibrium SO_2 concentration of 1.0×10^{-2} mol dm^{-3}, the intensity of the red colour decreases to **one tenth** of its original value.

(i) Write an expression for the equilibrium constant for equilibrium (1) and use the data to calculate its value. [2]

(ii) Would this decolourisation of the preserved fruit juice be more or less severe at pH = 4.0 compared to pH = 3.0? Explain your answer. [2]

(c) Primary fermentation of blackberries produces wine and carbon dioxide. It undergoes a secondary fermentation to convert compound **J** (M_r =134) to compound **K** (M_r =90) to decrease the acidity of the wine.

Compounds **J** and **K** undergo the following reactions.
- Both **J** and **K** react with sodium carbonate and hot acidified $K_2Cr_2O_7$, but not with 2,4–dinitrophenylhydrazine.

- Both **J** and **K** react with excess hot concentrated H_2SO_4, but only **J** gives a mixture with a pair of cis-trans isomers.

- 0.234 g sample of **J** reacts completely with 35 cm^3 of 0.10 mol dm^{-3} NaOH(aq).

- **K** give a yellow precipitate with alkaline aqueous iodine.

- 7.5×10^{-4} mol of **K** produces 18 cm^3 H_2 gas at r.t.p. when excess Na is added.

Use the information above to deduce the structures of compounds **J** and **K**. Explain all the reactions involved. [5]

(d) Pyruvic acid, CH_3COCO_2H, can be produced from compound **K**. Explain why pyruvic acid is more acidic than benzoic acid. [2]

(e) Trace amount of amino acids could be found in fruits.

One of the amino acids, alanine, has the following structure.
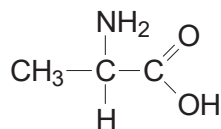
$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{NH_2}{|}}{C}}-C\overset{\nearrow O}{\underset{\searrow OH}{}}$$

(i) Suggest suitable reagents and conditions, and the structures of intermediate compounds formed, in the 3-steps synthesis of alanine from pyruvic acid. [4]

(ii) Describe a simple chemical test that you would carry out to distinguish alanine from asparagine.

$$H_2N-\overset{\overset{O}{||}}{C}-CH_2-\underset{\underset{H}{|}}{\overset{\overset{NH_2}{|}}{C}}-C\overset{\nearrow O}{\underset{\searrow OH}{}}$$

asparagine
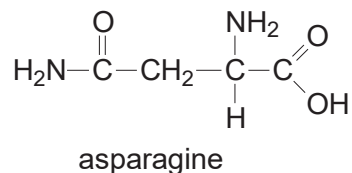
State the expected observations. [2]

[Total: 20]

Section B

Answer **one** question from this section.

4 (a) Alkenes are commonly used as a precursor to make halogenalkanes.

(i) Describe the mechanism for the reaction of 1 mol of buta−1,3−diene with 1 mol of HBr. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

The intermediate of the mechanism is shown below.

+
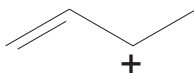
[3]

(ii) The intermediate in the above reaction in **(i)** can undergo a rearrangement to give a **primary** carbocation.

Draw the structure for the primary carbocation formed and show, with arrows, how the intermediate can be rearranged. [2]

(b) The diagram below shows the energy profile diagram for the formation of the products of the reaction of 1 mol of buta−1,3−diene with 1 mol of HBr.
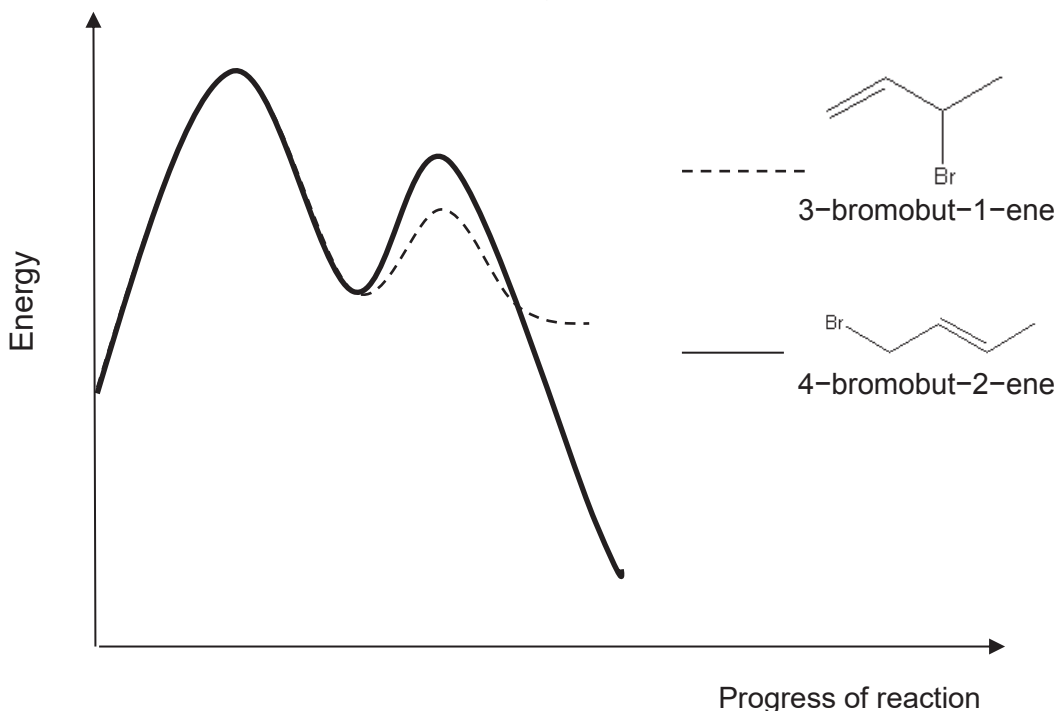
(i) Draw the Boltzmann distribution curve for the step 2 of the above reaction. Indicate their difference in activation energies that resulted in the two products formed. [2]

(ii) With reference to the Boltzmann distribution curve for the reaction, explain why 3−bromobut−1−ene is formed faster. [3]

(iii) With respect to the number of substituents on the C=C bond, suggest why 4−bromobut−2−ene is more stable than 3−bromobut−1−ene. [1]

(c) Separate bottles containing the following alkenes were mixed up.
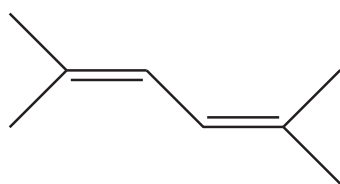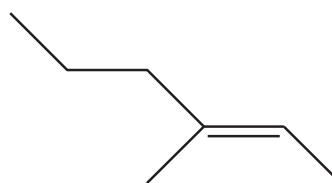
compound **L**   compound **M**

(i) Suggest a distinguishing test to determine the identity of the compounds and give the balanced equation for any reaction that occurs. [4]

(d) Arenes consist of 3 C=C bonds separated by C–C bonds, yet they exhibit different properties from alkenes.

(i) Explain why arenes cannot undergo electrophilic addition, unlike alkenes. [1]

(ii) Suggest suitable reagents and conditions, and the structures of intermediate compounds formed, for the synthesis of compound **N** from benzene.
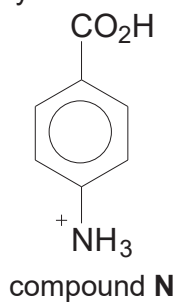
compound **N**   [4]

[Total: 20]

5 (a) Calcium chloride, $CaCl_2$, is commonly used as a desiccant to reduce humidity level of an enclosed space to allow the storage of articles that are prone to damage in high humidity. The lattice energy of $CaCl_2$ can be calculated from a Born–Haber cycle using the relevant data in the *Data Booklet* and the following data.

Enthalpy change of atomisation of calcium	= +177 kJ mol^{-1}
Enthalpy change of formation of calcium chloride, $CaCl_2$(s)	= −795 kJ mol^{-1}
First electron affinity of chlorine	= −364 kJ mol^{-1}

(i) Explain, with the aid of an equation, what is meant by *lattice energy* of $CaCl_2$. [1]

(ii) Construct a Born-Haber cycle for the formation of $CaCl_2$ and use it to calculate the lattice energy of $CaCl_2$. [4]

(iii) Explain how you would expect the magnitude of the lattice energy of aluminium oxide, Al_2O_3 (s) might compare to that of $CaCl_2$(s). [2]

(iv) Calcium chloride can be prepared by the reaction of calcium oxide and chlorine gas.

$$2CaO(s) + 2Cl_2(g) \rightarrow 2CaCl_2(s) + O_2(g)$$
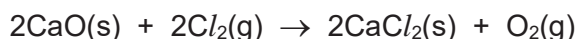
Using the data above and given that the enthalpy change of formation of calcium oxide is −635 kJ mol^{-1}, construct an energy cycle and use it to calculate the enthalpy change of reaction for the equation above. [2]

(b) Calcium chloride, $CaCl_2$ is a solid with a high melting point (775 °C) whereas aluminium chloride, $AlCl_3$, sublimes at 178 °C.

(i) Explain the difference in melting points between these two chlorides in terms of their structure and bonding. [3]

(ii) Aluminium chloride is a halogen carrier where it reacts with chloromethane gas to generate the electrophile in the electrophilic substitution of hydrogen atoms in benzene:

$$AlCl_3 + CH_3Cl \rightarrow AlCl_4^- + CH_3^+$$
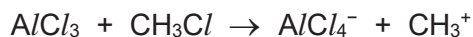
Explain why aluminium chloride can react with chlorine gas. Draw a diagram to illustrate the bonding in $AlCl_4^-$ [2]

(iii) The reaction in **(ii)** is an important step in the synthesis of 3–methylbenzoic acid, a precursor used to make DEET, a well-known insect repellent.

Suggest suitable reagents and conditions for a 3-steps synthesis of 3–methylbenzoic acid from benzene. [3]

(c) A 0.505 g sample of gaseous aluminium chloride takes up a volume of 90 cm^3 at 300 °C and 10^5 Pa.

    (i) Under what conditions of temperature and pressure would you expect the behaviour of gaseous aluminium chloride to be most like that of an ideal gas?

    [1]

    (ii) Calculate the M$_r$ of the vapour at this temperature. [1]

    (iii) With reference to your answer in **(ii)**, draw a displayed formula to show the type of bonding in the molecules of the vapour. [1]

[Total: 20]

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NATIONAL JUNIOR COLLEGE

SH2 Year-End Practical Examination

Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

Paper 4 Practical

Candidates answer on the Question paper

Additional Materials: As listed in the Confidential Instructions

9729/04

17 August 2017

2 hours 30 minutes

READ THESE INSTRUCTIONS FIRST

Write your identification number and name.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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

The use of an approved scientific calculator is expected, where appropriate. You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 19 and 20.

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.

Shift
Laboratory

For Examiner's use	
1	/ 12
2	/ 16
3	/ 10
4	/ 17
Total	/ 55

This document consists of **20** printed pages including this cover page.

[Turn over

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

1 **Determination of x in the formula of hydrated magnesium carbonate, $MgCO_3.xH_2O$.**

Magnesium carbonate is a white, powdery compound that occurs naturally as anhydrous and several hydrated forms. Due to its non-toxicity, it is widely marketed in common products such as cosmetics and toothpaste.

A sample of a hydrated magnesium carbonate mineral is analysed to find out the number of moles of water per mole of magnesium carbonate.

You are given the following:

FA 1 is $MgCO_3.xH_2O$ solid.

FA 2 is 2.00 mol dm^{-3} nitric acid, HNO_3.

FA 4 is 9.10 g dm^{-3} sodium hydroxide, $NaOH$.

Indicator: methyl orange

In this question, you will perform a back titration. The data from this titration will be used to determine the Mr of $MgCO_3.xH_2O$ and hence the value of **x**.

(a) In this titration, you will react $MgCO_3.xH_2O$ with an accurately measured amount of excess **FA 2**. The reaction mixture was then used to prepare bulk solution **FA 3**. The amount of unreacted **FA 2** in **FA 3** is then determined *via* titration with **FA 4**. The end-point is reached when the colour of the solution changes from pink to yellow.

(i) **Preparation of FA 3 by reacting FA 1 with excess FA 2**

Record all the mass measurements in the space provided on page **3**.

1. Weigh out accurately about 0.20 g of **FA 1** in a clean and dry weighing bottle.

2. Transfer **FA 1** to a clean and dry small beaker. Measure and record the mass of weighing bottle and residual solid. Calculate the actual mass of **FA 1** transferred.

3. Pipette 25.0 cm^3 of **FA 2** to dissolve ALL solid **FA 1.**

4. Transfer the resultant solution to a 250 cm^3 volumetric flask.

5. Use a small volume of deionised water to rinse the inner wall of the small beaker and the glass rod. Transfer ALL washings to the volumetric flask.

6. Add more deionised water to make up the volume to the mark. Stopper and shake to ensure complete reaction and to obtain a uniform solution.

7. Label this solution as **FA 3**.

(ii) **Titration of FA 3 against FA 4**

8. Fill the burette with **FA 4**.

9. Using a pipette, transfer 25.0 cm^3 of **FA 3** into a conical flask and titrate the unreacted HNO$_3$ with **FA 4**, using methyl orange as indicator.

10. Run **FA 4** from the burette into this flask until solution changes from pink to yellow.

11. Record your titration results in the spaces provided below. Make certain that your recorded results show the precision of your instrument used.

12. Repeat steps **9** to **11** until your results are within ± 0.10 cm^3.

Results

[5]

(iii) From your titrations, obtain a suitable volume of **FA 4** to be used in your calculations. Show clearly how you obtained this volume.

Volume of **FA 4** = …………………… [1]

(b) **(i)** Using your titration results, calculate the amount of unreacted HNO_3 in 25.0 cm³ of **FA 3**. Hence calculate the total amount of unreacted HNO_3 in 250 cm³ of **FA 3**.
[*Ar*: H, 1.0; O, 16.0; Na, 23.0]

Amount of unreacted HNO_3 in 250cm³ of **FA 3** = ……………… [1]

(ii) Determine the total amount of HNO_3 in 25.0 cm³ of **FA 2** before reacting with $MgCO_3.\textbf{x}H_2O$.

Amount of HNO_3 in 25.0 cm³ of **FA 2** = ………………...

(iii) Hence calculate the amount of HNO_3 used to react with $MgCO_3.\textbf{x}H_2O$.

Amount of HNO_3 reacted with $MgCO_3.\textbf{x}H_2O$ = ……………… [1]

(iv) Determine the relative molecular mass of $MgCO_3.xH_2O$.

M_r of $MgCO_3.xH_2O$ = ……………………..

