Name: **Index No.:** **CT Group: 11**

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CHEMISTRY 9647/03

Paper 3 Free Response **14 September 2012**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number and name on all 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 workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** out of five questions.
State the question number of the questions that you have attempted on the cover page provided.
The question numbers should be stated in sequence.

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.

This document consists of **15** printed pages.

Answer any **four** questions

1 Enzymes are biological molecules that catalyse chemical reactions. Almost all chemical reactions in a biological cell need enzymes in order to occur at rates sufficient for life.

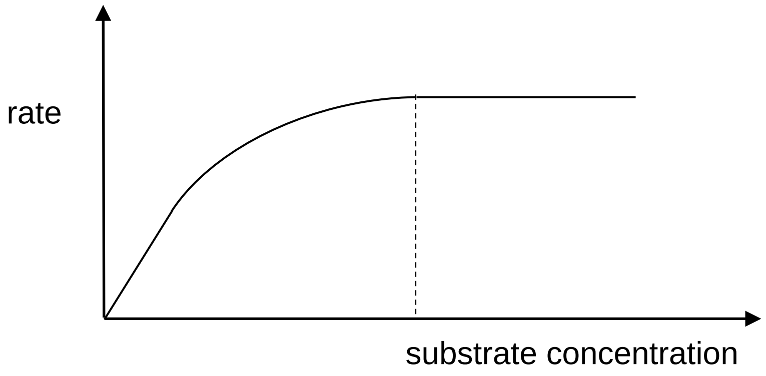
(a) Acquired Immuno-Deficiency Syndrome (AIDS) is a disease of the human immune system caused by the Human Immunodeficiency Virus (HIV). HIV-1 Protease is an enzyme which speeds up the reproduction of HIV. In the development of anti-HIV drugs, scientists often study the amino acid sequence of the HIV-1 Protease to understand how this enzyme displays its biological properties in the human body.

(i) A segment of the polypeptide structure of HIV-1 Protease, containing 10 amino acids, was digested using an enzyme and the following fragments were obtained.

leu – asn – phe
ile – gly – cys – thr – leu
leu – thr – glu – ile – gly

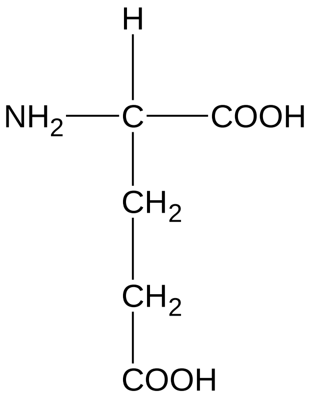
Deduce the primary structure of this segment of HIV-1 Protease.

(ii) A segment of the HIV strand acts as a substrate, which binds to the active site of the HIV-1 Protease which speeds up the reproduction of the HIV virus. The rate of this enzyme-catalysed reaction is investigated and can be represented by the following graph.



Explain the difference in the rate of reaction at high and low concentrations of substrate.

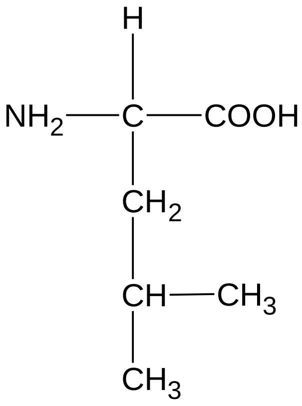
(iii) The structural formulae of the three most common amino acids present in the protein chain in HIV-1 Protease are shown below.



$NH_2CH(CH_2CH_2COOH)COOH$

glutamic acid

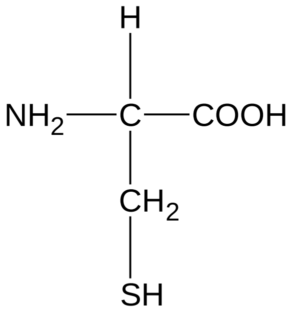
(glu)



$NH_2CH(CH_2CH(CH_3)CH_3)COOH$

leucine

(leu)



$NH_2CH(CH_2SH)COOH$

cysteine

(cys)

In how many different ways can these three amino acids be coupled by peptide bonds to form a tripeptide? Draw the structural formula of one such peptide.

(iv) The side chains of these three amino acids are responsible for maintaining the tertiary structure of HIV-1 Protease.

State and draw the type of side-chain interaction between two cysteine (cys) residues.

State the type of reaction that is involved in the formation of the side-chain interaction.

(v) Since its discovery in 1981, scientists have studied the protein structure of HIV in order to prevent its transmission. The World Health Organisation recommends heat treatment of breast-milk prior to giving it to the child, as a way to reduce the risk of HIV transmission to the baby in sub-Saharan Africa.
Explain how this treatment of breast-milk reduces the risk of HIV infection in infants.

