Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2016
Year 6

H1 CHEMISTRY 8872/02

Paper 2 Section A (Structured Questions) **16 September 2016**

Paper 2 Section B (Free–Response Questions) **2 hours**

Additional Materials: Data Booklet
Writing papers

INSTRUCTIONS TO CANDIDATES

1 Answer **all** questions in Section A, and any **two** questions in Section B.

2 Write your **name** and **class** on this cover page.

Section A

3 Write your answers in the spaces provided on this question paper.

4 You are advised to spend a maximum of 1 hour on Section A.

Section B

5 Write your **name** and **class** on the Cover Sheet provided.

6 Write your answers on the separate writing papers provided.

7 Answer any two questions.

8 Start each question on a fresh sheet of paper. ***Marks will be deducted if you fail to do so.***

9 At the end of the examination, fasten all your work securely together with the Cover Sheet on top.

10 You are advised to spend a maximum of 1 hour on Section B.

For Examiner's Use	
Question No.	**Section A Marks**
1	/10
2	/10
3	/6
4	/14
Total	/40

INFORMATION FOR CANDIDATES

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

You are advised to show all workings in calculations.

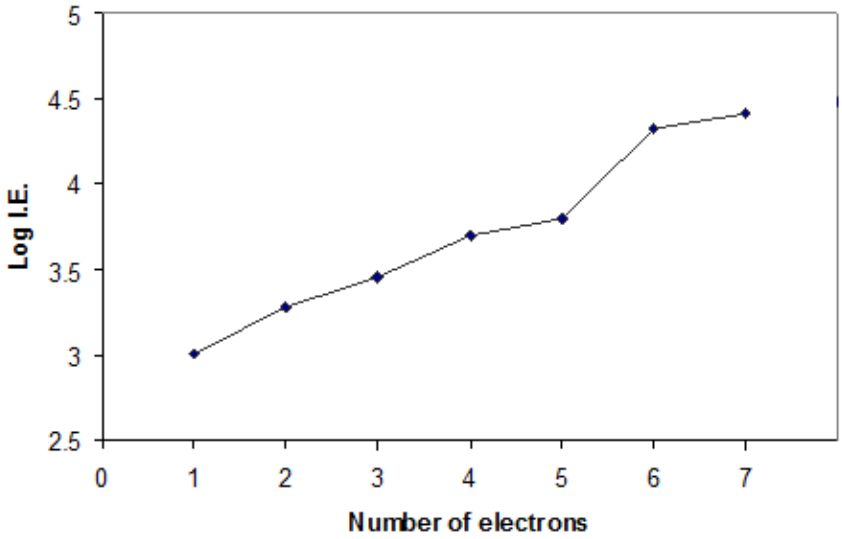
You are reminded of the need for good English and clear presentation in your answers.

[Turn over

Section A

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

1 The graph below shows the variation of the successive ionisation energies for the outermost seven electrons in an atom of an element.



(a) Explain why the graph above belongs to that of an atom of nitrogen.

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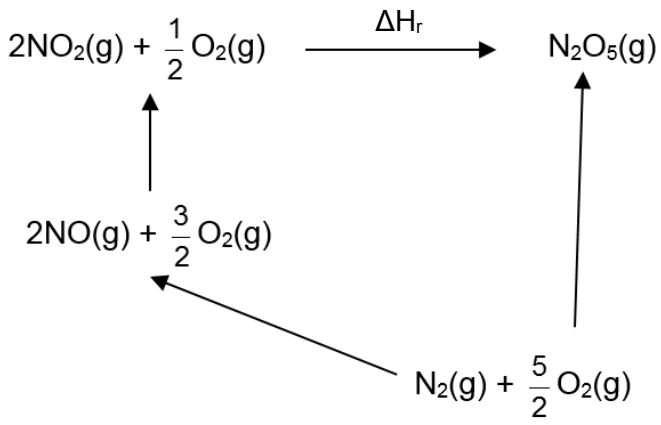
[2]

(b) Dinitrogen pentoxide, N_2O_5, is commonly used in chloroform. It can be produced by reacting nitrogen dioxide, NO_2, with oxygen as shown in the equation below.

$$2NO_2(g) + \frac{1}{2}O_2(g) \rightarrow N_2O_5(g) \qquad \Delta H_r$$

(i) Use the data and energy cycle given to calculate the enthalpy change of reaction, ΔH_r.