Hence calculate the value of **x** in $MgCO_3.xH_2O$. Give your answer to the nearest whole number.
[Ar: H, 1.0; C, 12.0; O, 16.0; Mg, 24.3]

x is ………..………[2]

(c) Another student repeated the experiment using the procedure in **(a)**, however in **step 6**, he made up the solution to the 250 cm³ mark by adding **FA 2** instead of deionised water. Explain the effect on his titre value and why it is unsuitable to do so.

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[Total:12]

2 **Determination of the enthalpy change for the formation of hydrated magnesium carbonate, $\Delta H_{reaction1}$.**

In this experiment, you are to determine $\Delta H_{reaction3}$.
$\Delta H_{reaction1}$ will be determined using Hess's law.

$Mg(s) + C(s) + (3+\textbf{x})/2\ O_2(g) + \textbf{x}H_2(g) \rightarrow MgCO_3.\textbf{x}H_2O(s)$ $\Delta H_{reaction1}$

$Mg(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$ $\Delta H_{reaction\ 2} = -490\ kJ\ mol^{-1}$

$MgCO_3.\textbf{x}H_2O(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + CO_2(g) + (\textbf{x}+1)H_2O(l)$ $\Delta H_{reaction3}$
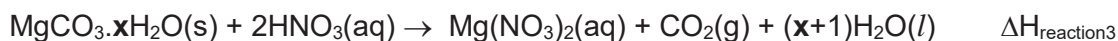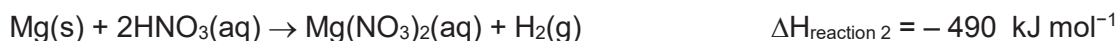
FA 1 is $MgCO_3.\textbf{x}H_2O$ solid.

FA 2 is 2.00 mol dm^{-3} nitric acid, HNO_3.

(a) You are to perform the experiment below.

Determination of $\Delta H_{reaction3}$

1. Place a Styrofoam cup with lid inside a second Styrofoam cup which is held in a glass beaker to prevent it from tipping over.
2. Using a measuring cylinder, place 40.0 cm^3 of **FA 2** into the first Styrofoam cup. Measure and record its initial temperature, T_i.
3. Measure accurately about 1.00 g of **FA 1** in a weighing bottle.
4. Transfer **FA 1** into the Styrofoam cup containing **FA 2** and quickly replace the lid. Stir and measure the highest/lowest temperature obtained. Record this temperature, T_f.
5. Reweigh the weighing bottle.
6. Wash and dry the Styrofoam cups.
7. Record your data in the space provided below. Make certain that the recorded results show the precision of the instrument used.

Results

[3]

(i) Using your results, calculate the amount of heat change, $\Delta q_{reaction3}$, by reaction 3:

[c = 4.18 $Jg^{-1}K^{-1}$, density of water = 1.00 g cm^{-3}]

$$\Delta H_{reaction3}$$
$$MgCO_3.\textbf{x}H_2O(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + CO_2(g) + (\textbf{x}+1)H_2O(l)$$
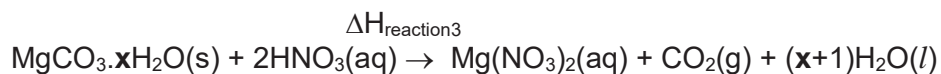
$\Delta q_{reaction3}$ = ...[1]

(ii) Calculate the $\Delta H_{reaction3}$.

(If you were unable to calculate **x** in **1(b)(iv)**, you may assume that **x** = 3 for the calculation here and in part **(b)**. Note: this is a hypothetical value.)

$\Delta H_{reaction3}$ = ...[1]

(b) Determination of $\Delta H_{reaction1}$

It is given that ΔH_f^θ of $CO_2(g)$ and $H_2O(l)$ is −393.5 kJ mol^{-1} and −285.8 kJ mol^{-1} respectively. Using these values together with $\Delta H_{reaction2}$ and $\Delta H_{reaction3}$, construct an energy cycle and calculate a value for $\Delta H_{reaction1}$.

$\Delta H_{reaction1}$ = ...[2]

[Turn over

(c) **(i)** Calculate the percentage error in the measurement of ΔT in the experiment.

percentage error = …………………[1]

(ii) Apart from errors associated with the thermometer, suggest one **significant** source of error in the procedure used in this experiment. Suggest an improvement that could be made to reduce this error.

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…………………………………………………………………………..[2]

(d) **Planning**

In another experiment, you are to plan an experiment to determine the identities of 3 unknown solutions using experimental techniques from thermochemistry.

You are provided with the following:
- solutions of **FB 1**, **FB 2** and **FB 3**, which can be any of the following:
  - 1 mol dm^{-3} aqueous ammonia
  - 1 mol dm^{-3} potassium hydroxide
  - 2 mol dm^{-3} hydrochloric acid
- the apparatus normally found in a school laboratory

In your plan, you should include
- appropriate quantities of solution used,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- an outline of how you would use your results to identify the 3 solutions. (Note: the use of indicator and litmus paper is not allowed)

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[Total: 16]

[Turn over

3   **Determination of the order with respect to Fe^{3+} of the reaction between iron(III) and iodide in acidified medium.**

Iodide ions are oxidised by iron(III) ions in the presence of acid.

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$
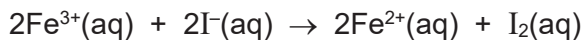
The rate of this reaction can be measured by adding thiosulfate ions, $S_2O_3^{2-}$, and some starch indicator to the mixture. As the iodine is produced, it reacts immediately with the thiosulfate ions and is reduced back to iodide ions.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$
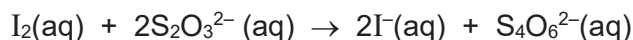
When all the thiosulfate ions have reacted, the iodine which continues to be produced then turns the starch indicator blue-black. The rate of reaction may be determined by timing how long it takes for the reaction mixture to turn blue-black.

You are to investigate how the rate of reaction is affected by changing the concentration of iron(III) chloride.

The general rate equation can be expressed as rate = $k\,[Fe^{3+}]^n[I^-]^p$

As the concentration of iodide is present in high concentration, its concentration stays relatively constant during the course of reaction.

Rate equation thus can be rewritten as: rate = $k'\,[Fe^{3+}]^n$

Taking the logarithm function of the whole equation gives:

$$\lg \text{rate} = \lg k' + n\lg[Fe^{3+}]$$

By plotting a suitable graph, the gradient gives the order of reaction with respect to Fe^{3+}.

You are provided with the following

FA 5 is 0.0500 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3$.

FA 6 is 0.500 mol dm^{-3} aqueous potassium iodide, KI.

FA 7 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.

FA 8 is 0.0500 mol dm^{-3} aqueous iron(III) chloride, $FeCl_3$.

Starch solution

(a) **Procedure**

Experiment 1
1. Fill a burette with **FA 5** and another burette with **FA 8**.

2. Run 20.00 cm^3 of **FA 8** from the burette into a 250 cm^3 conical flask.

3. Use a suitable measuring cylinder to add 20 cm^3 of **FA 7** to the flask.

4. Place a magnetic stir bar into the flask and set it stirring at a constant speed of 600 rpm.

5. Using another suitable measuring cylinder, transfer 20 cm^3 of **FA 6** into a 100 cm^3 beaker.

6. Add to the beaker from the burette 1.00 cm^3 of **FA 5**.

7. Add 1 cm^3 of starch indicator to the mixture in the beaker.

8. Tip the contents of the beaker into the conical flask and immediately start a stopwatch.

9. Observe the solution and stop the time when the solution turns blue-black.

10. Record the time taken to the nearest second.

Experiment 2
Repeat step 1 – 10 **except in step 2**, run 10.00 cm^3 of **FA 8** into the flask and using a suitable measuring cylinder to transfer 10 cm^3 deionised water into the flask.

Experiment 3 – 5
Carry out three further experiments to investigate how the reaction time changes with different volumes of iron(III) chloride.

Do not use a volume of **FA 8** that is less than 6.00 cm^3.

Record all your results in a single table. You should include the volume of **FA 8**, the volume of deionised water and the reaction time. Your recorded results should also include calculated values to enable you to plot

lg (1/time) against **lg (volume of FA 8)**

[5]

(b) (i) Use the grid below to plot a graph of **lg (1/time)** against **lg (volume of FA 8)**.
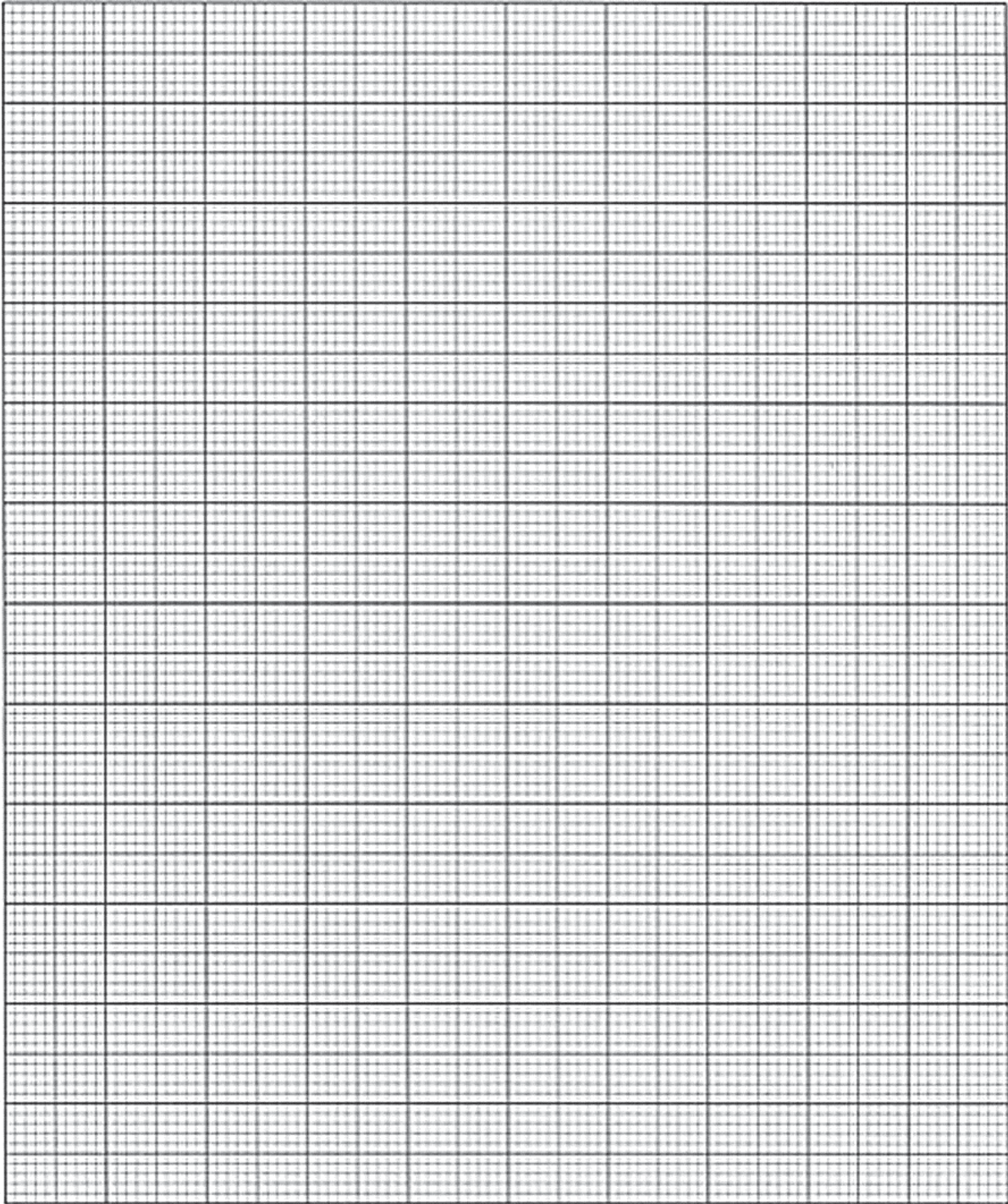
[3]

(ii) From your results, deduce the order of reaction with respect to Fe^{3+}.

order with respect to Fe^{3+} = ………………[2]

[Total: 10]

[Turn over

4   **Qualitative analysis**

In this question, you will deduce the two anions in solution **X** and a cation and an anion in solution **Y**. You will also work with an organic compound **Z**.

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

Test	Procedure	Observations
(a)	To 6 cm^3 of **X**, add barium nitrate solution until in excess.	
(b)	Filter the mixture from **(a)**. Wash and retain the residue for test **(c)**. Collect the filtrate for test **(d)** and **(e)**.	
(c)	To separate portions of the residue **(i)** add 2 cm^3 of hydrochloric acid	
	(ii) add 2 cm^3 of organic compound **Z** [You are to test for any gas evolved]	
(d)	To 1 cm depth of the filtrate from **(b)** in a test-tube **(i)** Add a few drops of organic compound **Z** and warm in a water bath **(ii)** followed by 1 cm^3 of nitric acid and 5 drops of silver nitrate. Add excess ammonia solution.	

(e)	To separate 1 cm depth of **Y** **(i)** add filtrate from **(b)** dropwise until in excess	
	(ii) add NaOH(aq), followed by one spatula of zinc powder and warm (CARE!)	

[5]

(f) **(i)** From the observation in part **(c)(i)** and **(e)(i)**, identify the anion in the residue and the filtrate.

……………………………………………………………………………….[2]

(ii) Suggest two functional groups present in organic compound **Z**. Justify your answer by quoting relevant evidence from the tests carried out.

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……………………………………………………………………………….[2]

(g) Suggest 1 possible identity for the cation and anion present in solution **Y**.

cation: ……………………………….. [1]

anion: ……………………………….. [1]

[Turn over

(h) Planning

Consider the following organic compounds.

benzaldehyde 2-methylpropan-2-ol butan-1-ol propanal

Plan an investigation, using test-tube reactions, which would allow you to identify each of these four organic compounds.

Each compound should be identified by at least one positive test results. It is **not** sufficient to identify a compound simply by eliminating all the others.

Your plan should include:
- details of the reagents and conditions to be used,
- an outline of the sequence of steps you would follow,
- an explanation of how you would analyse your results in order to identify each compound.

Once a compound has been clearly identified, your plan should concentrate on distinguishing the remaining compounds.