[9]

(b) An example of a copper-containing enzyme is superoxide dismutase (SOD) that aids in the disproportionation of the strongly oxidising superoxide ion, O_2^- to oxygen and hydrogen peroxide. Thus, they are an important antioxidant defense in nearly all cells exposed to oxygen, thereby protecting the body from harm.

$$2O_2^- + 2H^+ \longrightarrow O_2 + H_2O_2$$

(i) The activity of SOD hinges on the active site Cu^{2+} ion.

By referring to the following $E^\ominus$ data, suggest a mechanism for the catalysis of the disproportionation of O_2^- by SOD.

You may represent the oxidised and reduced forms of the enzyme as SOD- Cu^{2+} and SOD- Cu^+ respectively.

	$E^\ominus$/ V
$O_2 + e^- \rightleftharpoons O_2^-$	- 0.33
$O_2^- + e^- + 2H^+ \rightleftharpoons H_2O_2$	+0.89
SOD- Cu^{2+} + e^- $\rightleftharpoons$ SOD- Cu^+	+0.42

(ii) State the type of catalysis and explain how SOD–Cu^{2+} can act as a catalyst.

(iii) With the aid of a sketch of the Boltzmann distribution, explain how the presence of a catalyst affects the rate of reaction.

(iv) The secondary structure of SOD is composed mainly of beta-pleated sheets, as well as some regions of alpha-helices.

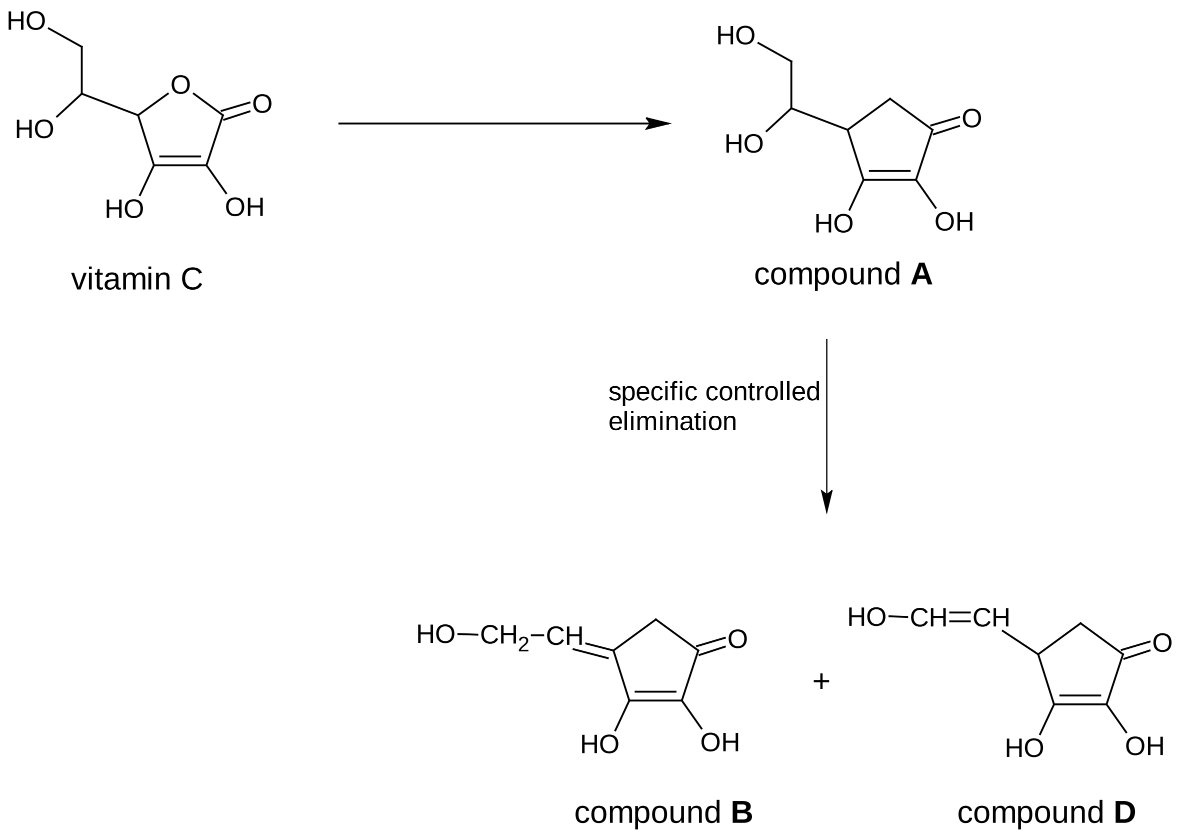
Draw a diagram of the beta-pleated sheet, showing the bonding which maintains the structure of the secondary structure of the enzyme.