Reactions		Enthalpy Change / kJ mol^{-1}
I	$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$	$\Delta H_1 = -57$
II	$N_2(g) + \frac{5}{2}O_2(g) \rightarrow N_2O_5(g)$	$\Delta H_2 = +11$
III	$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$	$\Delta H_3 = +90$



[1]

(ii) Hence, use the same energy cycle, or otherwise, to determine the enthalpy change of formation of nitrogen dioxide.

[1]

(iii) Name the enthalpy change of reaction **II**, ΔH_2.

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[1]

(c) Nitrogen dioxide, can be produced by reacting oxygen and nitrogen monoxide.

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

A student performed a series of experiments to determine the order of reaction with respect to O_2 and NO. The results were tabulated in the table below.

Expt	Initial $[O_2]$/ mol dm^{-3}	Initial [NO]/ mol dm^{-3}	Temperature/ K	Initial rate/ mol dm^{-3} s^{-1}
1	0.02	0.013	298	0.0033
2	0.02	0.013	318	0.0376
3	0.04	0.013	298	0.0066
4	0.08	0.026	298	0.0528

(i) Determine the order of reaction with respect to each reactant and hence, write the rate equation.

[3]

(ii) Explain, with the aid of a Boltzmann distribution curve, the difference in initial rates between Experiments 1 and 2.

[2]

[Total: 10]

2 Nitrogen dioxide is an extremely toxic gas with an acrid smell, while carbon dioxide is a primary greenhouse gas emitted through human activities.

At first sight, nitrogen dioxide (NO_2) seems similar to carbon dioxide (CO_2) due to the same number of atoms in the molecules.

(a) **(i)** Draw dot–and–cross diagrams of the NO_2 and CO_2 molecules.

[1]

(ii) With reference to your answer in **(a)(i)**, explain why NO_2 is more reactive than CO_2.

[1]

(b) Dinitrogen tetroxide, N_2O_4, forms an equilibrium mixture with nitrogen dioxide, NO_2.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57.2 \text{ kJ mol}^{-1}$$

As N_2O_4 is colourless and NO_2 is brown, the composition of an equilibrium mixture can be determined by its colour intensity.

(i) Write an expression for the equilibrium constant, K_c, of this dissociation reaction stating its units.

[1]

Experiments were conducted to study this equilibrium mixture at 100 ºC.

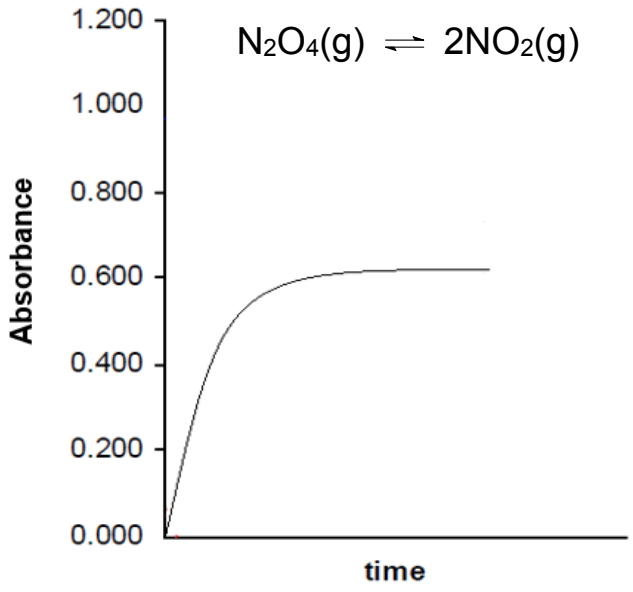
In the experiments, different quantities of N_2O_4 and NO_2 were left to reach equilibrium, in a gas syringe. The concentrations of N_2O_4 and NO_2 were monitored over a period of time.

