RAFFLES INSTITUTION
2015 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CHEMISTRY 9647/03

Paper 3 Free Response **September 2015**

Candidates answer on separate paper. **2 hours**

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

DO NOT open this question booklet until you are told to do so.

Write your name, class and index number in the spaces provided on the cover page.
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.
Begin each question on a fresh sheet of paper.
A Data Booklet is provided. Do not write anything on it.
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, with the cover page on top.

This document consists of **13** printed pages.

Answer any **four** questions.
Begin each question on **a fresh sheet of paper**.

1 Calcium is the fifth most abundant element found in the Earth's crust. It is commonly found in the form of salts and oxides as limestone, marble and chalk.

(a) Finely powdered calcium metal can cause spontaneous explosions in air. Explain briefly why this is so, writing chemical equations where appropriate. **[2]**

(b) Calcium metal is produced mainly by the electrolysis of molten calcium chloride at 800 °C.

(i) Determine the mass (in tonnes) of calcium metal that can be obtained when 1×10^5 A of current is passed through an electrolytic cell for 3 hours. [1 tonne = 1000 kg] **[2]**

(ii) With the use of the *Data Booklet*, explain why the electrolysis of calcium chloride cannot be conducted in aqueous medium. **[1]**

(c) When 2.0 g of calcium ethanoate, $Ca(CH_3CO_2)_2$, was heated to 450 °C, only propanone and a white solid, **M**, were produced.

(i) Write a balanced equation for the thermal decomposition of calcium ethanoate and state the identity of the white solid **M.** **[1]**

(ii) On further heating, partial decomposition of solid **M** occurs to give off carbon dioxide and a white residue. The white residue contains 70% by mass of solid **M**.

Calculate the mass of carbon dioxide evolved from the partial decomposition.
[M_r of $Ca(CH_3CO_2)_2$ = 158.1; CO_2 = 44.0] **[3]**

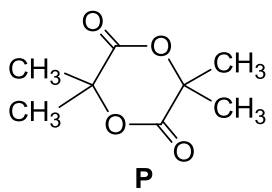
(iii) Predict whether barium ethanoate, $Ba(CH_3CO_2)_2$, decomposes at a higher or lower temperature than $Ca(CH_3CO_2)_2$. Explain your answer. **[1]**

Propanone is widely used as a solvent.

(d) **(i)** Propanone reacts with hydrogen cyanide in the presence of trace amounts of potassium cyanide to form a cyanohydrin.

Describe the mechanism, showing all partial and full charges and using curly arrows to show the movement of electron pairs. **[2]**

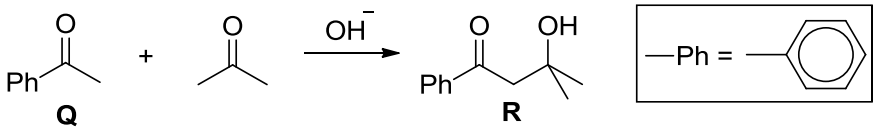
(ii) Suggest a two-step synthesis starting from the cyanohydrin in **(d)(i)** to form compound **P** as shown below.



P

[2]

(e) In aqueous solutions, propanone reacts readily with compound **Q** in the presence of hydroxide ions to form compound **R**, as shown in the equation below.

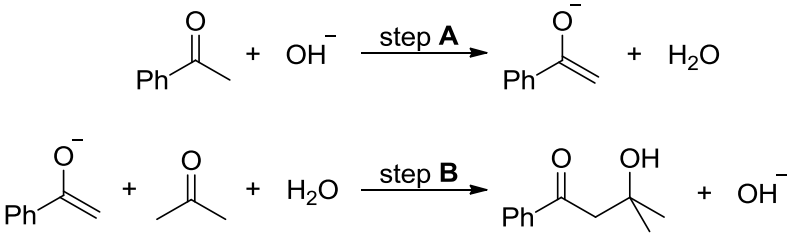


Four experiments were carried out to study the kinetics of the reaction.