[11]

[Total: 20]

2 Ginger has been used as a natural remedy for many ailments for centuries. Researchers around the world are finding that ginger works wonders in the treatment of everything from cancer to migraines. Ginger consists of many chemicals. Vitamin C and chlorogenic acid are two of the chemicals present in ginger.

(a) The structure of vitamin C and its reaction pathway is shown below.



(i) Draw the structural formula of the compound formed when vitamin C reacts with hot acidified potassium dichromate(VI).

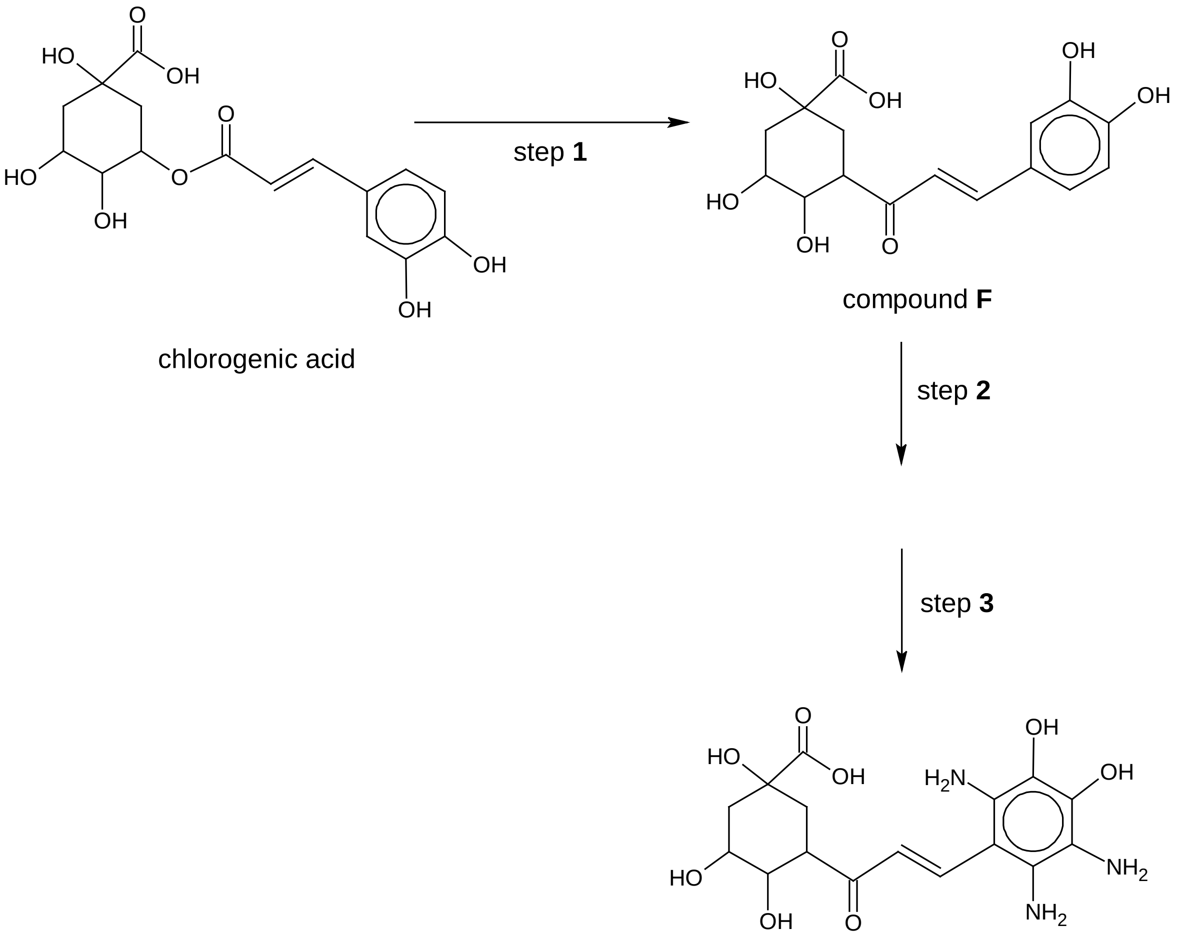
(ii) Compound **A** undergoes elimination to produce compounds **B** and **D**.

State and explain which compound is the major product.

(iii) Determine the maximum number of stereoisomers of compound **D**. Draw the pair that has the same boiling point.

[4]

(b) The structure of chlorogenic acid and its reaction pathway is shown below.



chlorogenic acid

compound **F**

compound **G**

(i) Compound **F** can be converted to compound **G** in two steps.