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[Total: 17]

[Turn over

GO TO NEXT PAGE FOR QUALITATIVE ANALYSIS NOTES

Qualitative Analysis Notes
[*ppt. = precipitate*]

(a) Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	**NH$_3$(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high $[Ca^{2+}$(aq)$]$	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

[Turn over

(b) Reactions of anions

anions	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated by dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous potassium manganite(VII) from purple to colourless

(d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

NJC H2 Chemistry Prelim Paper 1 Suggested Answers

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

1   Ans: **C**

SO$_2$ reacts with acidified KMnO$_4$
Total vol of SO$_2$ = 10 cm^3

Left over CO$_2$ reacts with NaOH(aq)
Vol of CO$_2$ = 2 cm^3

Vol of SO$_2$ produced from CS$_2$ = 4 cm^3
Vol of SO$_2$ produced from H$_2$S = 10 – 4 = 6 cm^3
Vol of CS$_2$: Vol of H$_2$S = 2 : 6
mole fraction of H$_2$S in the mixture = $\dfrac{6}{8}$ = 0.750

2   Ans: **D**

Step I: Oxidation state of Cr increases from +3 in Cr$_2$O$_4^{2-}$ to +6 in CrO$_4^{2-}$.
Step II: Oxidation state of Cr remains as +6 in both CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$.
$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$
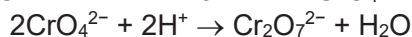
Step III: Oxidation state of Cr decreases from +6 in Cr$_2$O$_7^{2-}$ to +3 in Cr$_2$O$_3$.

3   Ans: **A**

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
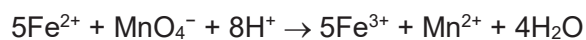
Amount of MnO_4^- required $= \frac{20}{1000} \times 0.40 = 0.008$ mol

Amount of $Fe^{2+} = 5 \times 0.008 = 0.040$ mol

At point X, the reaction is only half completed, $[Fe^{2+}] = [Fe^{3+}]$.

E_{cell} when connected to standard hydrogen electrode = +0.77 V

The colour change at end point is from yellow to first permanent pink.

Vol KMnO$_4$ added	Species present in conical flask	Colour of solution
0	Fe^{2+}(aq)	Pale green
Before eqv pt	Fe^{2+}(aq), Fe^{3+}(aq), Mn^{2+}(aq)	Yellow-green
At eqv pt	Fe^{3+}(aq), Mn^{2+}(aq)	Yellow
Just after eqv pt	Fe^{3+}(aq), Mn^{2+}(aq), small amt of MnO_4^-(aq)	Pink
In excess	Fe^{3+}(aq), Mn^{2+}(aq), large amt of MnO_4^-(aq)	Purple

4   Ans: **C**

Making reference to the I.E. values from Data Booklet, we can conclude that **I** is potassium.

Element **C** is Al, it is in Group 13.

Element **F** is S and it exists as S_8 molecules. The lowest boiling point is Ar gas (element **H**).

Ion of **E** (P^{3-}, 0.212 nm) is larger than that of **J** (Ca^{2+}, 0.099nm)

Element **D** and **G** are Si and Cl respectively. The compound formed is SiCl_4.

5   Ans: **C**

The ionic compound can form strong ion-dipole interaction with polar solvent, making it soluble in polar solvents. The long chain hydrocarbon can also form strong temporary dipole-induced dipole interaction with non-polar organic solvents, making it soluble in organic solvents.

Around S atom, there are 4 bond pair regions and 0 lone pair, the shape is tetrahedral.

All the C atoms are sp^3 hybridised with tetrahedral shape and bond angle of 109.5°

6 Ans: **B**

$pV = nRT$, with n and p kept constant.
As T increases,

Option **A**: V increases. [$V = \dfrac{nR}{p} \times T$]

Option **B**: $\dfrac{pV}{T}$ remains constant. [$\dfrac{pV}{T} = nR$]

Option **C**: Density of the gas deceases [$\dfrac{m}{V} = \dfrac{pM_r}{RT}$]

Option **D**: pV increases. [$pV = nRT$]

7 Ans: **D**

$\Delta H_{rxn} = \Sigma\, \Delta H_f^{\ominus}$ (products) $- \Sigma\, \Delta H_f^{\ominus}$ (reactants)
$-27 = 3 \times (-394) - [\Delta H_f^{\ominus}\ Fe_2O_3 + 3 \times (-110)]$
$\Delta H_f^{\ominus}\ Fe_2O_3 = -825\ kJ\ mol^{-1}$

8 Ans: **D**

The following processes are involved in the Born-Haber cycle for ionic compounds:
1) Enthalpy change of formation of $BaF_3(s)$
2) Enthalpy change of atomisation of $Ba(s)$
3) Bond energy of F−F
4) $1^{st} + 2^{nd} + 3^{rd}$ ionisation energies of $Ba(g)$
5) First electron affinity of F(g)

Ba^{3+} and F^- forms ionic compounds and would not have Ba−F bond energy.

9 Ans: **C**

Note since pressure is kept constant, ICE table **should NOT** be about change in pressure.

	X(g)	$\rightleftharpoons$	Y(g)	+ 2Z(g)
Initial / mol	x		0	0
Change / mol	−y		+y	+2y
Eqm / mol	x−y		y	2y

$P_Y + P_Z = p - 0.25p = 0.75p$
Since Y and Z are in a mol ratio of 1:2, $P_Y = 0.25p$, $P_Z = 0.5p$

$$K_p = \dfrac{(0.25p)(0.5p)^2}{0.25p} = 0.25p^2$$

10 Ans: **A**

Titration of a strong acid (H_2SO_4) with a weak base (NH_3). Equivalent point pH is less than 7 as NH_4^+ is a weakly acidic cation.

Methyl orange will be a suitable indicator as the working pH range of methyl orange coincides with the region of sharp pH change at equivalent point of this titration.

11 Ans: **B**

Since $Ca(OH)_2$ exist as aq and $Mg(OH)_2$ exist as a solid, K_{sp} of $Mg(OH)_2$ must be lower than $Ca(OH)_2$.
$|\Delta H_{hyd}| \propto$ charge density of ion, Mg^{2+} has a more exothermic ΔH_{hyd}.

$|L.E.| \propto \dfrac{q_+ \times q_-}{r_+ + r_-}$, magnitude of L.E. for $Mg(OH)_2$ is greater.

12 Ans: **D**

Since V_{total} is kept constant, volume of reactant used is proportional to its concentration in the final reaction mixture.
Comparing expt 3 and 4, when [P] × 2, initial rate also × 2. It is first order w.r.t **P**.
Comparing expt 4 and 2, when [R] × 2, initial rate × 4. It is second order w.r.t **R**.
Comparing expt 1 and 3, let rate = $k[P][Q]^y[R]^2$

$$\frac{\text{rate } 1}{\text{rate } 3} = \frac{k(10)(10)^y(10)^2}{k(5)(5)^y(10)^2}$$
$4 = (2)(2)^y$
$(2)^y = 2$
It is first order w.r.t **Q**

13 Ans: **A**

Since $E^{\ominus}(MnO_4^-, H^+/Mn^{2+}) = +1.52$ V is greater than $E^{\ominus}(Cu^{2+}/Cu) = +0.34$ V, the reduction half-cell is $MnO_4^-, H^+/Mn^{2+}$ and oxidation half-cell is Cu^{2+}/Cu.
$E^{\ominus}_{cell} = E^{\ominus}(MnO_4^-, H^+/Mn^{2+}) - E^{\ominus}(Cu^{2+}/Cu)$

A	When excess NH_3 is added to Cu^{2+}/Cu half-cell, the half-cell become $[Cu(NH_3)_4]^{2+}/Cu$, $E^{\ominus} = -0.05$ V and $E^{\ominus}_{cell}$ increases.
B	When additional H^+ is added into $MnO_4^-, H^+/Mn^{2+}$ half-cell, the position of equilibrium for $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ shifts to the right, $E^{\ominus}(MnO_4^-, H^+/Mn^{2+})$ increases and $E^{\ominus}_{cell}$ increases.
C	Size of electrode does not affect $E^{\ominus}(Cu^{2+}/Cu)$ as solids does not affect position of equilibrium.
D	When alloy of copper and zinc is present, Zn reacts with Cu^{2+} to give Zn^{2+} and $Cu(s)$. The concentration of Cu^{2+} decreases and position of equilibrium for $Cu^{2+} + 2e^- \rightleftharpoons Cu$ shifts to the left, $E^{\ominus}(Cu^{2+}/Cu)$ decreases and $E^{\ominus}_{cell}$ increases.

14 Ans: **C**

$E^o(Fe^{2+}/Fe)$ -0.44 V $E^o(H^+/H_2)$ +0.20 V $E^o(AgCl//Ag)$

Increasing E^o

-0.64 V
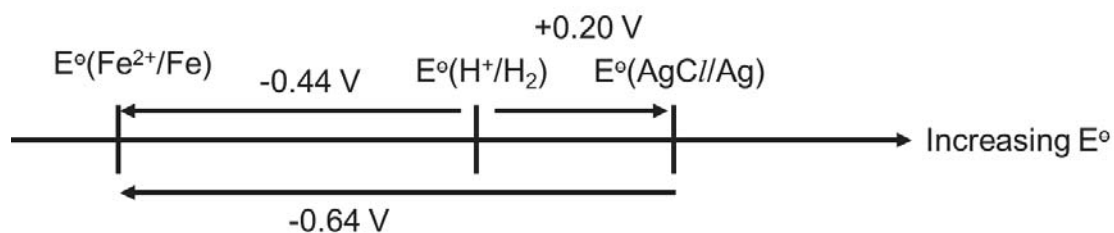
15 Ans: **C**

This is the simplified electrolytic cell.

e^- e^-

Zn   Cu

$NaNO_3(aq)$
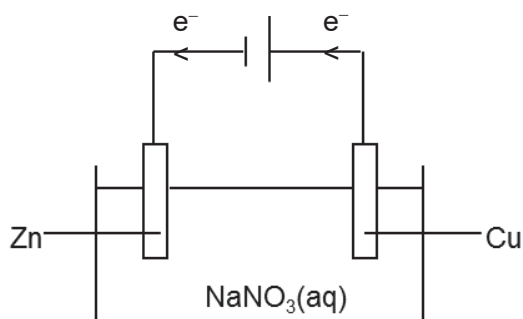
Species present: Na^+ (aq), NO_3^- (aq), H_2O, Zn cathode, Cu anode
At cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
At anode: $Cu \rightarrow Cu^{2+} + 2e^-$
The filter paper will turn blue due to the formation of $Cu^{2+}(aq)$
Note: this is not a litmus paper.

16 Ans: **C**

A	Melting point: $SiO_2 > Na_2O > P_4O_{10}$ SiO_2 (covalent lattice with strong covalent bond) Na_2O (ionic lattice with strong ionic bond) P_4O_{10} (simple molecular with weak IMF)
B	Covalent character: $P_4O_{10} = SiO_2 > Na_2O$
C	pH when mixed with water: Na_2O (pH = 14) > SiO_2 (pH = 7) > P_4O_{10} (pH = 3)
D	Na_2O is soluble in aq alkali due to reaction of Na_2O with H_2O to give NaOH. SiO_2 is insoluble in aq alkali due to strong covalent bond in the covalent lattice. P_4O_{10} is soluble in aq alkali due to reaction of P_4O_{10} with NaOH to give Na_3PO_4.

17 Ans: **B**

$M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + \frac{1}{2} O_2(g)$ (option 2 is correct)
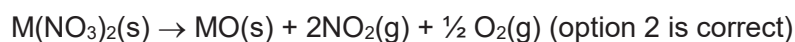
Ionic radius of Mg^{2+} is smaller than Ba^{2+}. Mg^{2+} has a higher charge density and stronger polarising power. Mg^{2+} is able to distort electron cloud of NO_3^- to a larger extent and N–O covalent bond in $Mg(NO_3)_2$ is weakened significantly. Hence $Mg(NO_3)_2$ decompose at a lower temperature. (option 1 is correct).

$|L.E.| \propto \dfrac{q_+ \times q_-}{r_+ + r_-}$, magnitude of L.E. for $Mg(NO_3)_2$ is greater. However, N–O covalent bond is broken during thermal decomposition and hence we should not even be comparing the lattice energy.

18 Ans: **A**

Before heating, YCl_n reacts with $AgNO_3$ to produce 8.368×10^{-3} mol of $AgCl$.
After heating, the product reacts with $AgNO_3$ to produce 5.021×10^{-3} mol of $AgCl$.

This shows that Y can form two chlorides with different oxidation state.
Y must be from Group 15 (e.g. PCl_5 and PCl_3)
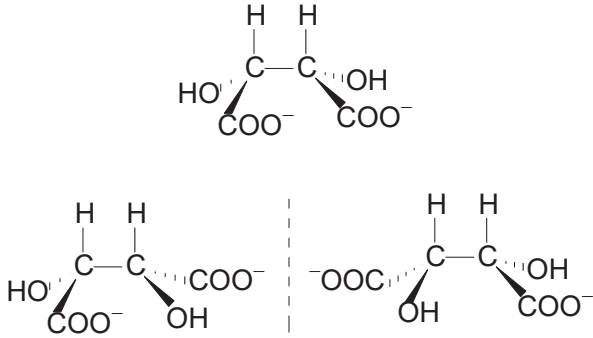
1 mol of YCl_5 gives 5 mol of Cl^-
Amount of $YCl_5 = (8.368 \times 10^{-3}) \div 5 = 1.674 \times 10^{-3}$ mol
M_r of $YCl_5 = 0.50 \div 1.674 \times 10^{-3} = 298.8$
A_r of Y $= 298.8 - 5 \times 35.5 = 121.3$
Y is Sb

19 Ans: **D**

Down Group 17,
- Thermal stability of HX decreases due to weaker bond energy
- Enthalpy change of formation becomes less exothermic (calculate using BE values)
- The ease of oxidation increases as $E^{\ominus}(X_2/X^-)$ decreases down the group.

20   Ans: **B**

A	The tartrate ion acts as a Bronsted acid, it donates 2 H^+ to react with 2 OH^- and form the new ligand.
B	There are 2 chiral carbons for tartrate ion with 4 possible stereoisomers. However due to internal line of symmetry, 2 of the isomers are identical (they are known as the meso compound). Hence there are only 3 stereoisomers.
C	The coordination number of the complex ion is 4. (4 dative bonds)
D	The oxidation number of Cu in the complex ion is +2. The ligands each have a charge of -3 after losing a H^+ from the tartrate ion.

21   Ans: **D**

There are a total of 6 central atoms with tetrahedral electron geometry. Hence, these 6 atoms are sp^3 hybridised. Take note that for the case of O and N in the molecule, the lone pair sits in the sp^3 orbital.

