JURONG JUNIOR COLLEGE
2013 JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY 9647/03

Paper 3 Free Response

17 September 2013
2 hours

Candidates answer on separate paper.

Additional Materials:	Answer Paper Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

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

Answer any **four** questions.

1 Nitric acid, HNO_3, is a common laboratory reagent and an important industrial chemical for the manufacture of fertilisers and explosives.

(a) Nitric acid can be used to prepare lead(II) nitrate, $Pb(NO_3)_2$, which does not occur naturally. When lead is dissolved in aqueous nitric acid, a brown gas is evolved during the reaction.

(i) Use the *Data Booklet* to construct an equation for the reaction of aqueous nitric acid with lead.

A 40 cm^3 sample of $Pb(NO_3)_2(aq)$ was prepared and then mixed with 60 cm^3 of 0.100 mol dm^{-3} $Al_2(SO_4)_3(aq)$, which is in excess. Upon mixing, a precipitate is formed which is removed. The final solution **X** that remained is found to be weakly acidic.

(ii) With the aid of an equation, explain why solution **X** is acidic.

(iii) Given that the acid dissociation constant, K_a, of solution **X** is 1.4×10^{-5} mol dm^{-3}, calculate $[H^+]$ in solution **X**.

[5]

(b) During the industrial manufacture of nitric acid, NO_2 is hydrolysed by passing the gas through water.

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g) \quad \Delta H_r$$

The following enthalpy changes are given:

	ΔH /kJ mol^{-1}
$N_2(g) + O_2(g) \rightarrow 2NO(g)$	+183
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	–116
$2N_2(g) + 5O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$	–256

(i) Using relevant data from the table above, calculate the enthalpy change of formation of $NO_2(g)$.

(ii) Using your answer in **(b)(i)** and any relevant data in the table, calculate ΔH_r, the enthalpy change of reaction for the hydrolysis reaction of NO_2.

[3]

(c) When concentrated nitric acid is reacted with concentrated sulfuric acid, the nitronium ion, NO_2^+, is produced, according to the following equation.

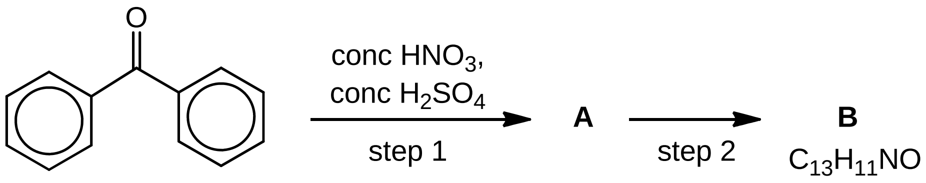
$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$$

(i) Draw a dot-and-cross diagram of the HNO_3 molecule.

(ii) Hence, suggest why HNO_3 acts as a *Bronsted base* in this reaction.

[2]

1 **(d)** Benzophenone can undergo the following two-step process.



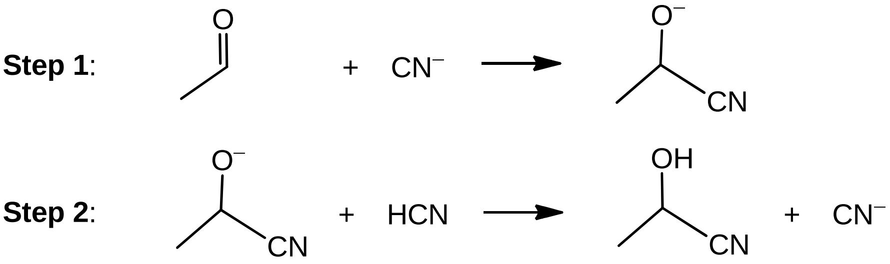
benzophenone

Draw the structural formulae of **A** and **B** and write a balanced equation for step 1. Suggest the reagents and conditions for step 2. [4]

(e) Unlike nitric acid which is a strong acid, HCN is a weak acid.

(i) With the aid of an equation, explain what is meant by the term *weak* acid using HCN as an example.