Experiment	Initial concentrations / mol dm^{-3}			Initial rate of formation of **R** /mol dm^{-3} s^{-1}
	[**Q**]	[Propanone]	[OH^-]	
1	0.0100	0.200	0.100	6.60×10^{-5}
2	0.0080	0.200	0.100	5.28×10^{-5}
3	0.0100	0.100	0.100	3.30×10^{-5}
4	0.0080	0.100	0.150	3.96×10^{-5}

(i) Use the data to deduce the order of reaction with respect to each of the three reagents, showing clearly how you arrived at your answer. Hence, write a rate equation for the reaction. **[3]**

(ii) It was proposed that the reaction between propanone and **Q** proceeds via the following mechanism.



Based on your rate equation in **(e)(i)**, suggest whether step **A** or step **B** is the rate determining step. Explain your choice. **[2]**

(iii) State the role of hydroxide ions in the reaction. **[1]**

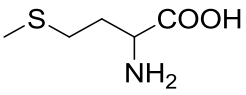
[Total: 20]

2 Methionine and tyrosine are two essential amino acids responsible for the structural conformation of prion proteins, which are linked to neurodegenerative diseases such as Creutzfeldt-Jakob disease (CJD), the human form of mad cow disease, and Alzheimer's disease.

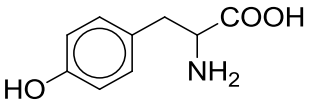
(a) (i) A common feature among these neurodegenerative diseases is the conversion of a protein, predominantly composed of α-helical structures, into highly ordered fibrous forms with structures rich in β-pleated sheets.

With the aid of a suitable diagram, describe the structure of a β-pleated sheet protein. **[2]**

The structures of methionine and tyrosine are shown below:



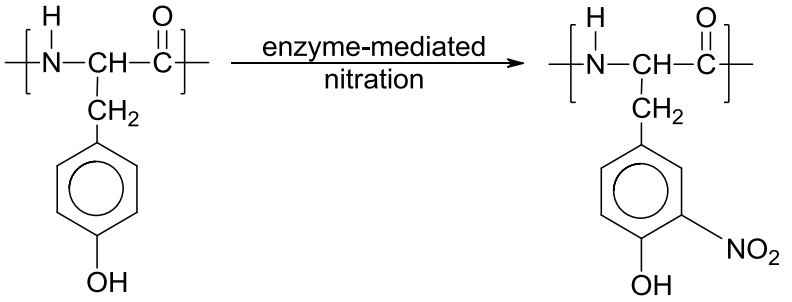
methionine



tyrosine

(ii) Both methionine and tyrosine dissolve readily in water. Explain why. **[2]**

(iii) Tyrosine residues in proteins are easily modified to 3-nitrotyrosine residues by enzymes.



tyrosine residue in normal prion protein

pK_a = 10.1

3-nitrotyrosine residue in infectious prion protein

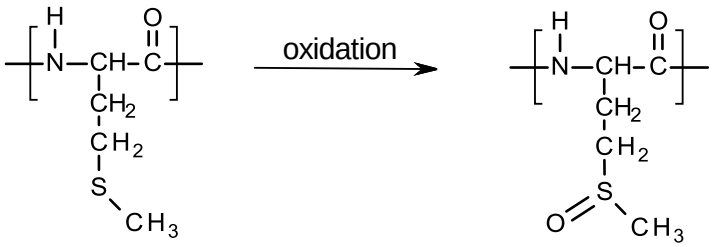
pK_a = 7.2

Explain why the pK_a of the 3-nitrotyrosine residue (pK_a = 7.2) is lower than that of the tyrosine residue (pK_a = 10.1). **[1]**

(iv) At physiological pH of 7.34–7.45, 3-nitrotyrosines residues were shown to induce conformation change in the tertiary structures of the prion proteins.

By considering the pK_a values given above, suggest a possible reason why this happens. **[2]**

(v) The oxidation of methionine to methionine sulfoxide inhibits the conformation change of α-helix to β-pleated sheet in a normal prion protein.



methionine residue　　methionine sulfoxide residue

One plausible suggestion is that methionine sulfoxide is able to form R-group interactions with other polar amino acids, like tyrosine, which then stabilise the normal prion proteins.