22 Ans: **B**

OH
|
H—C—CH$_2$CH$_3$
|
H
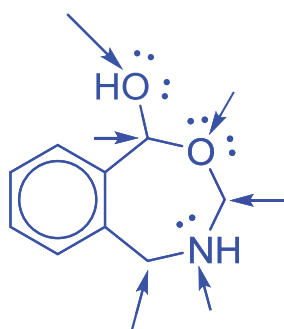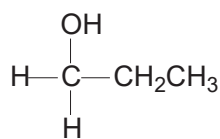
is the minor product from the addition reaction due to the lower stability of the carbocation intermediate.

23 Ans: **D**

4 moles of CO_2 can be obtained from the reaction of compound **A** with hot excess acidified $KMnO_4$.
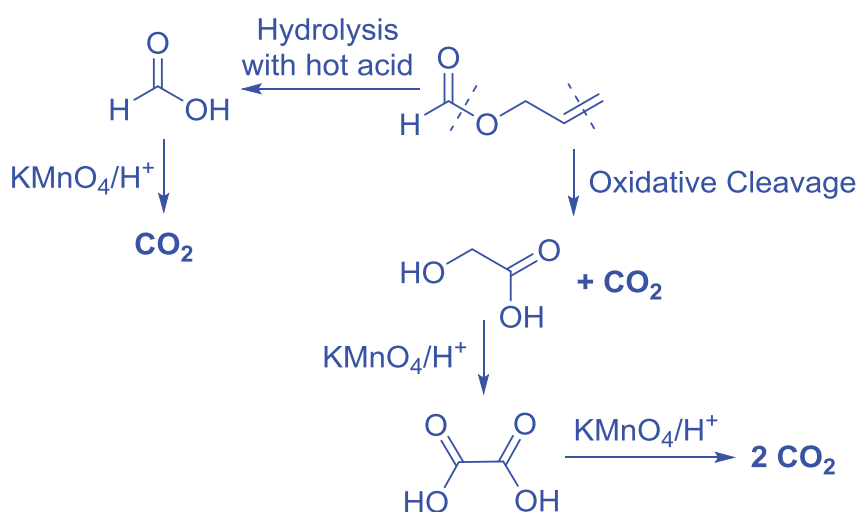
Since 1 mole of $CaCO_3$ can be obtained from every mole of CO_2 produced,
Mass of $CaCO_3$ = 4 x 100.1 = **400.4** g

24 Ans: **C**

The molecular formula is $C_8H_9NO_5$. **(option 1 is wrong)**

There are 2 chiral carbons with 1 C=C bond capable of cis-trans isomerism. Hence total number of stereoisomer = 2^3 **(option 2 is correct)**

HBr(g) reacts with alkene and alcohol groups, 2 Br atoms are found in the product. **(option 3 is correct)**

LiA*l*H$_4$ reduces carboxylic acid and amide but not alkene. Only 4 H atoms are found in the product. **(option 4 is wrong)**

25 Ans: **C**

The energy profile diagram suggests the substitution proceeds in 2 steps, meaning it is an S_N1 reaction. This would mean that the rate = k [$(CH_3)_3CCl$]. Overall order of reaction would be 1 (**option 2 is correct**). [OH^-] would not affect the rate of reaction (**option 4 is wrong**).Intermediate Z is the carbocation (**option 1 is wrong**).

Rate of reaction is also not based on products. There is also no equilibrium established in this question. Le Chatelier's Principle does not apply in this question. Removal of product does not cause any increase in the yield (**Option 3 is correct**).

26 Ans: **D**

$NaBH_4$ only reacts with carbonyl groups. $H_2(g)$, Ni(s) can react with alkene, carbonyl and nitrile group.

27 Ans: **B**

Acyl chloride reacts readily with water to give Cl^-.
Alkyl halide reacts with hot OH^-(aq) to give Cl^-.
$C-Cl$ bond in chlorobenzene and Cl bonded directly to C=C has a partial double bond character due to delocalisation of lone pair electron of Cl into the neighbouring π electron cloud. These $C-Cl$ bond will not break upon heating with OH^-(aq)

28 Ans: **A**

$-OH$ in phenol is 2, 4 directing w.r.t the $-OH$ group, dilute HNO_3 will only lead to mono nitration.

29 Ans: **C**

The cyanohydrin product from propanone does not contain a chiral centre, only one product $CH_3C(OH)(CN)CH_3$ is formed. Hence it cannot be considered as racemic mixture

$\delta+$ C atom in propanal experiences less steric hindrance and is able to react with the nucleophile CN^- at a faster rate. Furthermore, there are 2 electron donating alkyl groups bonded directly to the $\delta+$ C atom in propanone, decreasing the magnitude of $\delta+$ on the C atom. Hence propanone reacts with the nucleophile CN^- at a slower rate.

The cyanohydrin product $CH_3C(OH)(CN)CH_3$ reacts with hot NaOH(aq) to give pungent NH_3 gas which turns moist red litmus paper blue.

30   Ans: **C**

A CH_3CH_2CN $\xrightarrow[\text{D}Cl,\ \text{heat}]{\text{D}_2\text{O}}$ $CH_3CH_2COOD + NH_4^+$

B CH_3COCHI_2 $\xrightarrow[\text{D}_2\text{O, warm}]{\text{I}_2,\ \text{NaOD}}$ $CH_3COO^- + CDI_3$

C   ⬡—COCl $\xrightarrow[\text{KOD}]{\text{D}_2\text{O}}$ ⬡—COO$^-$ + KCl

D $CH_3CH_2CONHCH_3$ $\xrightarrow{\text{LiA}l\text{D}_4}$ $CH_3CH_2CD_2NHCH_3$ + D_2O
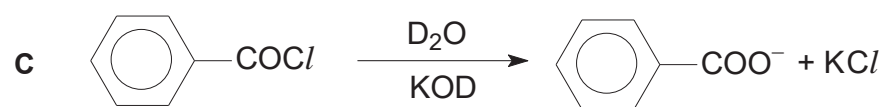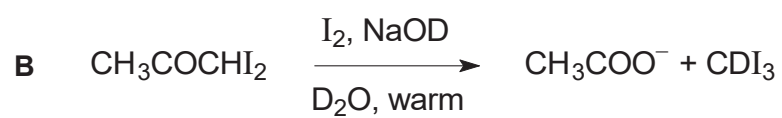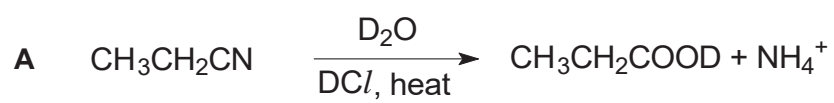
NJC H2 Chemistry Prelim Paper 2 Suggested Answers

1 **(a)** Due to **high temperature in the car engine**, **N_2 and O_2 from the air** can react to form NO_2.

NO$_2$ can be removed from the exhaust gas with the use of a **catalytic converter**, it can be **reduced by CO** to form harmless N_2.

(b) **(i)**

(ii) NO_2, being a **radical**, is **very reactive** and reacts with other gases in the air and gets destroyed more readily, hence a shorter atmospheric residence time

(c) **(i)** $\Delta H^\ominus = +9.2 - 2(+33.2) = -57.2$ kJ mol^{-1}

$\Delta S^\ominus = +304 - 2(+240) = -176$ J mol^{-1} K^{-1}

(ii) $\Delta H^\ominus$ has a negative sign since the dimerization is a **bond formation process**, hence heat is given out / reaction is exothermic.

$\Delta S^\ominus$ has a negative sign since the dimerization results in **fewer gas particles**, hence there is a decrease in the disorderliness of the system.

(iii) At equilibrium,

$\Delta G = 0$
$\Delta H^\ominus - T\Delta S^\ominus = 0$
$-57.2 - T(-176/1000) = 0$

$T = 325$ K

(iv) When N_2O_4 liquefies,
$\Delta G = 0$
$\Delta H_{vap} - T\Delta S_{vap} = 0$
$\Delta H_{vap} = T\Delta S_{vap} = 294 \times 88 = +25.9$ kJ mol^{-1}

(iv) Using **Hess's law**,
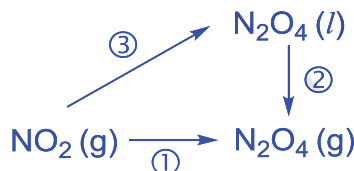
$② = ① - ③$
For $\Delta H_{rxn} = -57.2 - +25.9 = -83.1$ kJ mol^{-1}
For $\Delta S_{rxn} = -176 - 88 = -264$ J mol^{-1} K^{-1}

2 **(a)** **(i)** H_2O_2 oxidises the I$^-$, to aqueous I_2, so a **brown solution** / **black solid** would be obtained.
$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$

(ii) $E^{\theta}_{Cl_2/Cl^-} = +1.36$ V

$E^{\theta}_{H_2O_2/H_2O} = +1.77$ V

$E^{\theta}_{cell} = +0.41$ V > 0
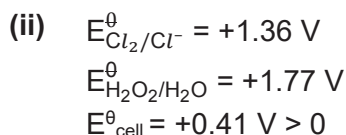
Since E^{θ}_{cell} is positive, reaction is spontaneous, H_2O_2 can oxidise chloride to chlorine while it itself is reduced to H_2O.

Hence, the oxidation of iodide may not be complete.

(iii) hexane / cyclohexane

The aqueous layer will **decrease in brown intensity** and the colourless organic layer will turn **purple / violet**.

(iv) Organic solvent is **flammable**, and can **cause a fire to break out**.

With higher temperature, iodine may **sublime** and escape.

(v) **Excess aqueous NH₃** should be added.

$AgCl$ is soluble in excess NH_3(aq) but AgI is not. If there was significant amount of silver chloride in the precipitate obtained, most of the precipitate dissolved upon adding excess aqueous NH_3

(b) **(i)** Amount of thioanisole used $= \frac{0.9 \times 1.06}{124.1} = 0.007687$ mol

Amount of $NaIO_4$ used $= \frac{107 \times {}^{15.40}/_{1000}}{214.0} = 0.0077$ mol
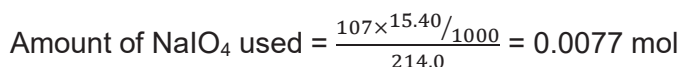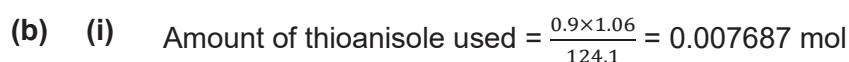
$\therefore$ $NaIO_4$ reacts with thioanisole in a 1:1 mol ratio.

(ii) $C_6H_5SCH_3 + NaIO_4 \rightarrow C_6H_5SOCH_3 + NaIO_3$

(iii)
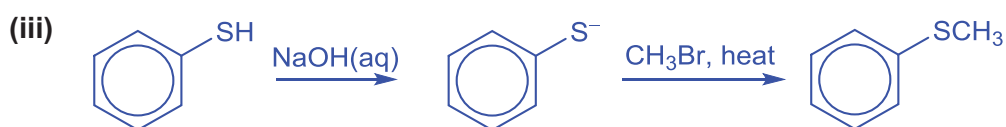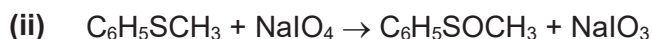
(c) As a reducing agent, H_2O_2 will be oxidized.
Quote both eqns and $E^{\ominus}$
(In acidic) $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^{\ominus} = +0.68$ V
(In alkaline) $O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$ $E^{\ominus} = -0.08$ V
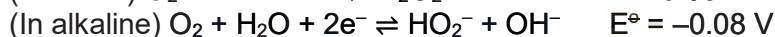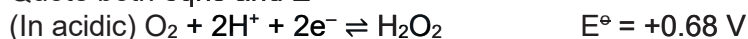
Due to a more negative $E^{\ominus}$ value, HO_2^- is more likely to be oxidised than H_2O_2. H_2O_2 is a better reducing agent in alkaline condition.

3 **(a)**

U
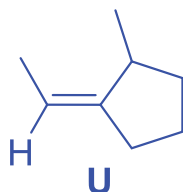
(b) Reagents : Dilute $KMnO_4$, NaOH(aq)

Conditions : cold

(c) Structure of carbocation intermediate
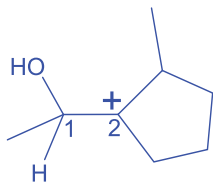
The carbocation ion would be formed at C_2 as it will form a more highly substituted carbocation than if the C+ is formed on C_1. OR

The carbocation would be formed at C_2 as it will have **more** electron donating alkyl group attached to C_2 than if the C+ is formed at C_1

(d)

X

Y

(e) **(i)**

W

(ii) $2^3 = 8$

(f)

W

Step **1**

OH

Step **2**

Z
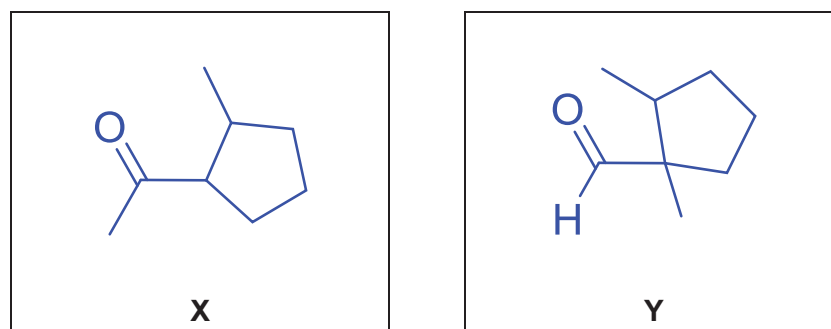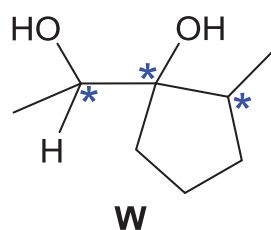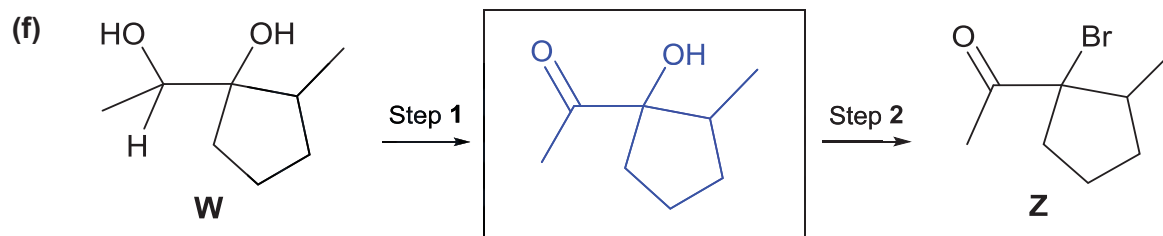
Reagents and Conditions

Step **1** $KMnO_4$, H_2SO_4(aq), heat (or $K_2Cr_2O_7$, H_2SO_4, Heat [under reflux])

Step **2** Anhydrous PBr_3 (or $SOBr_2$ or HBr(g))

4 **(a)** **(i)** NaOH(aq), heat

(ii) Since the [OH⁻] decreases linearly over time with fixed gradient, rate of reaction remains the same throughout the whole experiment, the order or reaction with respect to OH⁻ is 0.