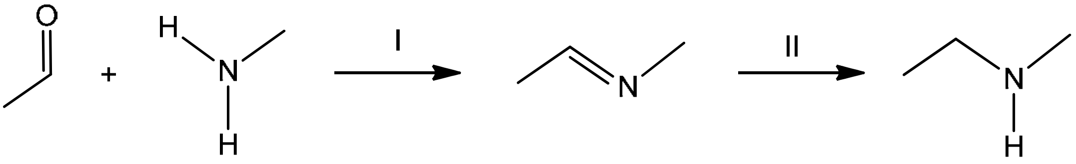
In organic reactions, HCN can react with aldehydes and ketones as shown in the mechanism below using ethanal as an example.



(ii) The reaction is carried out at a carefully controlled pH.

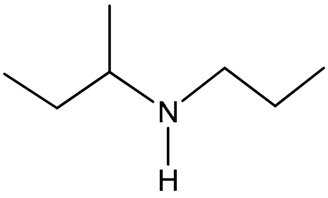
Suggest why this reaction occurs more slowly at both high and low concentrations of H^+ ions.

When primary amines are used instead of HCN, aldehydes and ketones react differently to form imines which can be converted to other amines, as illustrated by ethanal below.



(iii) State the *type of reaction* for reactions I and II.

(iv) Using the similar series of reactions as above, suggest the structural formulae of a possible pair of starting compounds that can be used to produce compound **C**.



compound **C**

[6]

[Total: 20]

2 Iron(III) chloride, $FeCl_3$, is an industrial scale commodity chemical compound.

(a) Anhydrous $FeCl_3$ can be prepared by passing chlorine gas over hot iron metal, kept heated at temperatures below 320 °C. However, if the metal is heated beyond 320 °C, the Fe_2Cl_6 vapour that is formed will slowly decompose to give $FeCl_2$ and Cl_2.

Fe_2O_3 can also be prepared by passing oxygen gas over hot iron metal. Unlike the preparation of $FeCl_3$, the metal can be heated at temperatures as high as 1000 °C.

(i) Explain why Fe_2O_3, unlike $FeCl_3$, can be prepared by heating iron metal with oxygen gas at very high temperatures.

(ii) $FeCl_3$ and Fe_2O_3 have the following melting points.

compound	melting point /°C
$FeCl_3$	305
Fe_2O_3	1565

Explain, in terms of structure and bonding, why the melting points of $FeCl_3$ and Fe_2O_3 are significantly different.

[4]

(b) One important industrial application of $FeCl_3$ is the etching of copper, via a two–step redox reaction as shown below, in the production of printed circuit board.

Step 1 $FeCl_3(aq) + Cu(s) \rightarrow FeCl_2(aq) +$ white solid **D**

Step 2 $FeCl_3(aq) +$ white solid **D** $\rightarrow FeCl_2(aq) +$ blue solution **E**

(i) Suggest the formula of compound **D** and of the complex ion present in **E**.

(ii) Explain fully why **D** is not coloured but **E** is coloured.

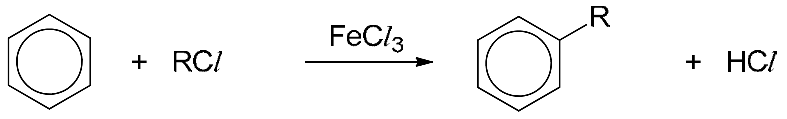
[6]

(c) In the laboratory, $FeCl_3$ is commonly employed as a Lewis acid (an electron–acceptor) as illustrated in the following example:

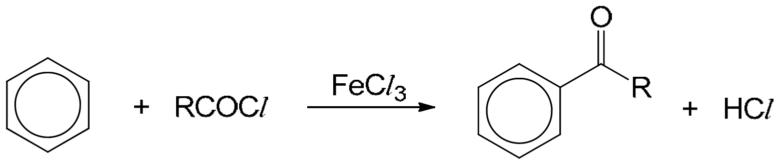
$$FeCl_3 + Cl_2 \rightarrow FeCl_4^- + Cl^+$$

It is used for catalysing Friedel–Crafts reaction of aromatic compounds as shown by benzene below.

