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.

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..... [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 $\Delta S^{\ominus}$.

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..... [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**.

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..... [2]

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

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[2]

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

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[2]

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

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[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.

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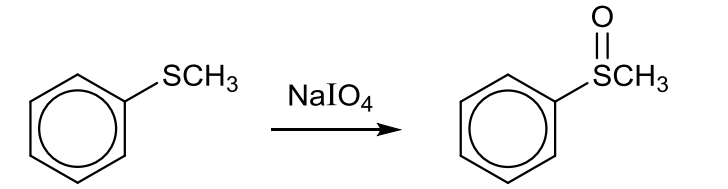
[2]

(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), $C_6H_5SCH_3$, 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, $C_6H_5SOCH_3$.



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_6H_5SH, 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.

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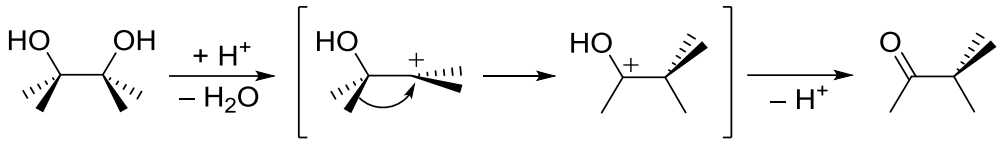
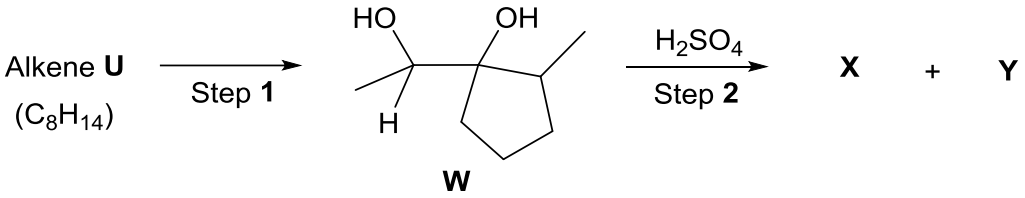
..... [2]

[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

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[2]

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

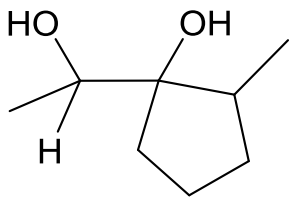
X

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 (*).



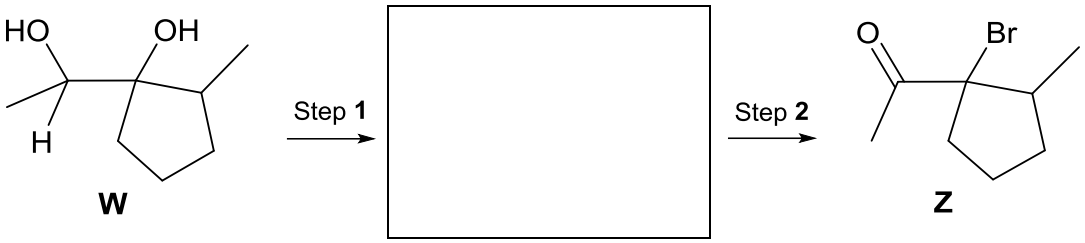
W

[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** .....

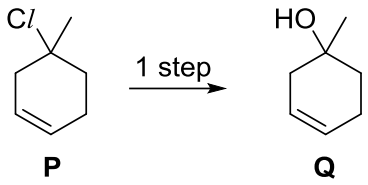
Step **2** .....

[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.