State the type of R-group interaction present between tyrosine residues and methionine sulfoxide residues. Illustrate your answer with a suitable diagram. **[2]**

(b) In the 1970s, biochemists discovered that methionine acts as a precursor to the production of ethene in plants. This process is known as the Yang cycle.

During the process, an intermediate, **X**, $C_4H_7NO_2$ is formed. **X** is both soluble in sodium hydroxide and hydrochloric acid. When irradiated with UV light together with chlorine, **X** forms only one monochlorinated compound (ignoring stereoisomers).

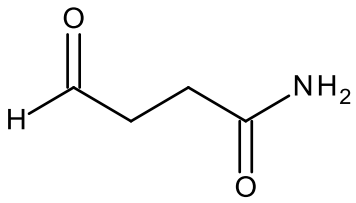
(i) Suggest a structure for intermediate, **X**. **[1]**

(ii) Compound **Y** is an isomer of **X**. It can be easily synthesised from a brominated carboxylic acid. **Y** does not decolourise aqueous bromine.

$$NH_2CH_2CH_2CH(Br)CO_2H \xrightarrow{\text{heat}} \mathbf{Y} + HBr$$

State the type of reaction, and hence suggest a structure for compound **Y**. **[2]**

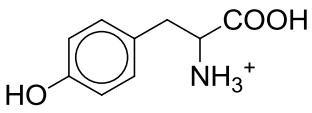
(iii) 4-oxobutanamide is another structural isomer of **X**.



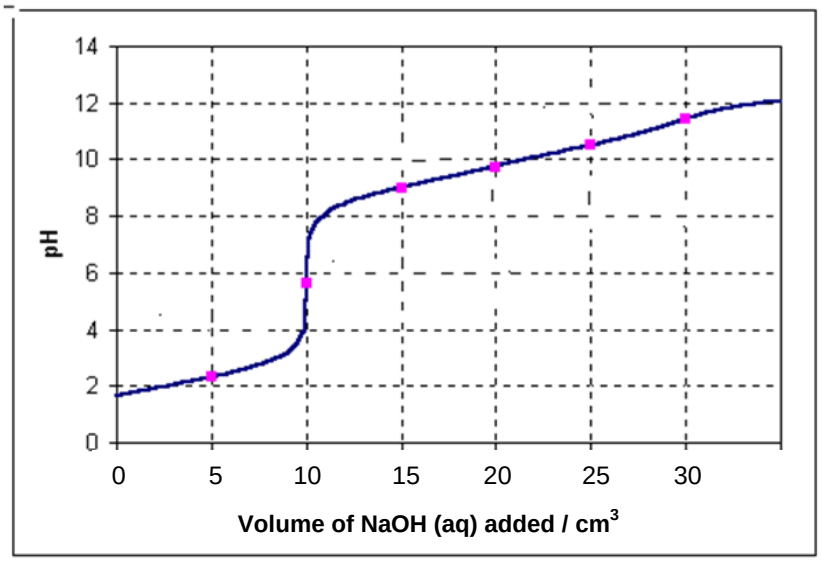
4-oxobutanamide

Describe what would be observed when 2,4-dinitrophenylhydrazine is added to 4-oxobutanamide. Draw the structure of the organic product formed. **[2]**

(c) When 10.0 cm^3 of protonated tyrosine, H_3T, was titrated with NaOH, the following curve was obtained. Both solutions have the same concentration.



Protonated tyrosine (H_3T)



(i) Given that the pK_a values of H_3T are 2.2, 9.1 and 10.1, explain why the titration curve appears to show only one equivalence point instead of three equivalence points. **[1]**

(ii) Draw the structures of the species present in the solution after 5.0 cm^3 of NaOH has been added. **[1]**

(iii) With the aid of an appropriate equation, explain why the first equivalence pH is acidic at 5.7. Determine the concentration of H^+ ions at the first equivalence point. **[2]**

(iv) With reference to answers in **c(iii)**, calculate the concentration of H_3T used in the titration. **[2]**

[Total: 20]