Comparing the time taken for 0.4 mol dm⁻³ of OH⁻ being reacted, it takes a half the time for sample with 0.5 mol dm⁻³ of **P** (13 mins) than that of 0.25 mol dm⁻³ of **P** (26.5 mins). This means when the [**P**] is doubled, the rate is also doubled. The order of reaction with respect to **P** is 1.

Rate Equation :   Rate = k [Compound **P**]

(iii) Nucleophilic Substitution (S$_N$1)
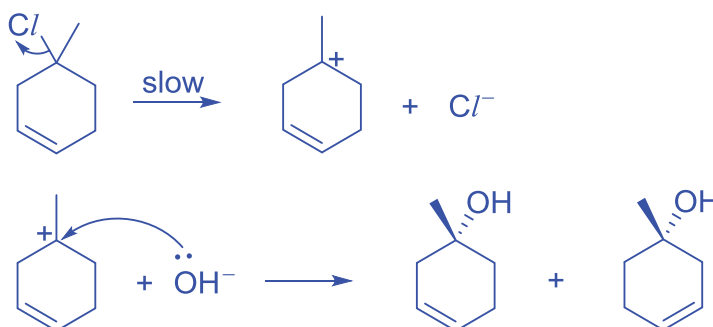
(iv) There is no optical activity present in the products.

Trigonal planar carbocation intermediate allows nucleophile to approach from top and bottom of the plane at equal probability producing equimolar of enantiomers forming a racemic mixture. The effect of rotation of plane polarised light by one enantiomer is <u>completely cancel</u> by the other enantiomer resulting in lack of optical activity.

(v) Trend: R–I, R–Br, R–Cl

Rate of this nucleophilic reaction depends on the breaking of the C–X bond. C–I bond (240 kJ mol⁻¹) is the weakest as compared to C–Br (280 kJ mol⁻¹) and C–Cl (340 kJ mol⁻¹). C–I bond is the easiest to be broken and hence would take the shortest time to complete the substitution (highest rate). C–Br bond is weaker than C–Cl, so C–Br would be easier to break and take shorter time than C–Cl.

(b) **(i)** 75% yield = 20 g
100% yield = 20 x 4/3 = 26.67g
Amount of diphenylethandioate = 26.67 ÷ 242 = 0.11021 mol
Amount of phenol = 0.11021 x 2 = 0.22042 mol
Mass of phenol used = 0.22042 x 94 = 20.7 g

(ii) Add neutral FeCl₃ (aq). Reaction is completed when there is no formation of violet complex, indicating that all phenol have been reacted.

OR

Add aqueous Br_2. Reaction is completed when orange aqueous Br_2 do not decolourise upon addition, indicating all phenol have been reacted. Reaction is incomplete when orange aqueous Br_2 decolorised and white precipitate formed.

OR

Add Br_2 in CCl_4. Reaction is completed when orange-red Br_2 do not decolourise upon addition, indicating all phenol have been reacted. Reaction is incomplete when orange-red Br_2 decolorised.

5 (a) (i) Oxidation state of C_1 in vitamin C   :   +1

Oxidation state of C_1 after oxidation :   +2

(ii)

$+$ $2 H^+$ $+$ $2e^-$
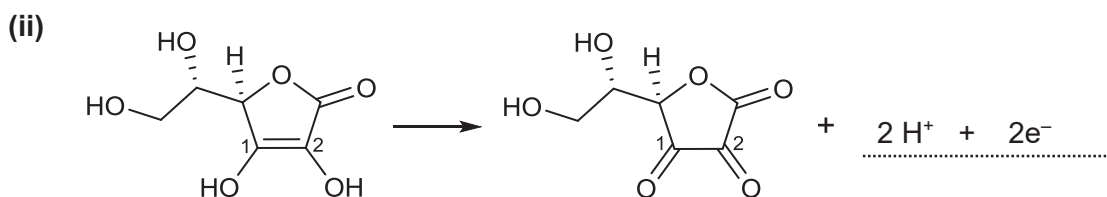
(b) (i) 5 million red blood cells contain 150 mg of haemoglobin.

Mass of haemoglobin in 10000 million red blood cells

$= \frac{10000}{5} \times 150 = 300000$ mg

Mass of iron in 10000 million red blood cells

$= \frac{4}{100} \times 300000$ mg $= 12000$ mg $= 12$ g

Amount of iron required $= \frac{12}{55.8} = 0.215$ mol

(ii) Red blood cell has a lifespan of 120 days. However, even when the red blood cells dies, some of the **iron still remains in the body for further use.**

(c) (i)

d_{z^2}

$d_{x^2-y^2}$

d_{xy}

d_{xz}

d_{yz}
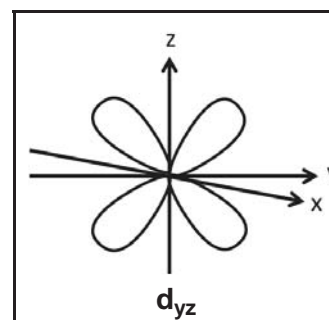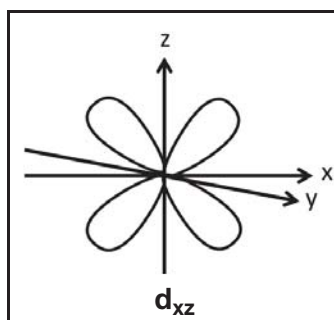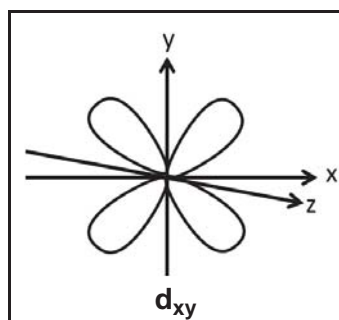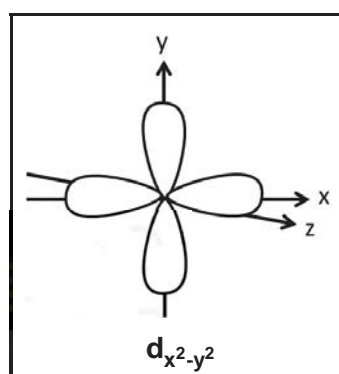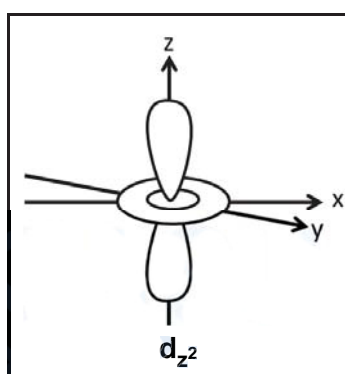
(ii) In the presence of ligands, the d-orbitals of the transition element ion are split into two different energy levels with a small energy gap, ΔE.

Electrons in the lower energy d-orbitals can absorb light of a certain wavelength with energy corresponding to the energy gap, ΔE, and be promoted to the higher energy d-orbitals **(d-d transition)**.

The light not absorbed would be reflected and the colour of the complex is the **complementary** of the wavelength absorbed.

(d)

(i) $1s^2\ 2s^2\ 2p^6\ \ \underline{3s^2\ 3p^6\ 3d^8}$

(ii)

Tetrahedral complex   Isolated gaseous Ni^{2+} Square planar complex
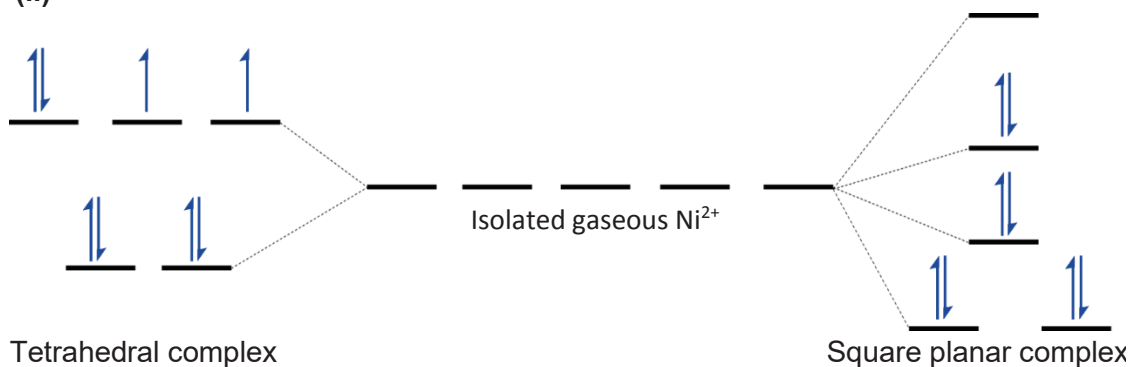
(iii) Square planar [only contains paired electrons in the d orbitals]

(e) **(i)** Condensation (also accept nucleophilic substitution or nucleophilic acyl substitution)

(ii) Heating under reflux with conc HCl will cause the hydrolysis of the amide group in luminol.

(iii) Luminol is less basic as compared to N_2H_4.
The lone pair on all N of luminol are involved in delocalization with the neighbouring benzene and C=O groups. As such, they are less available for donation to H$^+$ and act as a base. The lone pair on N of N_2H_4 do not undergo such delocalization and is more available for donation to H$^+$.

NJC H2 Chemistry Prelim Paper 3 Suggested Answers

1 (a) (i) $BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$
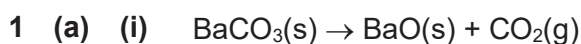
(ii)
- Down the group, cations of Group 2 metals have the same charge but their size increases. The $\frac{charge}{size}$ ratio of the cation decreases. This leads to a decrease in polarising power.
- The electron clouds in the carbonate anion is being distorted to a smaller extent down the group and the weakening of C–O bond is less significant down the group.
- More energy is required to break the C–O bonds in the carbonate anion down the group.
- Therefore, the ease of thermal decomposition of the carbonates decreases down the group.

(b) (i)
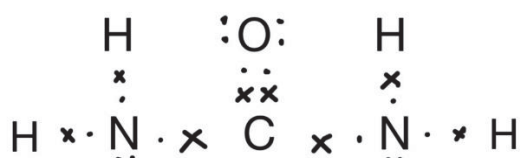
Shape: trigonal planar
Bond angle: 120 °

(ii) Reaction 1: $(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2$

Reaction 2: $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$
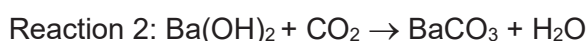
(c) (i) $K_a = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$

$K_a = \frac{(x)^2}{0.100-x} = 4.3 \times 10^{-7}$ mol dm^{-3}

$[H^+] = \sqrt{4.3 \times 10^{-7} \times 0.1} = 2.074 \times 10^{-4}$ mol dm^{-3}

pH = 3.68

(ii) $H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + 2H_2O$

Amount of $H_2CO_3 = \frac{25}{1000} \times 0.1 = 0.0025$ mol

Amount of NaOH required = 0.005 mol
Volume of NaOH required $= \frac{0.005}{0.125} = 0.04$ dm^3 = 40.0 cm^3

(iii) At maximum buffering capacity,
pH = pK_{a1}
= 6.37

(iv) From part (ii), 40 cm³ of NaOH is required to completely neutralise the 2 H⁺ from H_2CO_3.

When 20 cm³ of NaOH is added, only 1 H⁺ from H_2CO_3 will react with NaOH

	OH⁻	+ H_2CO_3	$\rightarrow$	HCO_3^-	+ H_2O
Initial / mol	0.0025	0.0025		0	-
Change / mol	−0.0025	−0.0025		+0.0025	-
Final / mol	0	0		0.0025	-

$[HCO_3^-]$ = 2.50 × 10⁻³/ (0.02 + 0.025) = 0.05556 mol dm⁻³

HCO_3^- acts as a weak base that dissociates partially.
$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$
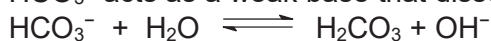
$K_b = \dfrac{[H_2CO_3][OH^-]}{[HCO_3\text{-}]}$

$K_b = \dfrac{(x)^2}{0.05556-x} = \dfrac{1\times10^{-14}}{4.3\times10^{-7}}$ = 2.325 × 10⁻⁸ mol dm⁻³

$x = [OH^-]$ = 3.595 × 10⁻⁵
$pOH = -lg[OH^-]$ = 4.44
pH = 9.56

(v)

(d) (i) $BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$
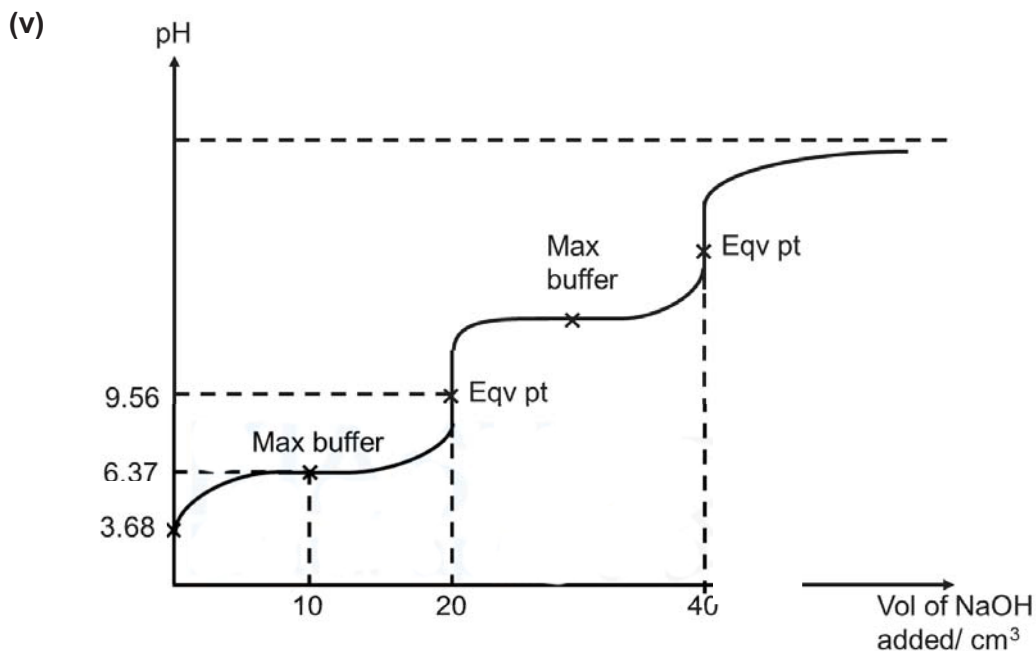
Let solubility of $BaCO_3(s)$ be s
$K_{sp} = [Ba^{2+}][CO_3^{2-}] = s^2 = 5.5 \times 10^{-10}$
s = 2.35 × 10⁻⁵ mol dm⁻³

(ii) $BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$ --- eqm (1)
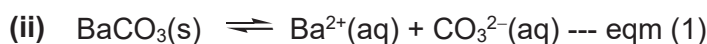
When ingested by mouth, the H^+ in stomach will react with CO_3^{2-} to form H_2CO_3 or CO_2. $[CO_3^{2-}]$ will decrease and equilibrium (1) will shift right. $BaCO_3$ will be more soluble in presence of H^+ and produces more Ba^{2+}, resulting in concentration of Ba^{2+} to exceed 0.100 mol dm^{-3}.