Suggest reagents and conditions for steps **2** and **3**.

(ii) Draw the structures of compounds formed when compound **G** reacts with

I H_2, Ni(s), 200°C

II $NaBH_4$ in methanol

[4]

(c) Ginger also contains nutrients like magnesium. Magnesium is a vital component of a healthy human diet. Magnesium taken in the proper amount plays a role in preventing both stroke and heart attack.

(i) Describe what is observed when a piece of magnesium ribbon is burnt in air.

(ii) The product obtained in **(i)** is placed in a beaker of water containing a few drops of universal indicator. State the observation(s) and write equations for the reaction(s) that occur.

[4]

(d) Sketch a graph of the pH of the solution when the chlorides of the elements from sodium to phosphorus are added separately to water. Label your graph clearly. [2]

(e) Hydrofluoric acid dissociates in water according to the following equation:

$$HF(aq) \xrightleftharpoons{DH^{\theta}_{dissociation}} H^{+}(aq) + F^{-}(aq)$$

The following are some enthalpy changes related to hydrogen fluoride.

First electron affinity of fluorine/ kJ mol^{-1}	-328
Standard enthalpy change of hydration of fluoride ion / kJ mol^{-1}	-506
Standard enthalpy change of reaction, HF(aq) → HF(g) / kJ mol^{-1}	+39
Standard enthalpy change of hydration of hydrogen ion / kJ mol^{-1}	-1090

(i) By using the data provided and other relevant data from the *Data Booklet*, construct an energy cycle and calculate the standard enthalpy change of dissociation of hydrofluoric acid.

(ii) Aqueous hydrofluoric acid is a weak acid under standard conditions. One explanation for the relatively weaker acid strength of hydrofluoric acid is its negative standard entropy change of dissociation, $\Delta S^{\theta}_{dissociation}$. Account for the sign of $\Delta S^{\theta}_{dissociation}$.

[6]

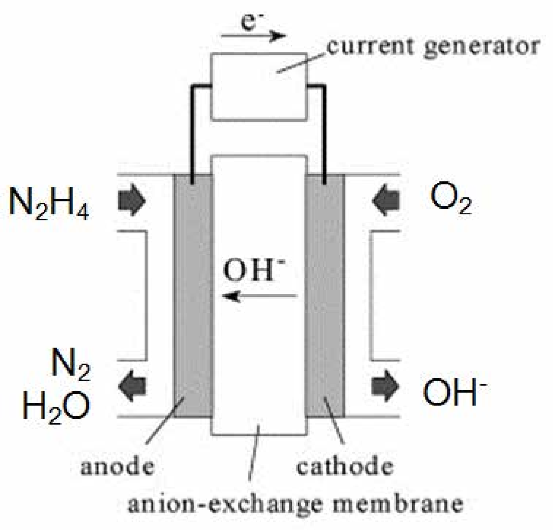
[Total: 20]

3 **(a)** Hydrazine (N_2H_4) is a colourless liquid with a slight odour like ammonia. However, the solubility of hydrazine in water is very much higher than that of ammonia.

Draw a diagram to show the bonding between a molecule of hydrazine and a molecule of water. Account for the difference in solubility of hydrazine and ammonia in water. [2]

(b) The Italian catalyst manufacturer *Acta* proposed using hydrazine as an alternative to hydrogen in fuel cells. The chief benefit of using hydrazine is that it can produce more energy than a similar hydrogen-oxygen cell.

The following diagram shows a typical hydrazine-oxygen fuel cell system incorporated with an anion exchange membrane between the electrodes.



(i) Write the two ion-electron half equations for the reactions that take place at each electrode. Hence, write an overall equation for the cell reaction.

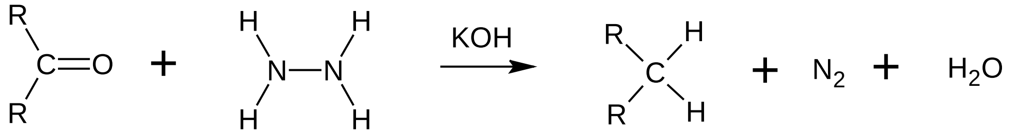
(ii) Given that $E^\ominus(N_2/N_2H_4)$ is -1.16 V, calculate the cell e.m.f. if the process takes place under standard conditions.

(iii) The hydrazine-oxygen fuel cell that is used to power a satellite produces an average current of 5 A per day. Assuming that the fuel cell is only 70% efficient, calculate the mass of hydrazine required in a day.