P **Q**

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

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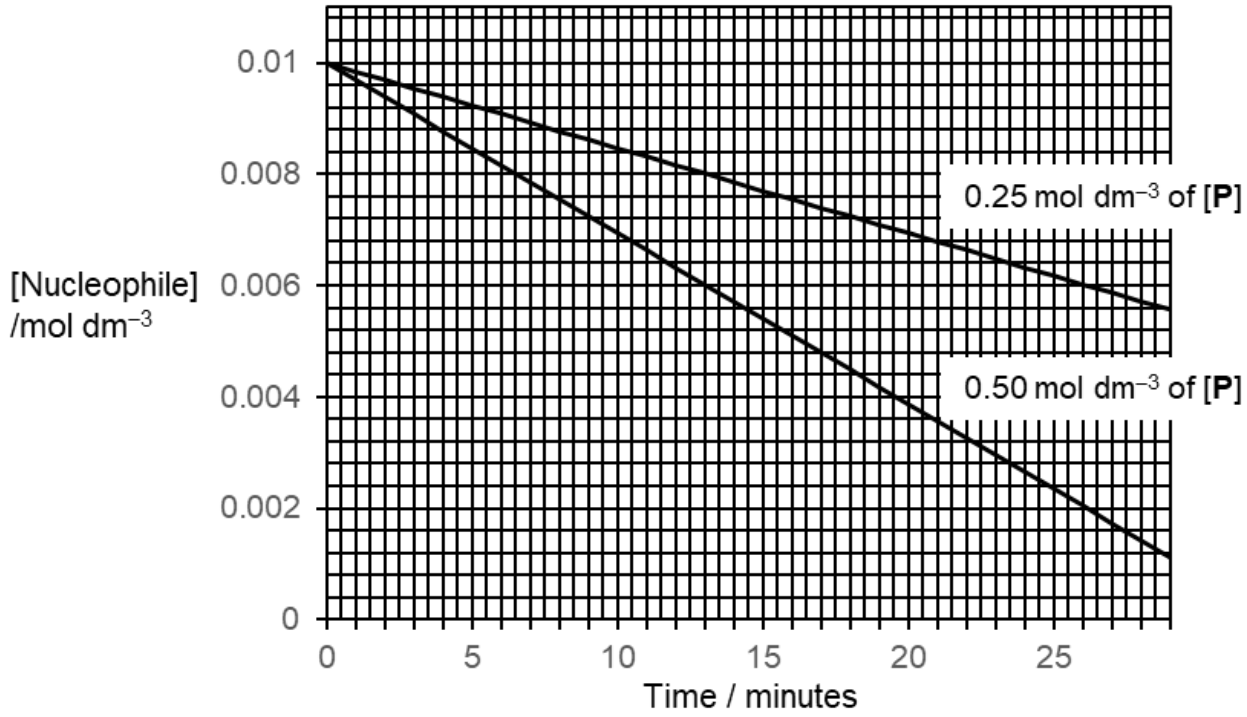
[1]

(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.

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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.

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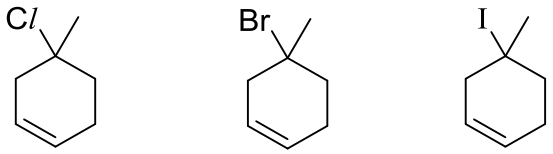
[3]

(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.

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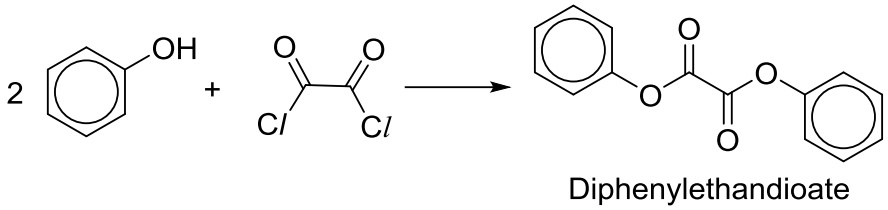
[2]

(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.

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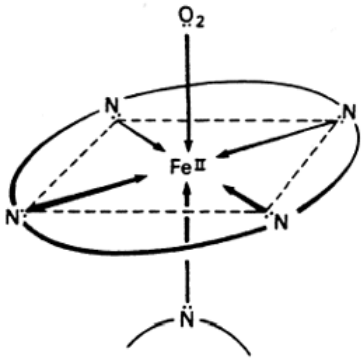
..... [2]

[Total: 16]

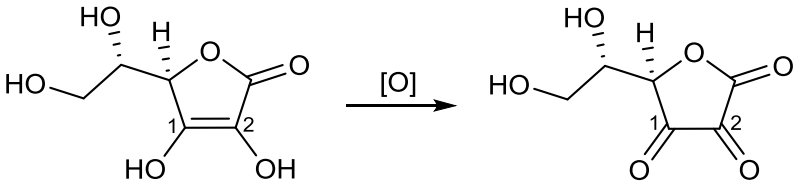
5 Haemoglobin reacts with oxygen to form oxyhaemoglobin as follows.

$$Hb + O_2 \rightleftharpoons HbO_2$$

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

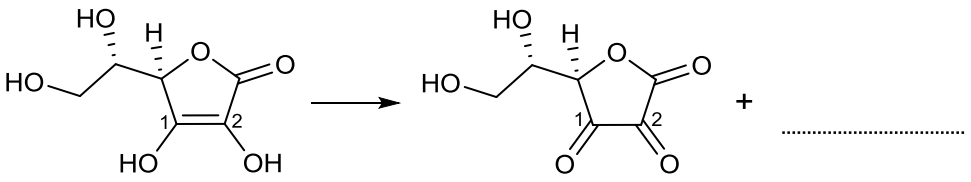
Approximately 10,000 million new blood cells are formed in the bone marrow daily. Red blood cells have a lifespan of 120 days. Each person should have about 150 mg of haemoglobin per cm^3 of their blood and a blood count of 5 million red blood cells per cm^3. Iron makes up 4% by mass of the haemoglobin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