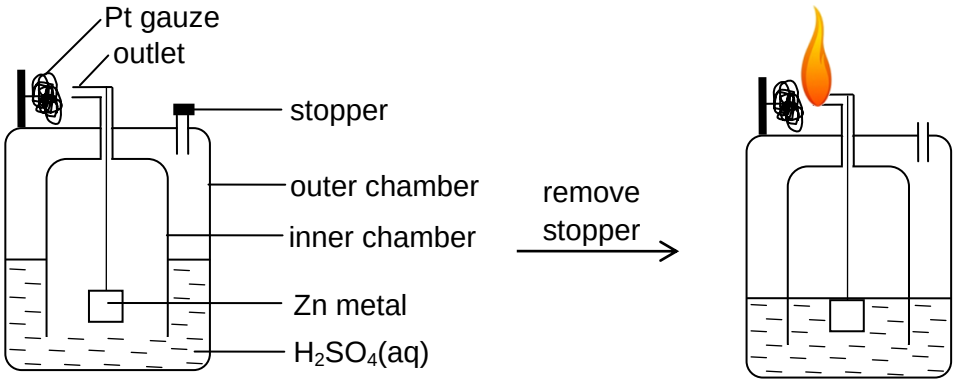
3 Platinum is an inert transition metal which has numerous applications in catalysis and electrochemical cells.

(a) **(i)** The reaction of hydrogen with oxygen is extremely exothermic, but takes place only in the presence of a spark or a heterogeneous catalyst, such as platinum.

$$2H_2(g) + O_2(g) \xrightarrow{\text{Pt catalyst}} 2H_2O(g) \quad \Delta H < 0$$

With reference to the stages in a heterogeneous catalysis, explain why a transition metal, such as Pt, is able to act as a heterogenous catalyst, and how its use speeds up the rate of the above reaction. **[3]**

(ii) The Döbereiner lighter, first demonstrated in 1823, was popular before the invention of matchsticks. The design incorporates a piece of platinum gauze as shown in the diagram below.



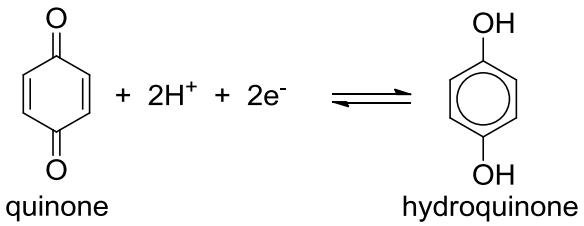
When the stopper is removed, sulfuric acid in the outer chamber flows into the inner chamber. A sequence of events occurs resulting in a flame at the outlet.

With the aid of information from **(a)(i)**, describe the sequence of events which leads to the formation of the flame. Your answer should include relevant chemical equation(s). **[3]**

(b) Use of the *Data Booklet* is relevant for this part.

A quinhydrone half-cell comprises a platinum electrode immersed in a solution which is prepared by dissolving a mixture of quinone and hydroquinone in acid.

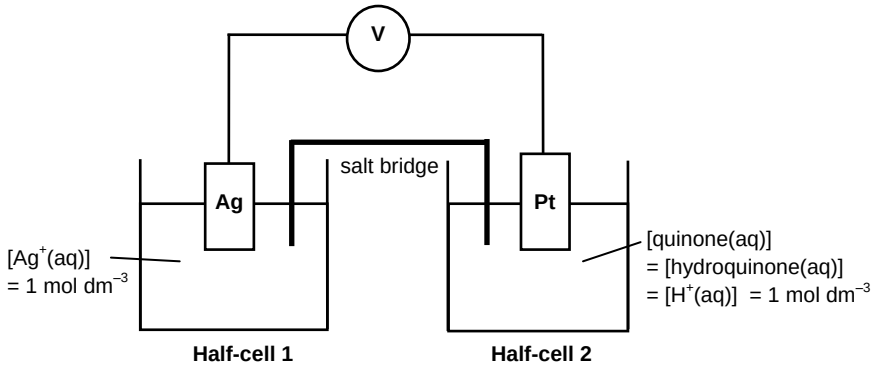
The standard reduction potential, $E^{\ominus}$, of the quinone-hydroquinone system is +0.70 V.



quinone hydroquinone

(i) By considering the oxidation states of the appropriate carbon atoms in quinone and hydroquinone, show that the conversion of quinone to hydroquinone is a reduction. **[2]**

An electrochemical cell, which consists of a standard quinone-hydroquinone half-cell and a standard Ag^+/Ag half-cell, was set up.