As NO_2 is coloured, its concentration can be measured using a spectrophotometer. The spectrophotometer measures the amount of light absorbed by NO_2.

The amount of light absorbed is directly proportional to the recorded absorbance value. The higher the concentration of NO_2 in the mixture, the higher is the absorbance value.

Experiment	Initial [N_2O_4] / mol dm^{-3}	Initial [NO_2] / mol dm^{-3}	Initial Absorbance / Au
1	1.00	0.00	0.00
2	0.00	1.00	0.80
3	0.50	0.50	0.40

The absorbance of the gas mixture was monitored over time and the graph for Experiment **1** is shown below.



(ii) Using the graph above and data given, calculate the equilibrium concentration of NO_2 for Experiment **1**.

[2]

(iii) Hence, calculate the value of K_c for Experiment **1**.

[1]

(iv) When the gas mixture at equilibrium in Experiment **3** was suddenly compressed in a gas syringe, the mixture first darkened and then slowly became paler. Explain why.

[2]

(v) State the effect, if any, of a higher temperature on the value of K_c. Explain your answer.

[2]

[Total: 10]

3 Citric acid can be isolated by precipitating it with calcium hydroxide to form calcium citrate. This forms part of the industrial process to produce citric acid. Citric acid is a known Brønsted–Lowry acid.

(a) State the Brønsted–Lowry theory of acids and bases.

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[1]

(b) Citric acid has the condensed structure, $HOOCCH_2C(OH)(COOH)CH_2COOH$. Write the first acid dissociation equation for citric acid and label the acid and conjugate base.

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[2]

(c) Calcium hydroxide is formed when calcium oxide in slaked lime reacts with water. Sodium hydroxide and magnesium hydroxide can be formed in a similar process.

The pH value of the solution formed when sodium oxide is shaken with water is greater than the pH value of the solution formed when magnesium oxide is shaken with water. The pH of the solution formed when sulfur trioxide is shaken with water is less than both of these.

Explain these observations with the aid of balanced equations.

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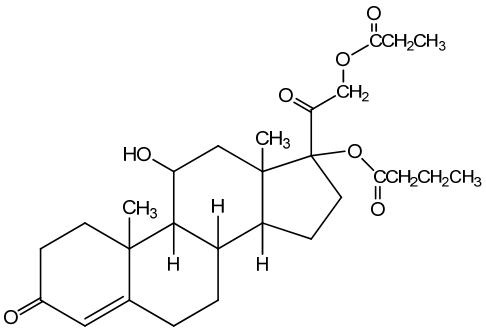
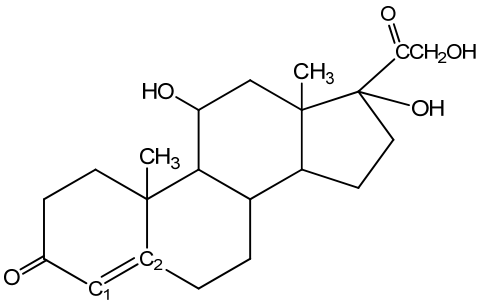
[3]

[Total: 6]

4 Hydrocortisone and cortisone are types of steroids which are applied to the skin to reduce inflammation, redness and swelling. Their structures are shown below:



Hydrocortisone



Cortisone

(a) For part (a), refer to cortisone only.

(i) Explain why geometric isomerism is **not** possible at carbons C_1 and C_2.