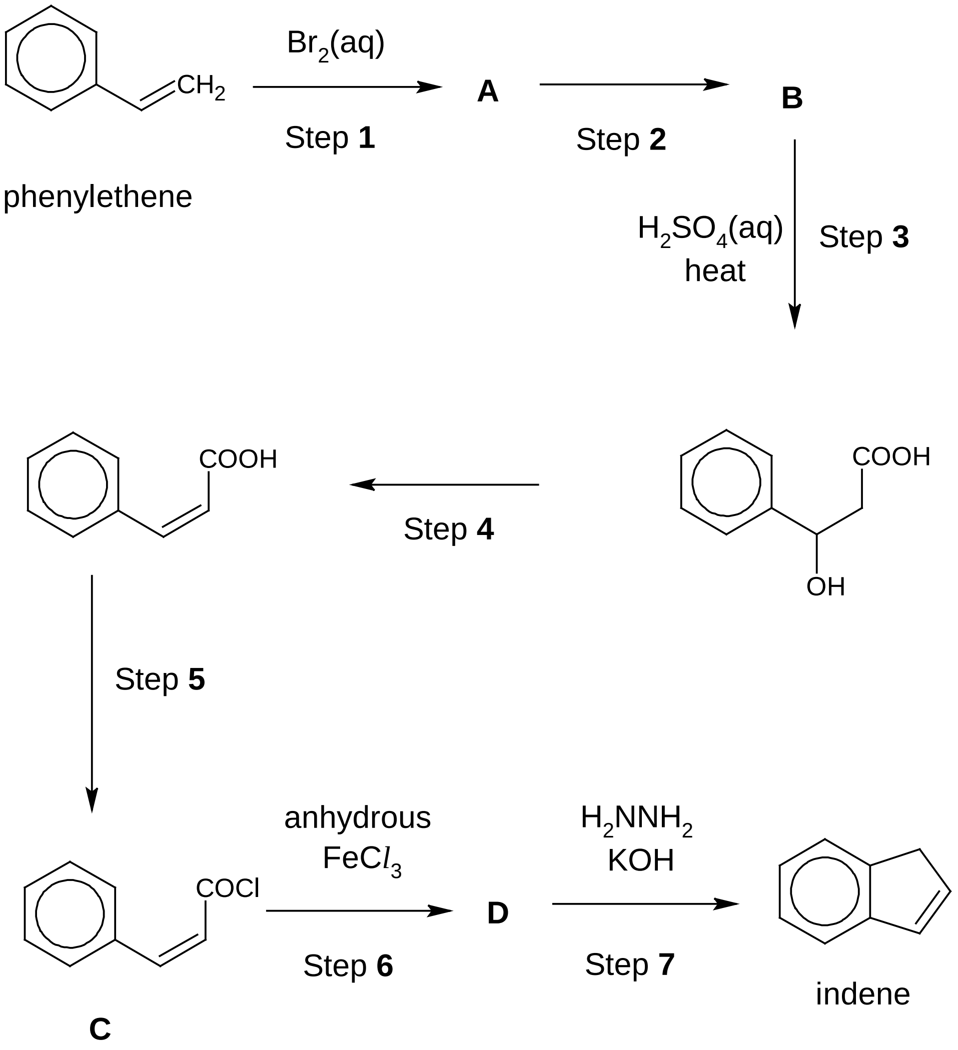
(iv) Based on the physical properties of hydrazine, suggest an advantage of the hydrazine-oxygen fuel cell over the hydrogen-oxygen fuel cell.

[6]

(c) Wolff-Kishner reaction was discovered independently in 1911 by Ludwig Wolff in Germany and N. M. Kishner in Russia. It is a valuable synthetic method for converting ketones or aldehydes into alkanes using hydrazine in the presence of potassium hydroxide.



Indene (C_9H_8) is a colourless organic liquid obtained from coal tar and used in preparing synthetic resins. It can be synthesised from phenylethene by the following route, incorporating Wolff-Kishner reaction.



(i) Give the structures of compounds **A**, **B** and **D**.

(ii) State the reagents and conditions for Steps **2**, **4** and **5**.

(iii) State the types of reaction occurring in Steps **6** and **7**.

(iv) When aqueous silver nitrate is added to compound **C**, a white precipitate is observed immediately. The precipitate dissolves when dilute aqueous ammonia is added to it. The addition of aqueous sodium iodide to the resulting mixture produces a yellow precipitate. Identify the precipitates formed and account for the observation.