Friedel-Crafts Alkylation:



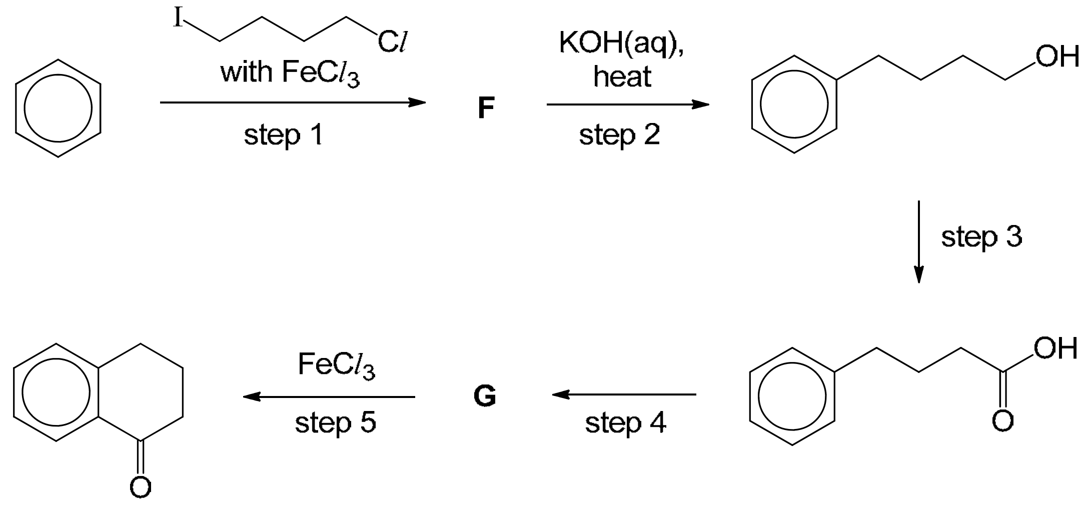
Friedel-Crafts Acylation:



(R represents an alkyl group.)

(i) State the *type of reaction* undergone by benzene during Friedel-Crafts reactions.

2 **(c)** Using the two Friedel-Crafts reactions described on **page 4** as parts of a synthesis route, a student suggested the following route to form 1–tetralone, from benzene.

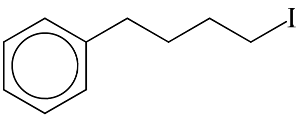


1-tetralone

(ii) Give appropriate reagents and conditions necessary for steps 3 and 4.

(iii) Predict the structure of **G**.

(iv) The student suggested that **F** has the following structure:

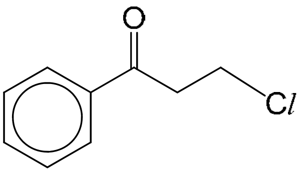


By quoting appropriate data in the *Data Booklet*, explain why the student's suggestion is **not** correct.

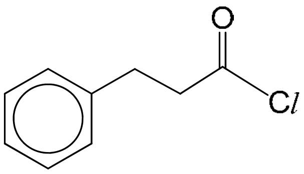
(v) Suggest a chemical test to be performed on **F** to prove that the student's suggestion is **not** correct.

(vi) Both **H** and **J** can also undergo Friedel–Crafts reactions in the presence of FeC*l*$_3$.

Suggest **two** reasons why **H** would require a harsher condition for Friedel–Crafts reaction to occur, as compared to **J**.



H



J

[10]

[Total: 20]

3 A breathalyser is a portable device used by the traffic police to estimate the blood alcohol content of intoxicated suspects via breath samples.

(a) One type of breathalyser uses the fuel cell technology and calculates the blood alcohol content based on the voltage measured.

The fuel cell contains platinum electrodes immersed in an acid electrolyte. At one electrode, ethanol from a breath sample is converted to ethanoic acid whereas at the other electrode, oxygen is converted to water.

(i) State the oxidation state of the carbon atom that is attached to the oxygen atom in one molecule of ethanol.

(ii) Write an overall equation for the reaction that occurs in the breathalyser.

(iii) Explain how the voltage of this breathalyser will change when the ethanol concentration increases.

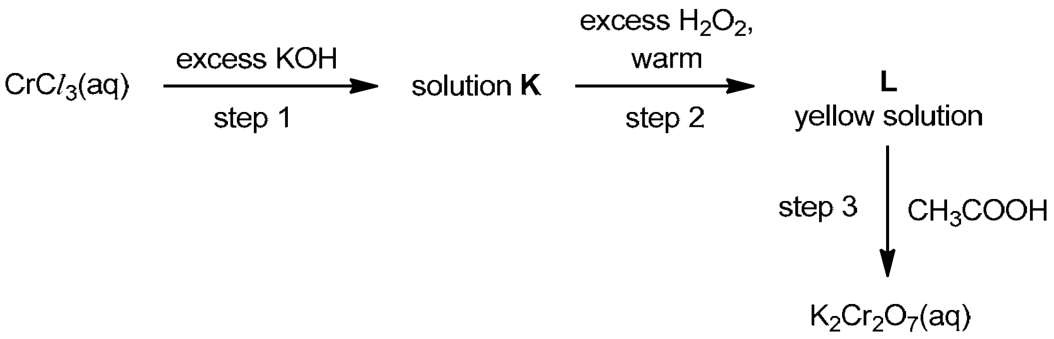
[3]