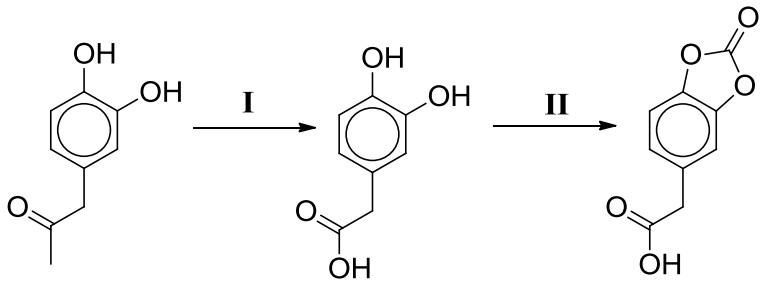
(ii) Write the half-equations of the reactions which occur at the cathode and anode. **[2]**

(iii) State the reading indicated on the voltmeter, when the above electrochemical cell is set up. **[1]**

(iv) Some solid $K_4[Fe(CN)_6]$ was added to the quinone-hydroquinone half-cell. Using relevant reduction potentials, explain the effect of this change on

- the concentrations of quinone and hydroquinone in the half cell, and
- the reading on the voltmeter. **[2]**

(c) Compound **T** is derived from the 1,2–isomer of hydroquinone. The conversion of **T** to **V** is shown below.



T **U** **V**

(i) Stage **I** comprises a two-step conversion. State the reagents and conditions for the two steps. **[2]**

(ii) Suggest the reagent(s) required for stage **II**. **[1]**

(iii) Describe a simple chemical test to distinguish between compounds **U** and **V**. You should provide observations for each compound. **[2]**

(iv) Predict the products of the alkaline hydrolysis of **V**. **[2]**

[Total: 20]

4 **(a)** The chemistry of some period 3 elements and their compounds are discussed here.

(i) Explain why the first ionisation energy of aluminium is lower than that of magnesium. **[1]**

Some information regarding three oxides, **E**, **F** and **G**, are given below.

oxide	melting point / °C	electrical conductivity when molten
E	1713	very poor
F	24	nil
G	2072	good

(ii) These three oxides, in no particular order, are Al_2O_3, SiO_2 and P_4O_6.
Identify **E**, **F** and **G**. **[1]**

(iii) With reference to their structure and bonding, account for your answer in **(a)(ii).** **[3]**

(iv) Suggest the pH values of the solutions formed when **E**, **F** and **G** are added separately to water. Write balanced equations for each of these reactions, where appropriate. **[2]**

(v) Molten sulfur and chlorine can react to form disulfur dichloride, S_2Cl_2.

$$S_8(l) + 4Cl_2(g) \longrightarrow 4S_2Cl_2(l)$$

	melting point / °C	boiling point / °C
sulfur	115	444
chlorine	–102	–34
disulfur dichloride	–80	137

Using the information provided, describe how a sample of S_2Cl_2 can be made from solid sulfur and chlorine gas, and how it can be purified. **[2]**

(b) Acid Mine Drainage (AMD) is metal-rich water formed from chemical reactions between surface water and rocks containing metal sulfides. The water is highly acidic and further dissolves heavy metals such as copper and iron. These metal ions can be removed by precipitation of their respective hydroxides.

In **Experiment 1**, solid NaOH was added to a 500 cm^3 sample of AMD to remove Al^{3+}, Cu^{2+}, Fe^{2+} and Zn^{2+}. The results are shown in **Figure 1**.