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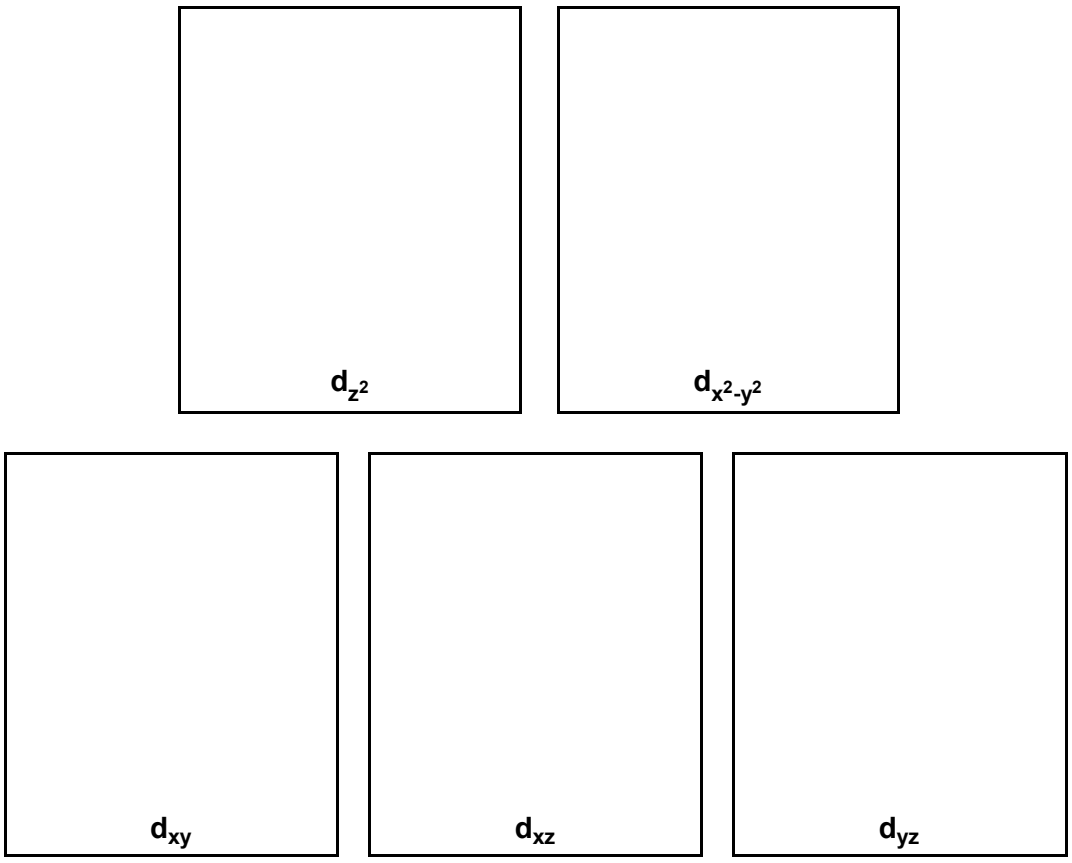
..... [1]

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



[2]

(ii) Account for the red colouration of blood.

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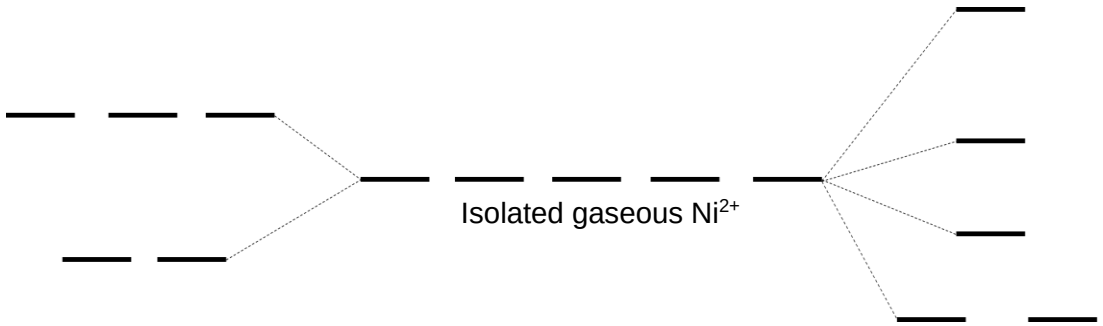
..... [3]

(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

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.

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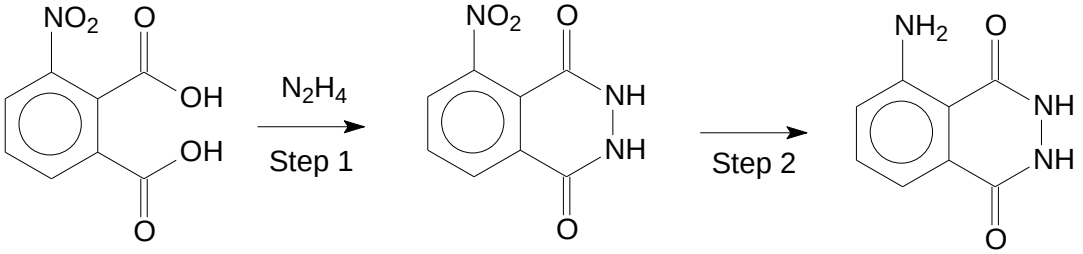
[1]

(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.



luminol

(i) State the type of reaction for Step 1.

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[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.

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[1]

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

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[2]

[Total: 18]

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