(b) An earlier version of a breathalyser consists of a chamber of acidified potassium dichromate(VI), $K_2Cr_2O_7$, which converts ethanol to ethanoic acid.

Ethanol in the breath sample will cause a colour change in the chamber in the presence of a silver nitrate catalyst. The instrument then calculates the blood alcohol content based on the degree of the colour change.

(i) With the aid of a suitable diagram, explain why the breathalyser can provide a test result within a very short period of time at normal ambient temperatures.

Potassium dichromate(VI) can be prepared in the laboratory using aqueous chromium(III) chloride, $CrCl_3$, via a series of reaction shown below.



(ii) Identify **K** and **L**.

(iii) Before adding CH_3COOH to **L** in step 3, the excess H_2O_2 needs to be removed.

Using relevant data in the *Data Booklet*, show why this is necessary.

(iv) To remove the excess H_2O_2, solution **L** is heated.

Suggest how you would confirm that all H_2O_2 has been removed and the heating can thus be stopped.

[7]

3 **(c)** In the liver of a human body, ethanol from the intake of alcoholic drink is first metabolised to ethanal, which is then converted to carbon dioxide and water. Alcohol dehydrogenase is the enzyme responsible for the first step.

(i) In a molecule of alcohol dehydrogenase, β-pleated sheets are found in localised regions. Sketch a diagram to show the structure of a β-pleated sheet.

(ii) When temperature rises beyond a particular value, the rate of an enzyme-catalysed reaction falls drastically. Explain the chemical basis of this phenomenon.

[4]

(d) A protein molecule can transit between its folded and unfolded states in water as shown below.

$$\text{folded state} \rightleftharpoons \text{unfolded state}$$

The unfolding process of a certain globular protein in water has a $\Delta H^{\ominus}$ of +200 kJ mol^{-1} and a $\Delta S^{\ominus}$ of +0.600 kJ mol^{-1} K^{-1}.

(i) Explain the significance of the sign of $\Delta S^{\ominus}$.

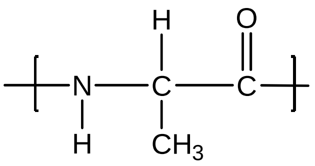
(ii) Calculate the temperature at which the protein molecule starts to unfold.

(iii) The equilibrium constant, K_c, can be related to $\Delta G^{\ominus}$ by the equation $\Delta G^{\ominus} = -\mathrm{RT}\ln K_c$.

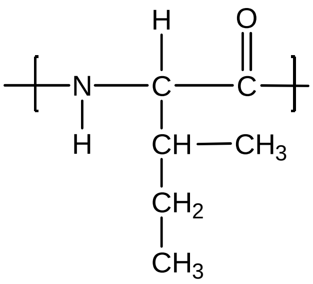
Calculate K_c for protein unfolding at 340 K and hence, calculate the proportion of the protein that will be properly folded at this temperature.

[5]

(e) A mutation occurs in the protein molecule such that an alanine residue normally buried at the core of the protein was replaced by an isoleucine residue.



alanine residue in a
normal protein molecule



isoleucine residue in a
mutant protein molecule

This mutational change did not affect the overall structure of the protein, but the measured $\Delta H^{\ominus}$ for the unfolding of the mutant protein differs from that of the unfolding of the normal protein by 40 kJ mol^{-1}.

Was the magnitude of $\Delta H^{\ominus}$ for the unfolding of the mutant protein most likely higher *or* lower? Justify your answer. [1]

[Total: 20]

4 **(a)** Metal hydroxide is a common component of antacids, which is administrated to neutralise gastric juice in the stomach to relieve acid indigestion.

To determine the solubility product, K_{sp}, of a metal hydroxide, **M**$(OH)_2$, in water at 25 °C, the following procedure was carried out.