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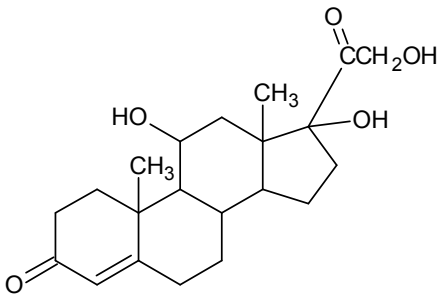
[2]

(ii) Draw the products formed after cortisone undergoes the following reactions:

Reaction		
I	heating with acidified $K_2Cr_2O_7$	
II	adding alkaline $KMnO_4$ at 10 °C	

[2]

(b) Show on the diagram below the possible forces of attraction that can be formed between cortisone and 3 molecules of ethanol. You are to represent ethanol as ROH. Hence, explain why cortisone is soluble in ethanol.



Cortisone

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[2]

(c) Calculate the mass of PCl_5 required to react with 1 mg of ***cortisone*** (M_r = 360). (1000 mg = 1 g)

[3]

(d) Name the functional groups present in hydrocortisone.

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[1]

(e) In general, in order for a drug that is to be taken orally to work, the chemical structure of the drug must be unchanged by the acidic condition in stomach. Predict and explain if hydrocortisone is suitable to be taken orally.

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[2]

(f) Describe the observation when 2,4–dinitrophenylhydrazine is introduced into a solution of hydrocortisone that is dissolved in CCl_4. State how many moles of 2,4–dinitrophenylhydrazine would react with one mole of hydrocortisone.

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[2]

[Total: 14]

Section B

Answer **two** questions from this section on separate answer paper.

1 Lactic acid ($CH_3CH(OH)COOH$) is formed in our muscles when we exercise. During exercise, lactic acid is produced from pyruvic acid ($CH_3COCOOH$).

(a) **(i)** State the reagent you would use to detect a small quantity of pyruvic acid in a sample of lactic acid and state your observations. [2]

(ii) State the reagents and conditions required for the conversion of pyruvic acid into lactic acid. [1]

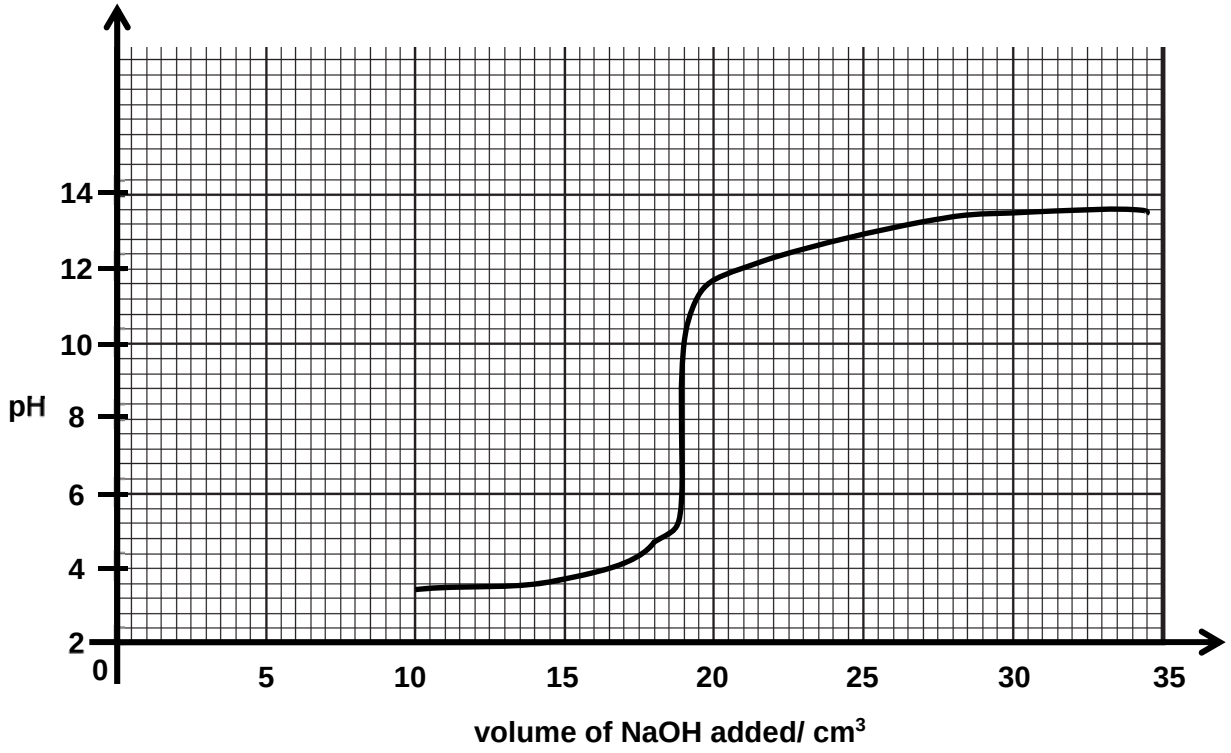
(b) **(i)** Lactic acid can be synthesised from ethanol in three steps.