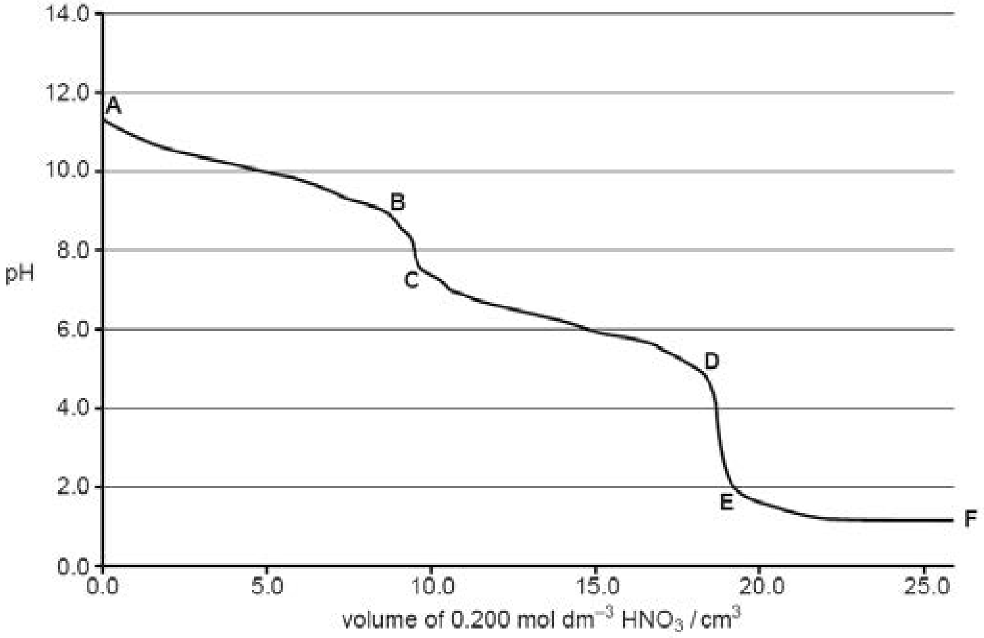
[12]

[Total: 20]

4 **(a)** A solution of carbonate reacts with H^+ in two stages.

$$CO_3^{2-} \xrightarrow[pK_{b1}]{+H^+} HCO_3^- \xrightarrow[pK_{b2}]{+H^+} CO_2 + H_2O$$

The pH changes during the addition of 0.200 mol dm^{-3} nitric acid to a 20.0 cm^3 solution of sodium carbonate and sodium hydrogencarbonate are shown below.



(i) A list of indicators and their p*K*a values is given below.

indicator	thymol blue	methyl yellow	methyl red	cresol red	thymolphthalein
p*K*a	1.7	3.1	5.1	8.3	9.2

From the given list of indicators, choose two suitable indicators that can be used to determine the two end-points in the titration. Explain your choice.

(ii) Calculate the concentration, in g dm^{-3}, of sodium carbonate present in the original solution, given that the end-point between **B** and **C** occurs after 8.40 cm^3 of nitric acid is added.

(iii) Calculate the concentration, in g dm^{-3}, of sodium hydrogencarbonate present in the original solution, given that the end-point between **D** and **E** occurs after 18.80 cm^3 of nitric acid is added.

[4]

(b) Dicarboxylic acids ionise in two stages.

$$HO_2C-(CH_2)_n-CO_2H \xrightarrow[pK_{a1}]{-H^+} HO_2C-(CH_2)_n-CO_2^- \xrightarrow[pK_{a2}]{-H^+} {}^-O_2C-(CH_2)_n-CO_2^-$$

The following table compares the pK_a values of three dicarboxylic acids.

acid	formula	pK_{a1}	pK_{a2}
oxalic	$HO_2C–CO_2H$	1.25	4.27
malonic	$HO_2C–CH_2–CO_2H$	2.85	5.70
succinic	$HO_2C–(CH_2)_2–CO_2H$	4.21	5.64

(i) Explain why succinic acid has the highest pK_{a1} value.

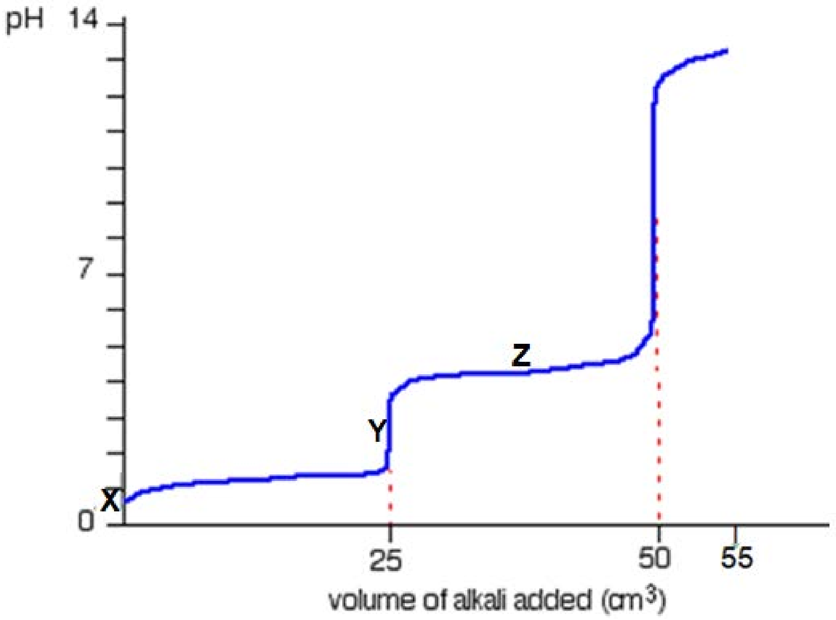
(ii) An amphiprotic species is one that reacts with an acid and a base. The monocarboxylate ion of a dicarboxylic acid, $HO_2C–(CH_2)_n–CO_2^–$, is an amphiprotic species.