- Anhydrous **M**$(OH)_2$ was crushed into fine powder and then added to a beaker containing 100 cm^3 of water, until no more solid could dissolve further.
- After filtration, 25.0 cm^3 of 0.000250 mol dm^{-3} HC*l* was titrated against the filtrate collected. 27.90 cm^3 of the filtrate was required for complete neutralisation.

(i) Explain, in terms of molecular collisions, why the solid should be crushed into fine powder before dissolving it in water

(ii) Using the information above, determine the K_{sp} of **M**$(OH)_2$ in water at 25 °C, stating its units.

(iii) Given that **M** is *either* Zn *or* Mg, suggest an appropriate inorganic reagent to determine the identity of **M**$(OH)_2$ and give the corresponding observations.

(iv) The following table contains information of some pH indicators.

Indicator	pK_a	colour in acidic form	colour in alkaline form
Methyl Orange	4.7	red	yellow
Bromothymol Blue	7.1	yellow	blue
Alizarine Yellow R	11.0	yellow	red

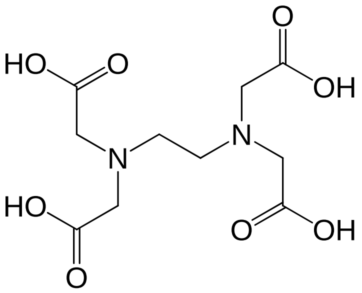
Using the information provided, suggest the **most** suitable indicator for the titration between $Mg(OH)_2$ and HC*l*.

State the colour change at end–point.

[9]

4 **(b)** Complexiometric titration is often used to determine the concentration of Mg^{2+} and Ca^{2+} in water using complexing agents such as ethylenediaminetetraacetic acid (widely abbreviated as EDTA).

The unionised form of EDTA has the following structure of H_4Y.



unionised form of EDTA (H_4Y)

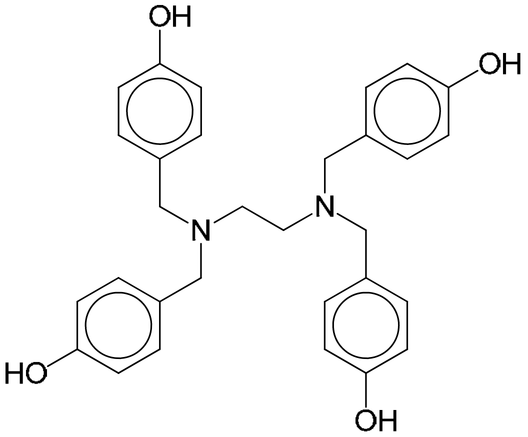
(i) EDTA is amphiprotic as it can both donate and accept protons.

Copy the structure of EDTA (H_4Y) and circle, with clear labelling, an atom or a group of atoms on EDTA that is capable of

I accepting a proton;

II donating a proton.

Similar to EDTA, compound **P** (shown below) is amphiprotic.



Compound **P**

(ii) State and explain how the acidity of EDTA (H_4Y) and compound **P** might differ.

(iii) It was found that the first base dissociation constant of compound **P** is lower than that of EDTA (H_4Y). Suggest why this might be so.

[4]

4 **(c)** The table below shows the different forms of EDTA and their corresponding pK_a values:

Form of EDTA	H_6Y^{2+}	H_5Y^{+}	H_4Y	H_3Y^{-}	H_2Y^{2-}	HY^{3-}	Y^{4-}
pK_a	0.0	1.5	2.0	2.6	6.2	10.2	–