Suggest reagents and conditions for each step and draw the structural formula of the intermediate compounds. [4]

(ii) Explain whether lactic acid has a larger or smaller K_a than propanoic acid. [2]

(iii) When lactic acid is treated with concentrated sulfuric acid, a compound with molecular formula $C_6H_8O_4$ is formed. Suggest a structure for $C_6H_8O_4$. [1]

(c) A 20.0 cm^3 solution of the weak monoprotic lactic acid, was titrated against a solution of 0.50 mol dm^{-3} of sodium hydroxide in which a few drops of indicator had been added. The pH readings were not recorded until 10 cm^3 of sodium hydroxide had been added.



(i) State the volume of sodium hydroxide needed to exactly neutralise lactic acid and hence calculate the initial concentration of lactic acid. [2]

(ii) Write an expression for the dissociation constant, K_a, of lactic acid. You may represent lactic acid as HA. [1]

(iii) Using **(c)(i)** and given that pH for the lactic acid solution is 2.10, calculate the K_a of lactic acid. [2]

(iv) Given the following information about three indicators, choose the indicator most suitable for determining the end–point of this reaction. Give a reason for your choice.

Indicator	pH range of colour change
methyl red	4.2 – 6.2
cresol red	7.2 – 8.8
alizarin yellow	10.1 – 12.0

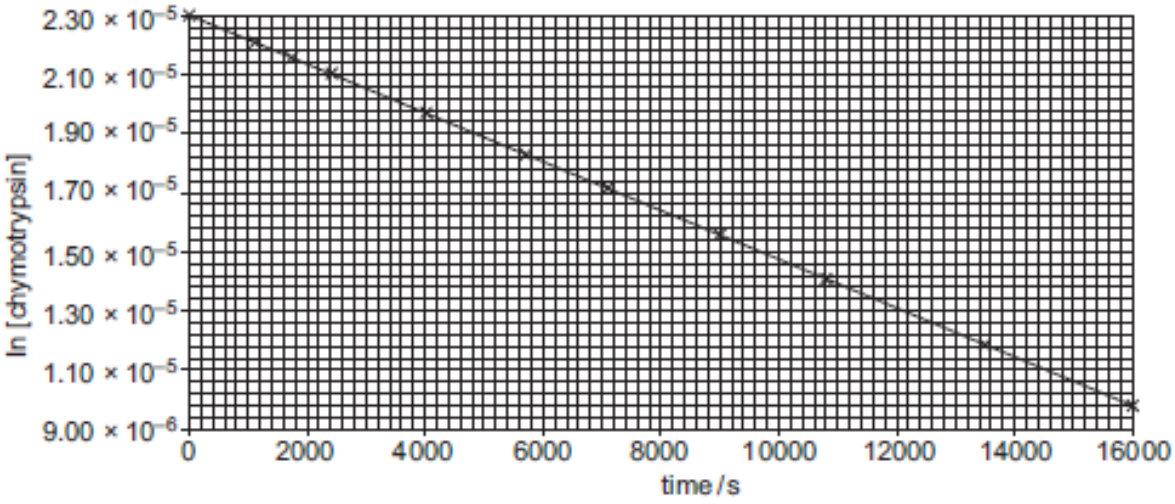
[1]