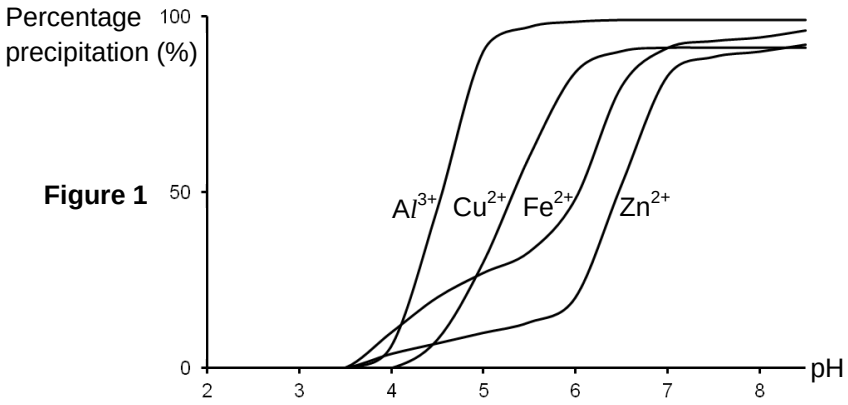


Figure 1

In **Experiment 2**, a separate 500 cm^3 sample of the same AMD was exposed to air for 5 days. The same procedure of precipitation using solid NaOH pellets was then carried out. The results are shown in **Figure 2**.

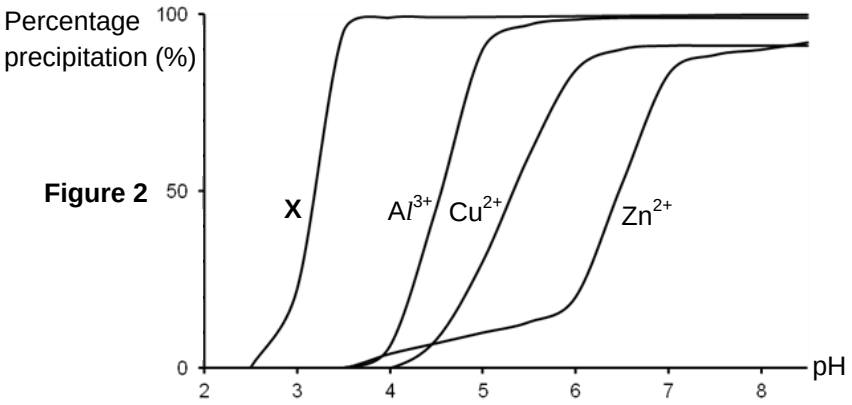


Figure 2

In **Experiment 1**, it was observed that $Fe(OH)_2$ was amongst the first precipitates formed.

(i) Write an expression for the solubility product of $Fe(OH)_2$, stating the units. **[1]**

(ii) The concentration of Fe^{2+} in the original AMD sample was 256.8 mg dm^{-3}.
At 25 °C, the K_{sp} of $Fe(OH)_2$ has a value of 8.0×10^{-16}.

Calculate the pH of the resultant solution in **Experiment 1** when 95% of the iron present had been precipitated as $Fe(OH)_2$. **[3]**

(iii) With the aid of **Figure 1**, estimate the minimum pH value where at least 50% of **each** metal ion present has been precipitated. **[1]**

The slight modification in procedure between **Experiments 1** and **2** produced different results as shown in **Figures 1** and **2**.

(iv) State the identity of the cation, **X**. **[1]**

(v) The pH of the original AMD sample was approximately 3. The pH of the solution used in **Experiment 2**, before any NaOH was added, was found to be approximately 2.

With the aid of a suitable equation, suggest an explanation for this decrease in pH. **[2]**

(c) In addition to heavy metals, other harmful metalloids such as arsenic can also be found in AMD. A common form of this substance is arsenic trioxide, As_2O_3.

As_2O_3 reacts with concentrated nitric acid to produce compounds **P** and **Q** in the balanced equation shown.

$$As_2O_3 + 2HNO_3 + 2H_2O \longrightarrow 2\mathbf{P} + \mathbf{Q}$$

(i) **P** has the following composition by mass: H, 2.1%; As, 52.8; O, 45.1%. Determine the molecular formula of **P**. **[1]**