The pH of an amphiprotic species is given by the following expression.

$$pH = ½(pK_{a1} + pK_{a2})$$

Using malonic acid as an example, write two equations to show that its monocarboxylate ion is an amphiprotic species.

(iii) The pH-volume added curve when 55 cm^3 of 0.20 mol dm^{-3} NaOH is added to 25 cm^3 of 0.20 mol dm^{-3} oxalic acid is shown below.

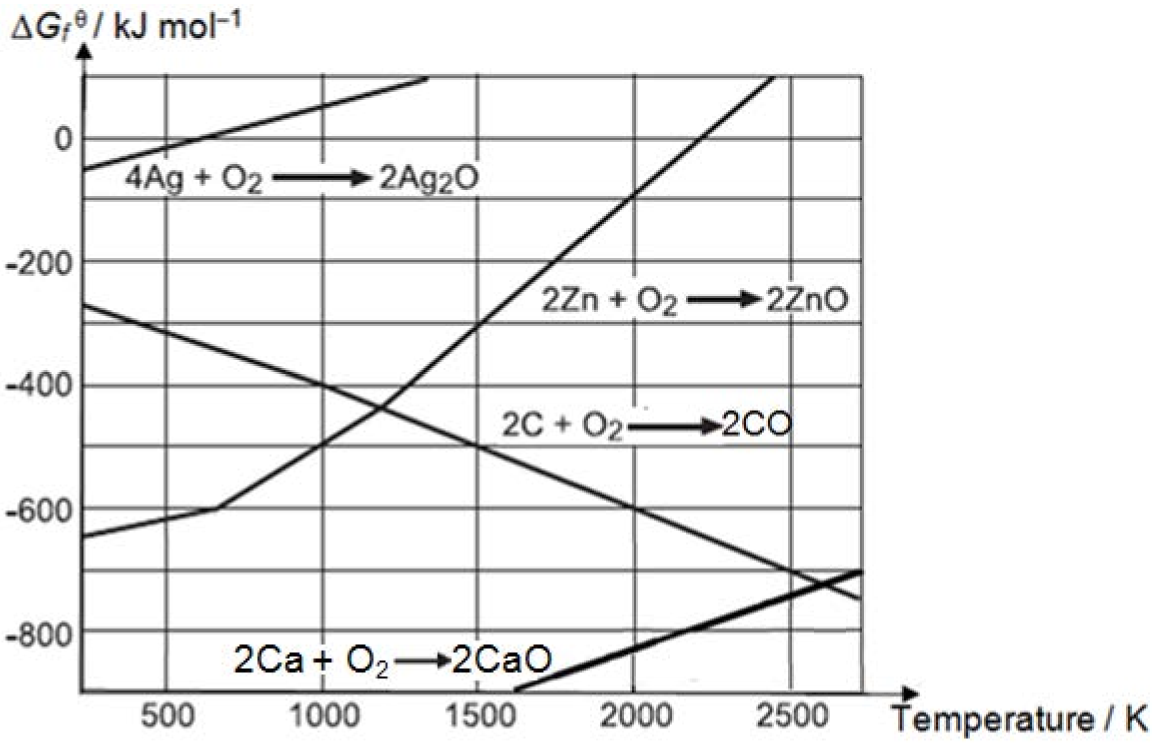


Calculate the pH of the curve at points **X**, **Y** and **Z**.

[6]

(c) Thermal decomposition of the calcium salt of oxalic acid, calcium oxalate, produces calcium oxide and oxides of carbon.

The graph below is an Ellingham diagram, which shows the variation in the standard Gibbs free energy change of formation, ΔG_f^{q}, with temperature, T, for various oxides.



(i) Which oxide, calcium oxide, zinc oxide or silver(I) oxide, could be decomposed by heat at 1000 K? Explain your choice.