(d) Sodium hydroxide can be used to denature the protein, chymotrypsin. Denaturation is the alternation of a protein shape through external stress in such a way that it will no longer be able to carry out its cellular functions.

At pH 12, the denaturation process is found to be first order with respect to both chymotrypsin and sodium hydroxide.

An experiment was carried out in the presence of excess sodium hydroxide and the denaturation of the chymotrypsin was monitored.

The results obtained are shown in the graph below.



Based on the integrated rate law, a first order rate equation can be written as:

$$\ln [\text{chymotrypsin}] = -kt + \ln [\text{chymotrypsin}]_0$$

[chymotrypsin] is the concentration of chymotrypsin at time t
$[\text{chymotrypsin}]_0$ is the initial concentration of chymotrypsin
t is the time since the start of reaction

(i) Explain how the graph plotted confirms that the denaturation process is first order with respect to [chymotrypsin] and how the conditions used give rise to first order kinetics overall. [2]

(ii) Use the graph plotted to calculate the value of the first order rate constant, *k*, for this denaturation. [2]

[Total: 20]

2 (a) Ethanamide, CH_3CONH_2, can be converted into methylamine, CH_3NH_2, as follows via a reaction known as the Hofmann rearrangement.

$$CH_3CONH_2 \xrightarrow[Br_2,\ NaOH]{\text{step 1}} CH_3NCO \xrightarrow[H_2O]{\text{step 2}} CH_3NH_2$$

(i) State the oxidation number of the carbonyl carbon atom in ethanamide. [1]

(ii) Suggest the identity of the by–product formed in step 2 and write a balanced equation for the reaction between CH_3NCO and H_2O. [2]

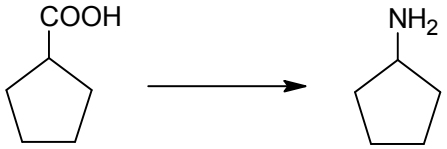
(iii) Draw a dot–and–cross diagram to illustrate the bonding in CH_3NCO. [1]

(iv) Predict and explain the shape and bond angle around the nitrogen atom in CH_3NCO. [2]

(v) Amides, $RCONH_2$, can be prepared from acyl chlorides as shown below.

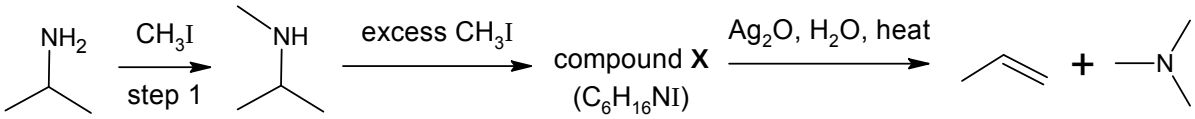
$$RCOCl \xrightarrow{NH_3} RCONH_2$$

Use this information to suggest a synthetic route involving the Hofmann rearrangement to carry out the following conversion. Identify reagents and conditions, and the structures of the organic intermediates.



[4]

(b) Another reaction, the Hofmann elimination, is used to convert an amine into an alkene. An example of this reaction is shown below.