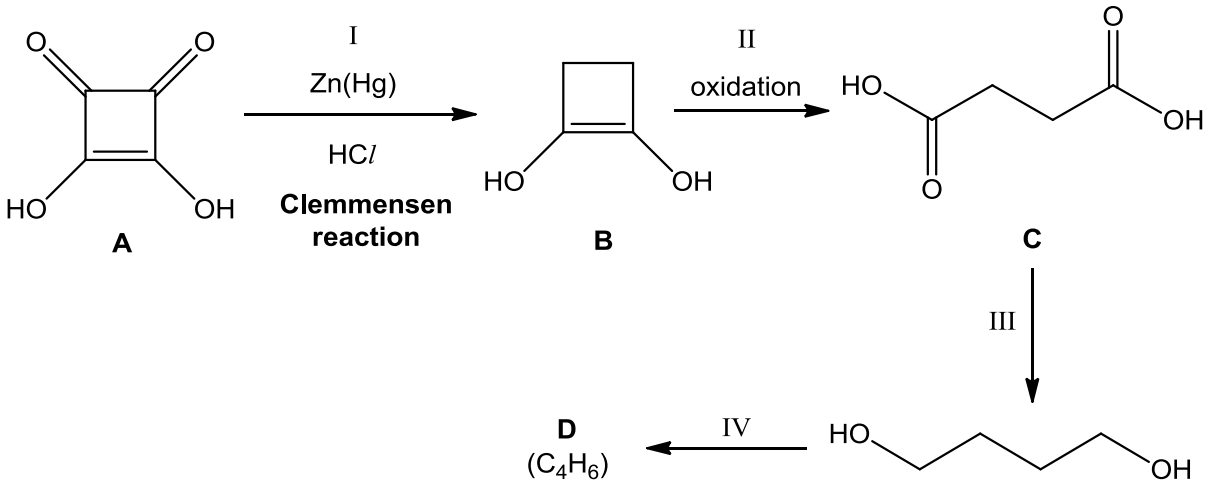
(ii) State the molecular formula of **Q**. **[1]**

(iii) Given that **Q** contains an N–N bond, suggest the structure of **Q**. **[1]**

[Total: 20]

5 **(a)** Oxocarbons are a series of organic compounds with the general formula $C_nH_2O_n$. Compound **A**, $C_4H_2O_4$, is one such example. It is a white crystalline powder with a melting point of 245 °C.

A reaction scheme using compound **A** as the starting reagent is shown below. The first step of the reaction is known as the Clemmensen reaction. This reaction reduces carbonyls to alkanes.



(i) Write the balanced equation for the reduction of compound **A** to **B**.
Use [H] to represent the formula of the reducing agent. **[1]**

(ii) The pK_{a1} values of compounds **A** and **C** are given below.

	pK_{a1}
Compound **A**	1.5
Compound **C**	4.2

With reference to the pK_{a1} values given, comment on and explain the relative acidity of compounds **A** and **C**. **[2]**

(iii) Suggest reagents and conditions for reactions III and IV. **[2]**

(iv) Suggest the structure of compound **D**. **[1]**

(b) The use of the *Data Booklet* is relevant in part **(b)**.

(i) Write a chemical equation for the enthalpy change of atomisation of compound **A** in its gaseous state. **[1]**

(ii) Calculate the enthalpy change of atomisation of compound **A** in its gaseous state. **[2]**

(iii) Using your answer to **(b)(ii)** and the following additional data, construct an energy cycle to determine the enthalpy change of sublimation of compound **A**.

- Standard enthalpy change of combustion for compound **A** is –1210 kJ mol^{-1}
- Standard enthalpy change of vaporisation of water is +40.7 kJ mol^{-1}
- Bond energy of C=O in CO_2 is +805 kJ mol^{-1}

[4]

(c) Ester **J** ($C_6H_{10}O_2$) decolourises Br_2 in CCl_4 to form $C_6H_{10}Br_2O_2$.

Upon prolonged heating with excess acidified $KMnO_4$, 1 mol of **J** produces 1 mol of **K** ($C_4H_6O_3$) and 2 mol of CO_2.

K gives a yellow precipitate when warmed with aqueous alkaline iodine. **K** also undergoes the Clemmensen reaction to give **L** ($C_4H_8O_2$). Both **K** and **L** produce effervescence when reacted with aqueous Na_2CO_3.

Deduce the identities of **J**, **K** and **L**. **[7]**

[Total: 20]