(ii) What does the gradient of the graph in the Ellingham diagram represent? Hence, explain why the gradient for $2C + O_2 \rightarrow 2CO$ is as shown.

(iii) From the Ellingham diagram, find the ΔG^{θ} values of the following reactions at 1500 K.

I $2C(s) + O_2(g) \rightarrow 2CO(g)$
II $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$

(iv) Use your answer in **(iii)** to calculate ΔG^{q} value for the reaction in which carbon reduces zinc oxide at 1500 K.

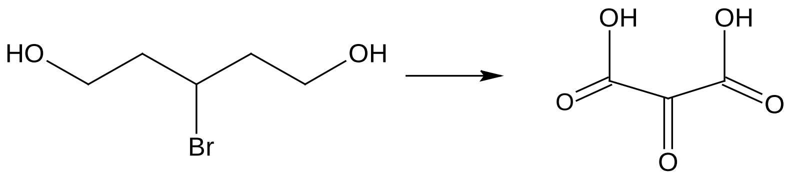
$$2ZnO + 2C \rightarrow 2Zn + 2CO$$

Hence, comment on the feasibility of the reaction at 1500 K.

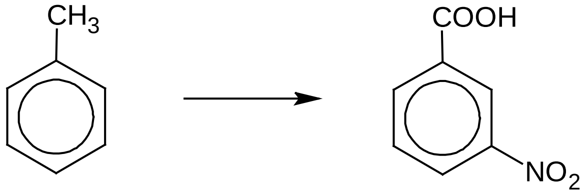
[5]

(d) In **no more than 3 steps**, suggest how each of the following transformations can be achieved. You are required to state the reagents and conditions for each step and give the structures of the intermediate compounds.

(i)



(ii)



[5]

[Total: 20]

5 **(a)** Magnesium carbonate occurs naturally in several forms. Due to its hygroscopic properties, anhydrous magnesium carbonate is used in organic reactions to remove moisture.

The decomposition temperature of magnesium carbonate is 540 °C. Explain how you would expect the decomposition temperature of barium carbonate to differ from magnesium carbonate. [3]

(b) The solubility of magnesium carbonate is 0.267 g dm^{-3}.

(i) Calculate the solubility product, K_{sp}, of magnesium carbonate.

(ii) To a 1.0 dm^3 saturated solution of magnesium carbonate, 50.0 cm^3 of 1.00 mol dm^{-3} aqueous magnesium chloride was added. Find the mass of precipitate formed.

[4]

(c) Compound **A** ($C_{11}H_{22}$) decolourises aqueous bromine. Compound **A** was heated with a mixture of aqueous sodium hydroxide and potassium manganate(VII). After the reaction was completed (assuming 100% yield), the reaction mixture was extracted several times with an organic solvent.

The aqueous and organic layers were then collected separately. Acidification of the aqueous layer yielded compound **B** (M_r = 102), which rotated the plane of polarised light. Compound **B** produced a colourless gas with sodium metal.

(i) Use **all** of the information to determine the identity of functional group present in

I compound **A**,
II compound **B**.

For each functional group you identify, explain how you came to your decision.

(ii) Deduce the molecular formula of compound **B** and hence, draw its displayed formula.

(iii) Explain why the salt of compound **B** was found in the aqueous layer after the separation of the reaction mixture.

The organic layer was then distilled to give compound **C** ($C_6H_{12}O$). Warming compound **C** with aqueous alkaline iodine, followed by controlled addition of concentrated hydrochloric acid produced compound **B**.

(iv) Propose the structure of compound **C** and give a balanced equation for its reaction with aqueous alkaline iodine.

(v) Hence or otherwise, deduce the structure of compound **A**.

Compound **C** was converted to compound **E** via the following reaction scheme.

$$\begin{tikzcd}[column sep=huge, row sep=huge]
\begin{array}{c}\text{Compound }\mathbf{C}\\(C_6H_{12}O)\end{array} \arrow[r, "\text{1. HCN(aq), NaCN, 10-20 }^{o}\text{C}", "\text{2. }H_2SO_4\text{(aq)}"'] & \begin{array}{c}\text{Compound }\mathbf{D}\\(C_7H_{14}O_3)\end{array} \arrow[d, "\begin{array}{c}\text{concentrated }H_2SO_4\text{,}\\ \text{heat under reflux}\end{array}"'] \\
 & \begin{array}{c}\text{Compound }\mathbf{E}\\(C_{14}H_{24}O_4)\end{array}
\end{tikzcd}$$

(vi) Draw the structures of compounds **D** and **E**.

(vii) Describe a simple chemical test to distinguish between compounds **C** and **D**, clearly stating how each compound behaves in the test. You should **not** use any of the reagents and conditions outlined in this question.

[13]

[Total: 20]

End of Paper