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ --- eqm (2)
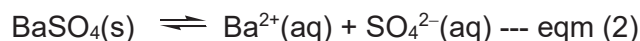
$[SO_4^{2-}]$ remains unchanged as SO_4^{2-} does not react with H^+. Hence, there is no shift in the position of equilibrium in (2). Concentration of Ba^{2+} is not affected and will not exceed the lethal level of 0.100 mol dm^{-3}

(e) $\Delta H_{sol}^{\ominus} = \Sigma\Delta H_{hyd}^{\ominus} - LE$

$\Delta H_{sol}^{\ominus}$ of $CaSO_4 = -1577 - 1099 + 2374$
$\qquad\qquad = -302$ kJ mol^{-1} [1]

$\Delta H_{sol}^{\ominus}$ of $BaSO_4 = -1305 - 1099 + 2480$
$\qquad\qquad = +76$ kJ mol^{-1} [1]

The $\Delta H_{sol}^{\ominus}$ of $CaSO_4$ is more negative compared to $BaSO_4$. $CaSO_4$ is more soluble than $BaSO_4$.

A negative $\Delta H_{sol}^{\ominus}$ shows that the aq ions of $CaSO_4$ are more stable than the ionic solid. Linking to $\Delta G = \Delta H - T\Delta S$, a more negative ΔH value will give a more negative ΔG value. Hence the reaction is more likely to be energetically feasible.

2 (a) (i)
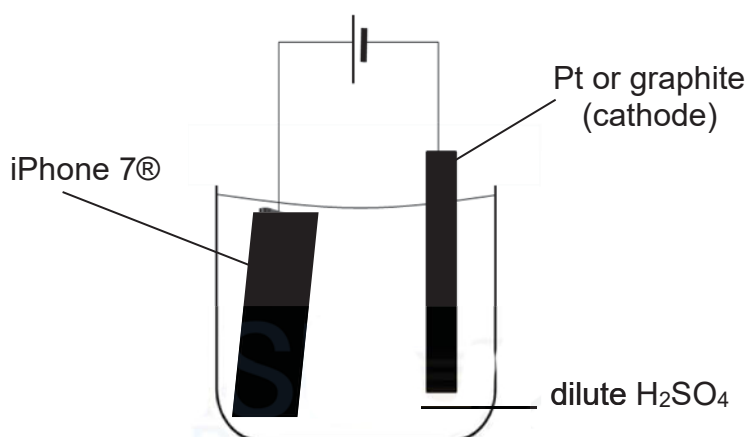
Item **to be anodised placed at anode**

Correct inert metal / graphite used as cathode

Clear and labelled diagram

Use of battery

(ii)
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
$2Al(s) + {}^3/_2O_2(g) \rightarrow Al_2O_3(s)$
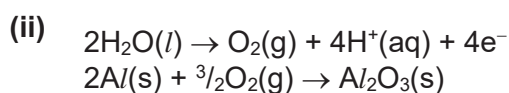
(iii) Volume of Al_2O_3 required $= 93.0 \times 0.02 = 1.86$ cm^3
Mass of $Al_2O_3 = 3.95 \times 1.86 = 7.347$ g
No. of moles of $O_2 \quad = {}^3/_2 \times$ No of moles of Al_2O_3
$\qquad\qquad\qquad\qquad = {}^3/_2 \times \dfrac{7.347}{102} = 0.1080$ mol

No of moles of electrons passed $= 0.1080 \times 4 = 0.4322$ mol
$Q = 0.4322 \times 96500 = 41705$ C

Time needed $= 41705 \div 2.0 = 20853 = 2.09 \times 10^4$ s (3 s.f.)

(b) **(i)** Fe^{3+} has high charge/size and is able to distort the electron cloud of water molecules, breaking the O-H bonds and release H^+
OR $[Fe(H_2O)_6]^{3+} \;\rightleftharpoons\; [Fe(H_2O)_5(OH)]^{2+} + H^+$
H^+ reacts with carbonate to form CO_2. $Fe(OH)_3$ is the red-brown ppt.

(ii) $Fe^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Fe(OH)_2(s)$ green ppt
$[Fe(H_2O)_6]^{2+}(aq) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{4-}(aq) + 6H_2O(l)$ formation of coloured solution
OR $Fe(OH)_2(s) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{4-}(aq) + 2OH^-(aq)$

(c)

	Ru	N	Cl	H
Mass in 100 g	36.9	30.7	25.8	6.6
Amount	36.9 / 101.1 = 0.365	30.7 / 14 = 2.193	25.8 / 35.5 = 0.7268	6.6 / 1.0 = 6.6
Simplest ratio	0.365 / 0.365 = 1	2.193 / 0.365 = 6	0.7268 / 0.365 = 2	6.6 / 0.365 = 18

There are 2 moles of free Cl^- ions. The remaining N and H must be from 6 NH_3 ligands.
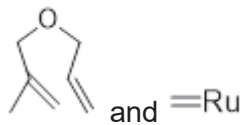
Hence, molecular formula of orange compound is $[Ru(NH_3)_6]Cl_2$.
accept $RuN_6H_{18}Cl_2$
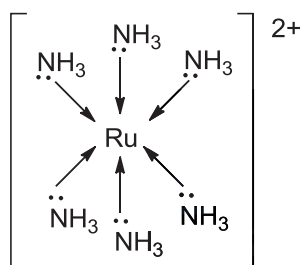
(d) **(i)** Ethene

(ii) Two possible answers:

Step 4: $\longrightarrow$ $+$ $=$Ru

Step 4: $\longrightarrow$ $+$ $=$Ru

(iii) and $=$Ru

(e)

T:

U:

V:

 undergoes internal acid-base reaction to give V
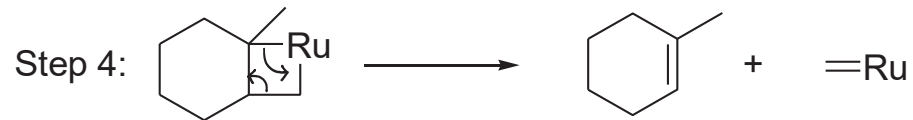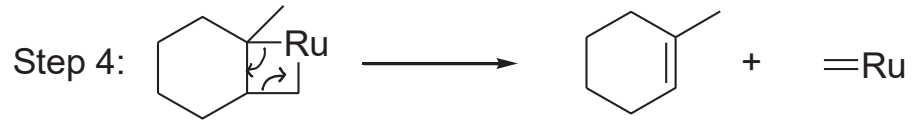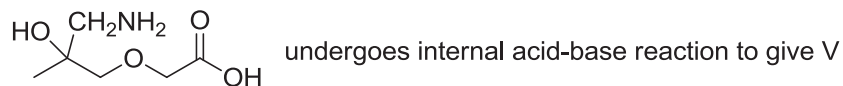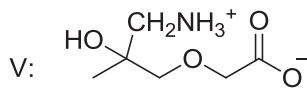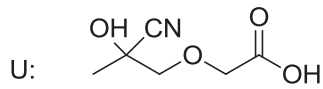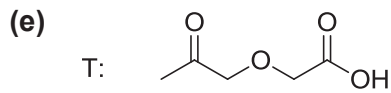
3 (a) (i)

$$K_a = \frac{[Cy][H^+]}{[CyH^+]}$$

(ii) $[H^+] = 10^{-5.3}$

$$K_a = \frac{[Cy][H^+]}{[CyH^+]}$$

$$5 \times 10^{-5} = \frac{[Cy][10^{-5.3}]}{[CyH^+]}$$

$$\frac{[CyH^+]}{[Cy]} = \frac{[10^{-5.3}]}{[5 \times 10^{-5}]}$$

$$= 0.100$$

OR pH = pK_a + lg $\frac{[Cy]}{[CyH^+]}$

$$5.3 = -\lg(5 \times 10^{-5}) + \lg \frac{[Cy]}{[CyH^+]}$$

$$\lg \frac{[Cy]}{[CyH^+]} = 0.9990$$

$$\frac{[Cy]}{[CyH^+]} = 10^{0.9990} = 9.976$$

$$\frac{[CyH^+]}{[Cy]} = (1 \div 9.976) = 0.100 \text{ (3sf)}$$

Since concentration of Cy is much greater than CyH^+, the dominant species is Cy. Hence, the colour of the solution will be purple colour.

(b) (i)

$$K_c = \frac{[CySO_3H_2][H^+]}{[CyH^+][SO_2]}$$

$[H^+] = 10^{-3.0}$ mol dm^{-3}

Let initial concentration of CyH^+ be x mol dm^{-3}

$$[CyH^+]_{eqm} = \frac{1}{10}x \text{ mol dm}^{-3}$$

$$[CySO_3H_2]_{eqm} = \frac{9}{10}x \text{ mol dm}^{-3}$$

$$K_c = \frac{[CySO_3H_2][H^+]}{[CyH^+][SO_2]} = \frac{[(9/10)x][10^{-3.0}]}{[(1/10)x][1 \times 10^{-2}]} = 0.9$$

(ii) The decolourisation of the preserved fruit juice will be more severe at pH = 4.0.
At higher pH, $[H^+]$ is lower. According to Le Chatelier's principle, position of equilibrium (I) will shift to the right to increase $[H^+]$, thereby reducing the amount of cyanidin to a greater extent.

(c)

Information	Deduction
Both **J** and **K** react with sodium carbonate	**J** and **K** undergoes acid base reaction with sodium carbonate. ➜ Both compounds contain –carboxyl (COOH) group.
Both **J** and **K** react with acidified $K_2Cr_2O_7$, but not with 2,4–dinitrophenylhydrazine.	**J** and **K** undergoes oxidation reaction with $K_2Cr_2O_7$. ➜ Both compounds are not carbonyl compound and contain 1°/2°alcohol.

Both **J** and **K** react with excess hot concentrated H_2SO_4, but only **J** gives a mixture with a pair of cis-trans isomers.	**J** and **K** undergoes elimination of H_2O to form alkene. Alkenes obtained from **J** exhibited cis-trans isomerism, but not that of **K** (terminal alkene).
A 0.234 g sample of **J** reacts completely with 35 cm³ of 0.10 mol dm⁻³ NaOH.	**J** undergoes neutralisation/acid base reaction with NaOH. Amt of **J** = $\dfrac{0.234}{134}$ = 1.746 x10⁻³ mol Amt of NaOH = 3.5 x 10⁻³ mol Mole ratio of **J**: NaOH is 1:2 **J** is dibasic acid which contains two COOH groups. Given M_r of **J** = 134, $2 \times M_r(COOH) + M_r(OH) + M_r(C_xH_y) = 134$ 2(45) + (17) + x(12) + y(1) = 134 107 + x(12) + y(1) = 134 x(12) + y(1) = 27 x = 2 and y = 3
K give a yellow precipitate with alkaline aqueous iodine.	**K** undergoes mild oxidation with alkaline aqueous iodine. **K** contains the following structure
A 7.5 x 10⁻⁴ mol of **K** produces 18 cm³ H_2 gas at r.t.p. when excess Na is added.	**K** undergoes redox/ acid metal reaction with Na. Amt of H_2 liberated = 18/24000 = 7.5 x 10⁻⁴ mol Mole ratio of **K**:H_2 is 1:1 **K** contains two OH groups (make up of 1 COOH and 1 OH group). Given M_r of **K** = 90, $1 \times M_r(COOH) + M_r(CH_3CH(OH)) = 90$

J:

K:

(d) In conjugate base of pyruvic acid, <u>the negative charge on O of COO⁻ can delocalise over **3** oxygen atoms</u> which <u>disperse the negative charge to greater extent</u> as compared to the <u>delocalisation of the negative charge of O of COO⁻ between **2** oxygen atoms and the benzene ring in the benzoate ion</u>.

or Presence of the additional <u>electron withdrawing C=O group</u> in conjugate base pyruvic acid <u>disperses the negative charge on O of COO⁻ to greater extent compared to the carboxylate group and benzene ring in the benzoate ions.</u>

Hence, $CH_3COCO_2^-$ is more stabilised as compared to $C_6H_5COO^-$ and <u>position of equilibrium shifts to right favouring the dissociation of the pyruvic acid into H⁺</u>.

e) (i)

Step 1:	H_2, Pt *or* H_2, Ni, heat *or* NaBH₄, ethanol
Step 2:	If X = Br,
	HBr(g) *or* KBr, conc H_2SO_4, heat
	If X = C*l*,
	HC*l*(g) with anhydrous ZnC*l₂* catalyst
Step 3:	excess NH_3 in ethanol, heat in sealed tube

(ii) Add NaOH(aq) and heat

<u>Observation:</u>
alanine: **No alkaline gas evolved. Moist** red litmus paper remains red.
asparagine: Pungent **alkaline** gas evolved which turn **moist** red litmus paper blue

4 **(a)** **(i)** Electrophilic Addition

Step 1:

slow

Step:2

Correct product
Correct Partial charges and arrows

(ii)