(i) State the type of reaction occurring in step 1. [1]

(ii) Suggest the structure and bonding present in compound **X**, given that it conducts electricity when dissolved in propanone. [1]

(iii) Use your answers in **(b)(i)** and **(b)(ii)** to deduce the structure of **X**. [1]

(c) A mixture of but–1–ene and but–2–ene is obtained when an amine undergoes a similar Hofmann elimination reaction in **(b)**.

(i) Describe one chemical test that could distinguish between but–1–ene and but–2–ene. [2]

(ii) One of the alkenes exhibits geometric isomerism. Explain how this isomerism arises and draw the pair of geometric isomers. [2]

(iii) A pure sample of but–2–ene was treated with aqueous bromine and the organic product formed was purified before it was warmed with alkaline aqueous iodine, giving a positive test.

Describe the observations you would make and write an equation for **either** of the reactions occurring. [3]

[Total: 20]

3 This question is about Period 3 elements and the uses of its compounds.

(a) A sample of magnesium oxide is suspected to be contaminated with a substantial amount of aluminium oxide. A simple experiment with a quantitative analysis of the mass of the solid is performed to prove that the contamination has taken place. The following steps are proposed with some information missing in the procedure. Write out the incomplete steps 5 and 6 with the missing information and give an equation for step 3.

Procedure:
1. Weigh the original sample first.
2. Add aqueous sodium hydroxide in excess.
3. Only aluminium oxide will dissolve to form a soluble complex:
   Equation for reaction: _____
4. The mixture is then filtered.
5. Dry the residue and _____ the sample again.
6. If there is contamination, _____.

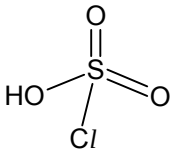
[3]

(b) Another Period 3 oxide, sulfur trioxide dissolves in water to form sulfuric acid, H_2SO_4 which can be converted into peroxodisulfuric acid, $H_2S_2O_8$ via the two–step process below, with chlorosulfonic acid, HSO_3Cl, as an intermediate:

$$H_2SO_4 + HCl \rightarrow HSO_3Cl + H_2O$$

$$H_2O_2 + 2HSO_3Cl \rightarrow H_2S_2O_8 + 2HCl$$

(i) The structure of HSO_3Cl is given below.



The boiling point of H_2SO_4 is 290 °C whereas that of HSO_3Cl is 152 °C. By making reference to the structures of the two compounds, explain the difference in the boiling points. [2]

(ii) Draw the Lewis structure of $H_2S_2O_8$ molecule, showing the spatial arrangement and estimated bond angle around any one sulfur atom. The $H_2S_2O_8$ molecule contains a O–O bond. [2]

(c) Chlorine forms an oxide, Cl_2O_7, with the structure $O_3ClOClO_3$ and a boiling point of 82 °C. Its standard enthalpy change of formation is –546 kJ mol^{-1}.

(i) Write the equation which corresponds to the standard enthalpy change of formation of Cl_2O_7. [1]

(ii) Given that the bond energy of Cl–O bond is 269 kJ mol^{-1} and using relevant data from the *Data Booklet*, estimate the average bond energy of the Cl=O bond. [2]

(iii) The bond energy calculated in **(c)(ii)** could have been more accurate if the value of an additional enthalpy change is known. State what process this enthalpy change corresponds to. [1]

(d) Aluminium oxide is used extensively in organic synthesis as a dehydrating agent.

An organic compound **A**, $C_8H_{10}O$, contains a benzene ring and has one carbon atom which is bonded to 4 different substituents.

When **A** is treated with Al_2O_3, compound **B** is formed. **B** can be converted into compound **C** by reacting with dry gaseous HCl. Compound **C** also has one carbon atom which is bonded to 4 different substituents.

When **C** is refluxed with acidified $KMnO_4$, compound **D**, $C_7H_6O_2$, is produced. Treatment of **D** with PCl_5 produces compound **E**.

Identify the five compounds **A** – **E**. State the type of each reaction described above.

[9]

[Total: 20]

- END OF PAPER -