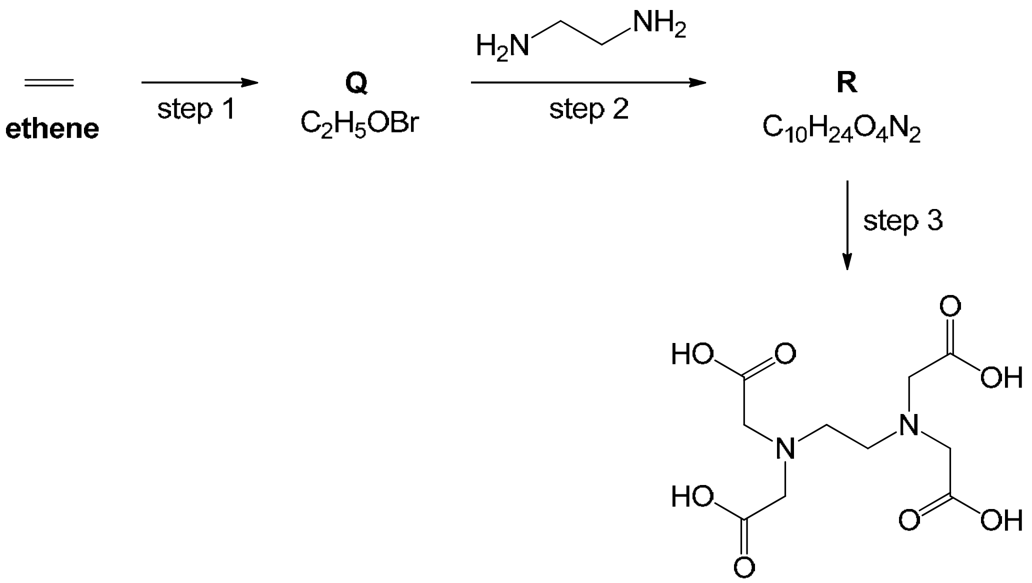
(i) Given that the most stable form of EDTA is able to form a stable complex ion with Mg^{2+} in a 1:1 ratio with an overall charge of 2–, identify the most stable form of EDTA.

(ii) In order to obtain a solution containing the most stable form of EDTA as identified in **(c)(i)**, the solution of EDTA used in complexiometric titration is typically buffered.

State whether an acidic buffer *or* basic buffer should be used to maintain the solution of EDTA at the desired pH level and suggest a pH value for the buffer.

[2]

(d) Synthesis of the unionised form of EDTA (H_4Y) can be carried out in the laboratory, using ethene as the starting material.



unionised form of EDTA (H_4Y)

(i) Draw the structures of **Q** and **R**.

(ii) Suggest appropriate reagents and conditions for steps 1 to 3.

[5]

[Total: 20]

5 Fluorine, chlorine, bromine and iodine are members of the halogen family.

(a) Chlorine is made commercially by the electrolysis of brine (concentrated sodium chloride) using inert electrodes. In the cell, the anode and cathode compartments are separated by a diaphragm.

(i) Write ion-electron equations for the reactions occurring at the anode and cathode.

(ii) Using the relevant half-equation in **(a)(i)**, calculate the current needed to produce 100 tonnes of Cl_2 per day.
[1 tonne = 1 × 10^6 g]

(iii) Suggest what products might be formed at room temperature if the diaphragm was removed, writing a balanced equation for the reaction that occurs.

On the other hand, fluorine cannot be obtained by electrolysing aqueous sodium fluoride using inert electrodes.

(iv) With reference to relevant data from the *Data Booklet*, predict the gas formed at the anode when dilute sodium fluoride is used. Explain your reasoning.

(v) Explain clearly why fluorine is not formed even if concentrated sodium fluoride is used.

[7]

(b) HBr and HI form acidic white fumes in moist air under room temperature and pressure conditions. Addition of concentrated sulfuric acid to these two hydrogen halides separately can be used as a distinguishing test.

State what you would observe for **each** compound when concentrated sulfuric acid is added. Write balanced equations with state symbols for any reactions that occur. [3]

(c) In the production of CH_3Cl using methane and chlorine under certain conditions, it has been noticed that a small quantity of chloroform, $CHCl_3$, has been produced.

Using CH_3Cl as the starting material, describe the mechanism of this reaction that would result in the production of chloroform. [2]

(d) Compound **S**, $C_6H_{10}Cl_2$, exists in **two** stereoisomeric forms.

When vigorously oxidised with hot potassium manganate(VII) in excess alkali, followed by acidification, **T**, $C_4H_6O_3$, is the only organic compound produced. **T** gives yellow crystals with alkaline aqueous iodine solution and carbon dioxide with aqueous sodium carbonate respectively.

When reacted with hot ethanolic potassium cyanide, **S** gives **U**, $C_8H_{10}N_2$, which is then reduced by hydrogen gas to give **V**, $C_8H_{20}N_2$. With dilute hydrochloric acid, **V** gives a white crystalline solid when the mixture is evaporated. **U**, when heated under reflux with a dilute acid, gives **W**, $C_8H_{12}O_4$.

Identify the compounds **S**, **T**, **U**, **V** and **W**. State the *type* of **each** reaction described above. [8]

[Total: 20]