Correct arrow
Correct product

b **(i)**
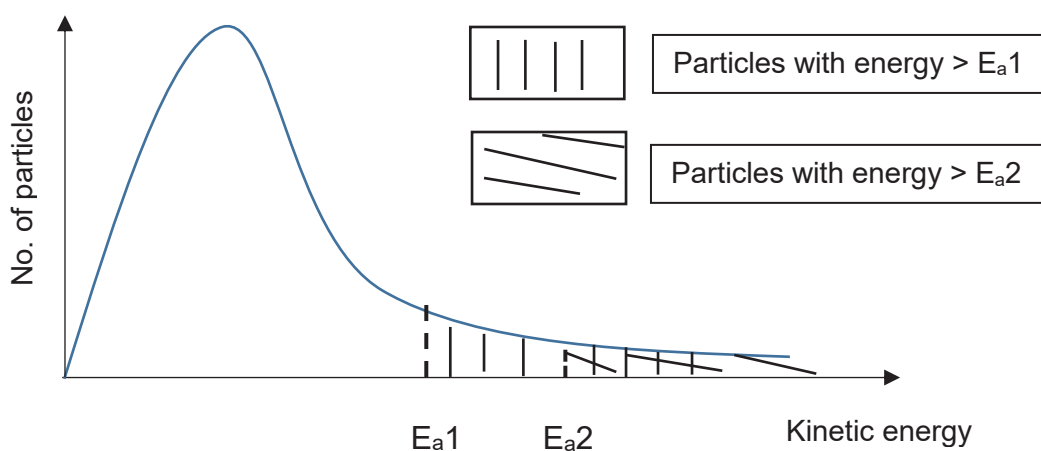
E_a1 is the E_a for **the formation of 3−bromobut−1−ene**
E_a2 is the E_a for **the formation of 4−bromobut−2−ene**
Axis labelled
Peak of graph should be before plateau off
Graph plateau off
Graph starts from origin
Legend for shaded area
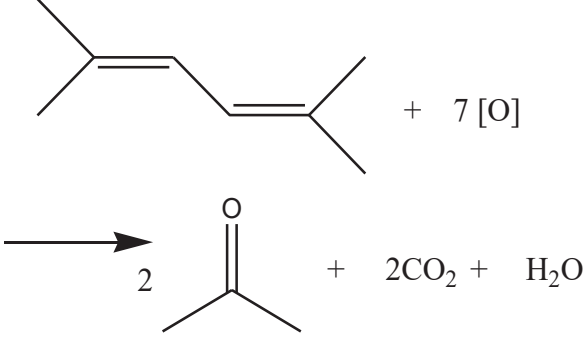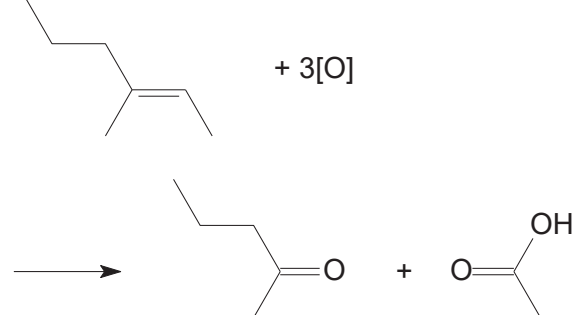
(ii) The activation energy for the formation of the 3−bromobut−1−ene is lower, hence there are more particles with energy larger than the activation energy. This leads to an increase in the frequency of effective collision and hence the rate of forming 3−bromobut−1−ene is faster.

(iii) 4−bromobut−2−ene is a more substituted alkene hence it is more stable.

(c)

KMnO$_4$ (aq), H$_2$SO$_4$ (aq), heat

Compound L	Purple KMnO4 decolourises Effervescence observed. The gas forms white ppt in limewater	
Compound M	Purple KMnO4 decolourises	

d) **(i)** Electrophilic addition to an arene will disrupt the resonance stability as the p orbitals cannot form a continuous overlap.

(ii)
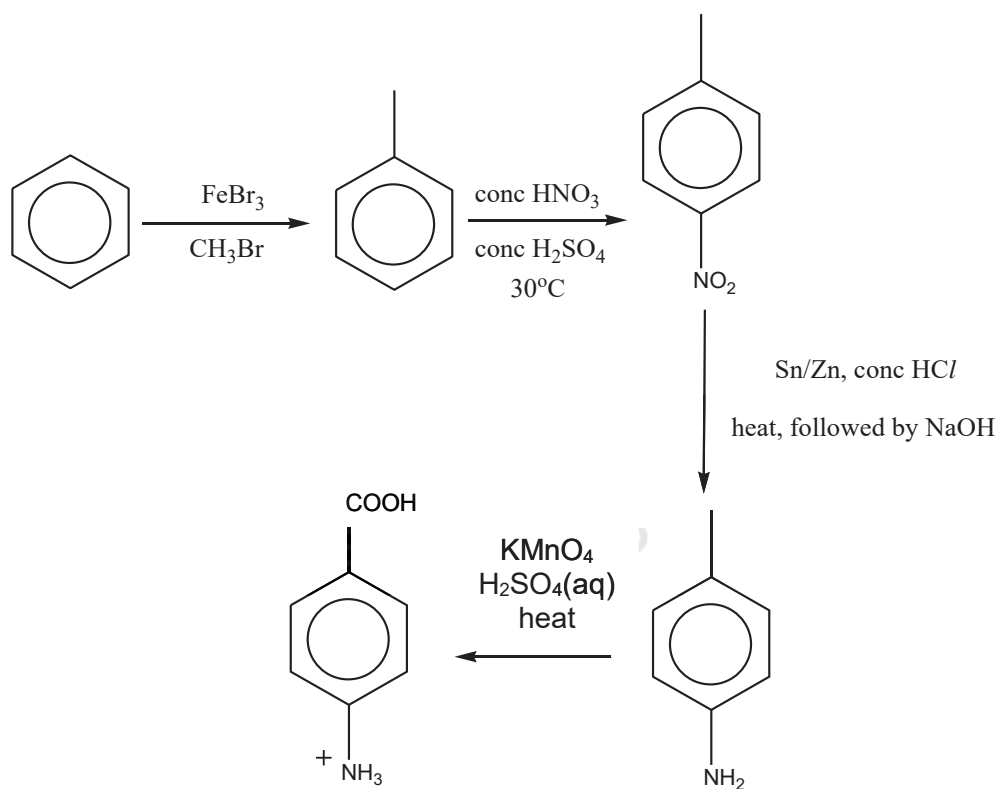
5 a) (i) Lattice energy of $CaCl_2$ is the heat evolved when one mole of solid $CaCl_2$ is formed from isolated gaseous Ca^{2+} and Cl^-.

$$Ca^{2+}(g) + 2Cl^-(g) \rightarrow CaCl_2(s) \qquad L.E = \text{negative}, <0$$
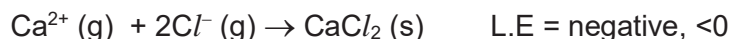
(ii)
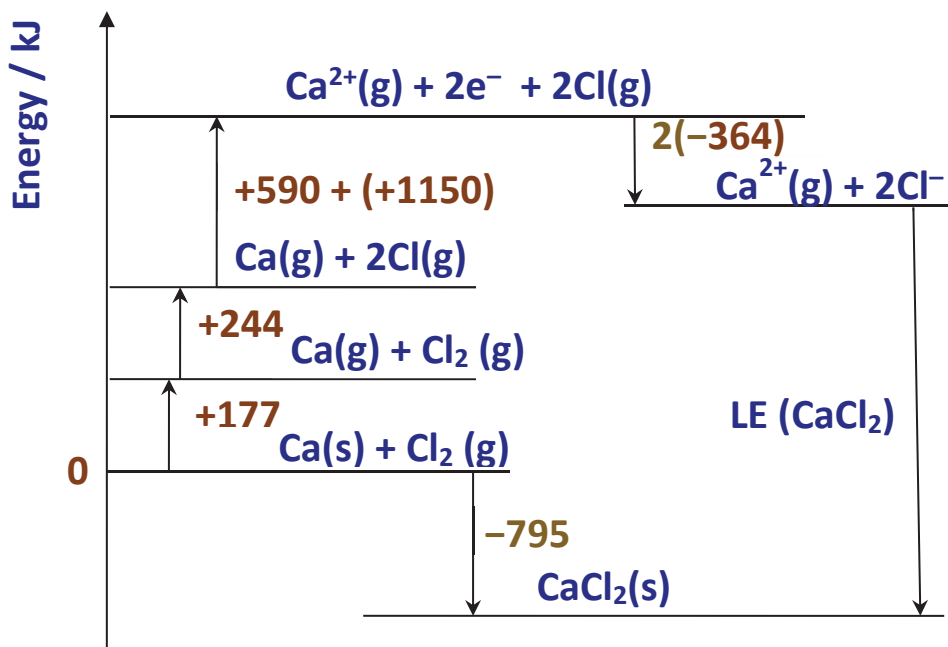
$$L.E. = -795 - 177 - 244 - 590 - 1150 - 2(-364) = -2228 \text{ kJ mol}^{-1} \approx -2230 \text{ kJ mol}^{-1}$$

(iii)

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

Al_2O_3 has larger $q^+ \times q^-$ than $CaCl_2$

Al_2O_3 has smaller interionic distance than $CaCl_2$

Hence, magnitude of LE of Al_2O_3 > magnitude of LE of $CaCl_2$

(iv)
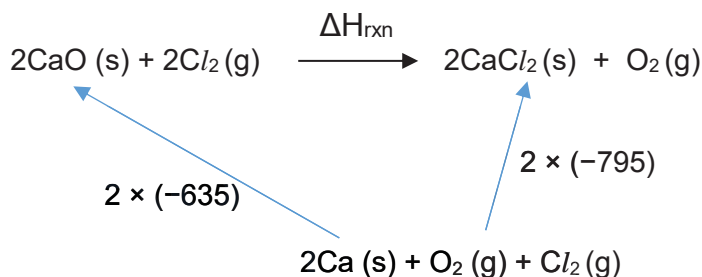
correct energy cycle that is balanced and labelling of relevant enthalpy change symbol or value.

$$2 \times (-635) + \Delta H_{rxn} = 2 \times (-795)$$

$$\Delta H_{rxn} = 2 \times (-795) - 2 \times (-635)$$

$$= -320 \text{ kJ mol}^{-1}$$

b) (i) $CaCl_2$ has giant ionic structure. Large amount of energy required to overcome strong ionic bonds between Ca^{2+} and Cl^- ions.

$AlCl_3$ has simple molecular structure. Small amount of energy required to overcome weak intermolecular temporary dipole – induced dipole interactions.

Hence melting point of $CaCl_2$ is higher than $AlCl_3$.

(ii) Al does not have a full octet structure in $AlCl_3$ (or Al is electron deficient) so it is able to accept another pair of electrons from Cl^-.

(iii)
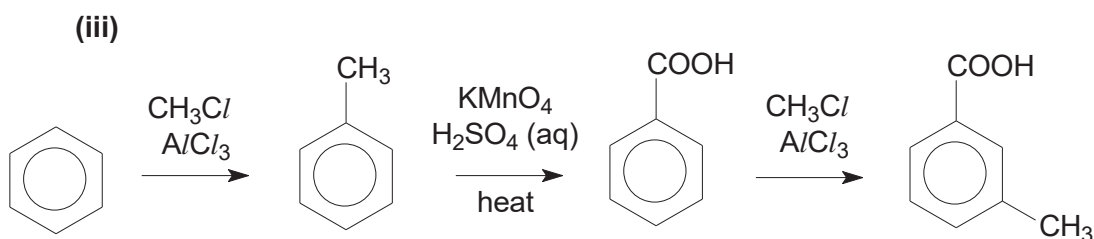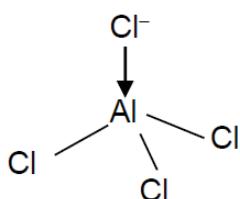
c) (i) High temperature and low pressure.

(ii) $$M_r = \frac{mass \times RT}{PV} = \frac{0.505 \times 8.31 \times (273 + 300)}{10^5 \times 90 \times 10^{-6}} = 267.2$$

(iii)
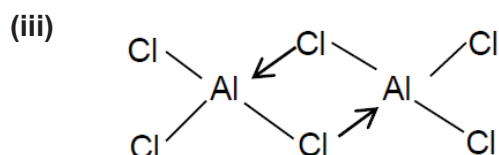
Suggested solution for 2017 SH 2 Prelim Practical

1 (a) (ii) Table 1: Weighings of FA1

Mass of weighing bottle and **FA1** / g	3.696
Mass of weighing bottle and residual **FA1** / g	3.497
Mass of **FA1** transferred / g	0.199

Table 2: Titration of FA3 with FA4 using screened methyl orange as indicator

	1	2
Final burette reading / cm^3	30.00	36.90
Initial burette reading / cm^3	9.00	16.00
Volume of **FA4** used / cm^3	21.00	20.90

(iii) average volume = $\dfrac{21.00 + 20.90}{2}$ = 20.95 cm^3

(b) (i) amount of HNO$_3$ in 25.0 cm^3 = amount of NaOH = 20.95 / 1000 x (9.10/40.0) = 4.77 x 10^{-3}

amount of HNO$_3$ in 250.0 cm^3 = 4.77 x 10^{-2}

(ii) amount of HNO$_3$ in 25.0 cm^3 = 25/1000 x 2 = 0.05 mol

(iii) amount of HNO$_3$ = 0.05 – 4.77 x 10^{-2} = 2.34 x 10^{-3}

(iv) amount of MgCO$_3$.xH$_2$O = 2.34 x 10^{-3} / 2 = 1.17 x 10^{-3}

M_r = 0.208 / 1.15 x 10^{-3} = 170.2

x = [180.7 – (24.3 + 12.0 + 16.0 x 3)] / 18 = 4.77 ≈ 5

(c) The acid **will not be diluted** and close to 2.00 mol dm^{-3}, the titre value required to neutralise 25 cm^3 of FA 3 will be **about 250 cm^3 / more than 10 times greater**. Since this **exceeds the capacity of burette**, it is unsuitable.

2 **(a)** **Table 1: Weighings of FA1**

Mass of weighing bottle and **FA1** / g	4.495
Mass of weighing bottle and residual **FA1** / g	3.478
Mass of **FA1** transferred / g	1.017

Table 2: Measurement of temperature

T_i / °C	30.3
T_i / °C	33.3
ΔT / °C	3.0

(i) $\Delta q_{reaction3} = -mc\Delta T = -40 \times 4.18 \times 3.0 = -502$ J

(iii)

$$\Delta H_{reaction1}$$
$$Mg(s) + C(s) + (3+x)/2\ O_2(g) + xH_2(g) \rightarrow MgCO_3.xH_2O(s)$$

$+ 2HNO_3(aq)$ -490 -86.0 $+ 2HNO_3(aq)$

$-393.5 + 6 \times -285.5$

$Mg(NO_3)_2(aq) + C(s)$
$+ (3+x)/2\ O_2(g) + (x+1)H_2(g)$

$Mg(NO_3)_2(aq) + CO_2(g)$
$+ (x+1)H_2O(l)$
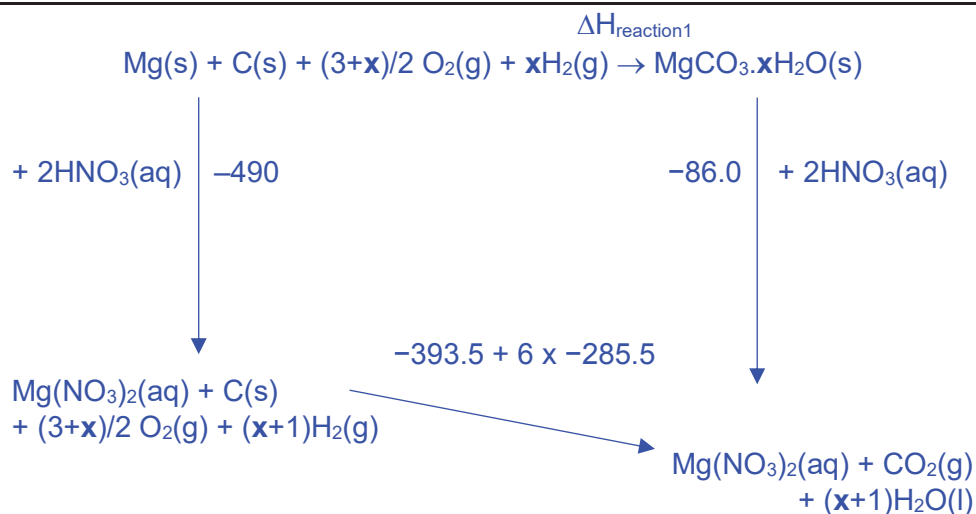
By Hess's law,

$\Delta H_{reaction1} = -490 -393.5 + 6 \times -285.5 - (-86.0) = -2510$ kJ mol^{-1}

OR

If they use $x = 3$

By Hess's law,

$\Delta H_{reaction1} = -490 -393.5 + 4 \times -285.5 - (-68.3) = -1957.2$ kJ mol^{-1}
$= -1960$ kJ mol^{-1}

(c) **(i)** percentage error = $(\pm 0.1 \times 2) / 3.0 \times 100 = \pm 6.67$ %

(ii) $\Delta H_{reaction3}$ = −502 / (1.017 / 174.3) = −86.0 kJmol^{-1}
OR

If they use $x = 3$
$\Delta H_{reaction3}$ = −502 / (1.017 / 138.3) = −68.3 kJmol^{-1}

(ii) **Error:**
The experiment did not take into account **heat exchange with surrounding** / **calorimeter / heat loss to surrounding / calorimeter**.

Improvement 1:
Use **cooling curve method** where **temperature changes after mixing are measured at 30s intervals** for about 3 min, then **max temperature is extrapolated to time of mixing**. This accounts for heat exchange with surrounding, hence a more accurate ΔT is obtained.

Improvement 2:
Calibration of the calorimeter by **making use of reaction with accurately known enthalpy change**. The calibrated heat capacity, C of the calorimeter takes into account heat exchange with surrounding, hence a more accurate ΔT is obtained.

OR

Error:
The experiment did not **repeat experiment to ensure consistent results**.

Improvement:
Repeat experiment until **$\Delta T/m$ between a pair of experiments is within 5%**.

(d) **Suggested solution:**

Procedure:
1. Using three **10.0 cm^3 measuring cylinders**, measure 5.0 cm^3 of **FB 1**, **FB 2** and **FB 3**.
2. Mix separately, 5.0 cm^3 of **FB 1** to 5.0 cm^3 of **FB 2** and 5.0 cm^3 of **FB 1** to 5 cm^3 of **FB 3**, into 2 **test-tubes**
3. Measure for the rise in temperature using a **0.2 °C division thermometer**

Deduction:
- If both reaction mixture gives a temperature rise, **FB 1** is **HCl**.
- If one of the 2 reaction mixture does not give a temperature rise, then this pair of solutions must be NH$_3$(aq) and KOH(aq). **HCl** can be identified.

Upon identifying **HCl**,
4. Using a 10.0 cm^3 measuring cylinder, add 10.0 cm^3 of **HCl** to a **Styrofoam cup** and measure the initial temperature, T$_1$, using a a **0.2 °C division thermometer**.

5. Using another 10.0 cm^3 measuring cylinder, transfer 10 cm^3 of **one of the bases** into another Styrofoam cup.
6. Wash and dry the thermometer
7. Measure the initial temperature, T_2, of the **base** solution.
8. Add **HCl** to **base** and stir with the thermometer and note the highest temperature reached, T_f and determine ΔT.
9. Wash and dry the Styrofoam cup.
10. Repeat steps 4 – 9 but replace base with the other base solution.

Assuming if **FB 1** is **HCl**

	FB 2	FB 3
T_i / °C		
T_f / °C		
ΔT / °C		

Deduction of results:
Since **HCl** is 2 mol dm^{-3}, the limiting reagent is the base and the same amount of base is used / same amount of H_2O is produced in each reaction.

When total volume of reaction mixture is kept constant and the no of moles of water formed in the reaction is the same, ΔT depends only on the strength of the base used.

As weak acid dissociates partially, a portion of the energy released from neutralisation is used to complete the dissociation of the weak acid. Therefore less energy is released compared to a neutralisation between a strong acid and a strong base.

The reaction mixture that gives a lower ΔT must contain 1 mol dm^{-3} aqueous ammonia.

Procedure:
1. To 1 **test-tube**, add 5.0 cm³ of **FB 1** using a **10.0 cm³ measuring cylinder** and measure the initial temperature, T_1, using a **0.2 °C division thermometer**.
2. Using another 10.0 cm³ measuring cylinder, measure 5.0 cm³ of **FB 2**.
3. Wash and dry the thermometer.
4. Measure the initial temperature, T_2, of **FB 2**.
5. Transfer **FB 2** into the test-tube. Stir with the thermometer and note the highest temperature reached, T_f and determine ΔT.
6. Wash and dry the test-tube.
7. Repeat steps 1 – 6 but by mixing 5.0 cm³ of **FB 1** to 5 cm³ of **FB 3** and 5.0 cm³ of **FB 2** to 5 cm³ of **FB 3** respectively.

	FB 1	**FB 2**	**FB 3**
FB 1		$T_1 =$ $T_2 =$ $T_f =$ $\Delta T =$	$T_1 =$ $T_2 =$ $T_f =$ $\Delta T =$
FB 2			$T_1 =$ $T_2 =$ $T_f =$ $\Delta T =$

Results analysis: similar to first solution of using ΔT to identify the 3 solutions.

3 (a)

Expt	Vol of FA 8 / cm³	Vol of DI / cm³	time / sec	lg $V_{FA\ 8}$	lg 1/t
1	20.00	0.0	46	1.30	-1.66
2	10.00	10.0	116	1.00	-2.06
3	15.00	5.0	64	1.18	-1.81
4	12.00	8.0	87	1.08	-1.94
5	8.00	12.0	251	0.903	-2.40

3   (b)   (i)   Use the grid below to plot a graph of lg (1/time) against lg (volume of FA 8).

$lg\left(\frac{1}{t}\right)$

The graph has axes labelled lg(1/t) (vertical) and $lg\ V_{FA8}$ (horizontal). Points marked: (0.93, -2.10) and (1.25, -1.725). Vertical axis values: -1.70, -1.80, -1.90, -2.00, -2.10, -2.20. Horizontal axis values: 0.700, 0.800, 0.900, 1.00, 1.10, 1.20, 1.30, 1.40, 1.50.
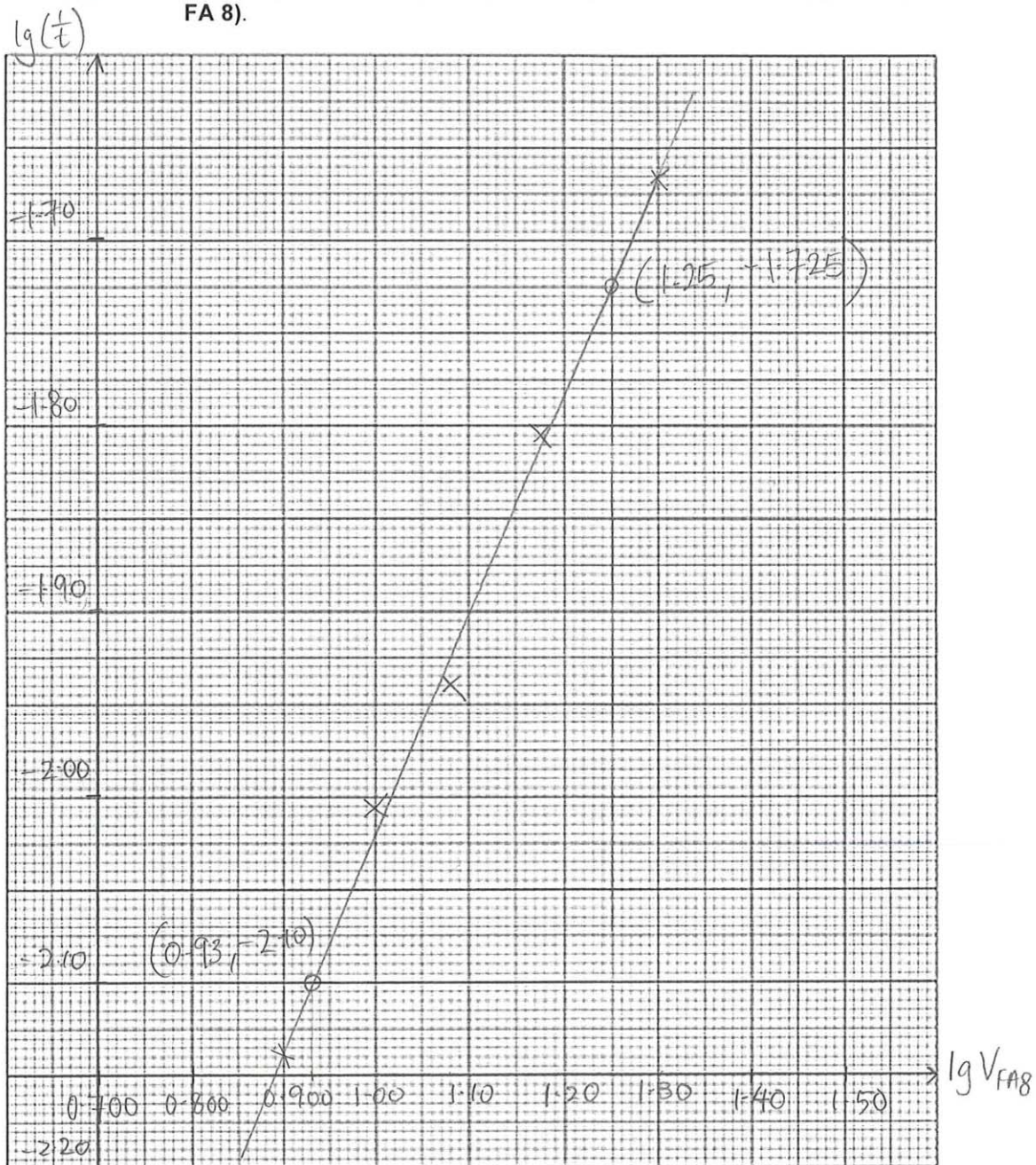
(ii)   Order of reaction wrt Fe^{3+} = gradient of graph
= (-1.725 – -2.10) / (1.25 – 0.93) = 1.17 ≈ 1

Test	Procedure	Observations
(a)	To 6 cm^3 of **X**, add barium nitrate solution until in excess.	**White ppt.** formed, insoluble in excess.
(b)	Filter the mixture from **(a)**. Wash and retain the residue for test **(c)**. Collect the filtrate for test **(d)** and **(e)**.	
(c)	To separate portions of the residue **(i)** add 2 cm^3 of hydrochloric acid	A **colourless and odourless gas** evolved, which forms a **white ppt with Ca(OH)$_2$**
	(ii) add 2 cm^3 of organic compound **Z** [You are to test for any gas evolved]	A **colourless and odourless gas** evolved, which forms a **white ppt with Ca(OH)$_2$**
(d)	To 1 cm depth of the filtrate from **(b)** in a test-tube **(i)** add a few drops of organic compound **Z** and warm in a water bath for 5 minutes	Solution remains colourless.
	(ii) followed by 1 cm^3 of nitric acid and 5 drops of silver nitrate. Add excess ammonia solution.	**white ppt.** formed, **soluble in excess NH$_3$**
(e)	To separate 1 cm depth of **Y** **(i)** add filtrate from **(b)** dropwise until in excess	Pale **blue ppt**. formed, **insoluble in excess**
	(ii) add NaOH(aq), followed by one **spatula of zinc powder** **and** **warm.** (CARE!)	Pale **blue ppt.** formed upon adding NaOH(aq). Vigourous effervescence, **colourless and pungent gas evolved**, which **turns damp red litmus paper blue**

(f)	**(i)**	carbonate / CO_3^{2-} in residue hydroxide / OH^- in filtrate
	(ii)	**Carboxylic acid** is present. From test (c)(ii), **CO_2 is produced from the reaction of Z with carbonate** in the residue from **(b)**, which suggests an acidic group is present. **Halogenoalkane** / **chlorine-containing** organic compound / **alkyl halides** / is present. From test (d)(i), a white ppt. is produced upon heating with OH^- and adding nitric acid and $AgNO_3$, which dissolves in excess NH_3, which suggests that the **white ppt. is AgCl**. Hence Cl is present in **Z**.
(g)		cation: Cu^{2+} anion: NO_3^- / NO_2^-
(h)		Possible solution:

Step	Procedure	Observations and conclusions
1	Add Cu^{2+} complex in NaOH(aq) to each sample in a test-tube, warm	For **propanal**, **brick-red ppt** is formed due to the presence of aliphatic aldehyde. For other compounds, **blue solution remains**.
2	Add 2,4-dinitrophenylhydrazine to a new sample of the remaining 3 unknowns, warm	For **benzaldehyde**, **orange ppt.** is formed due to the presence of carbonyl group. For remaining compounds, **no orange ppt. form**.
3	Add $KMnO_4$, dil H_2SO_4 to a new sample of the remaining 2 unknowns, heat	For **butanol**, **purple $KMnO_4$ decolourises** due to oxidation of primary alcohol. For the last compound, purple $KMnO_4$ remains.
4	Add PCl_5(s) to a new sample of the last unknown	For **2-methylpropan-2-ol**, **white fumes of HCl** observed due to presence of OH / alcohol group.