Class	Reg Number

Candidate Name _____

Meridian Junior College
2009 JC 2 Preliminary Examination
H2 Chemistry 9746

14 September 2009 **2 hours**

Paper 3

Free Response

Additional Materials
Data Booklet
Writing paper

INSTRUCTION TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer *any* 4 out of 5 questions.

Begin each question on a fresh page of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1 & 2** and **Cover Page for Questions 3, 4 & 5** respectively.

Hand in Questions 1 & 2 and 3, 4 & 5 separately.

You are advised to spend about **30 min** per question **only**.

INFORMATION FOR CANDIDATES

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

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

This question paper consists of 15 printed pages.

Answer any 4 out of 5 questions in this paper.
Begin each question on a ***fresh page*** *of writing paper.*

1 Sulphuryl chloride, SO_2Cl_2, is often used as a source of Cl_2 for various organic reactions. Sulphuryl chloride is also a highly reactive gaseous compound. When heated, it decomposes endothermically as follows:

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

A 7:2 mole ratio of SO_2Cl_2 and Cl_2 is placed in an evacuated vessel at 375 K and 6 atm. After 10 minutes, the mixture reached equilibrium and the partial pressure of SO_2 is found to be 0.625 atm.

(a) Write an expression for the equilibrium constant, K_p, and calculate its value.

[3]

(b) Suggest, with a reason, how the position of equilibrium might alter when the temperature is increased at the 20th minute.

Hence, draw labelled sketches on the same graph to show how the number of moles of sulphuryl chloride and sulphur dioxide gas would change from the start of the decomposition till the new equilibrium is reached.

[3]

(c) Sulphuryl chloride is commonly confused with thionyl chloride, $SOCl_2$. Equimolar amounts of $SOCl_2$ and SO_2Cl_2 are added separately to water to yield an acidic solution with the evolution of some white fumes.

Suggest, with the aid of suitable equations, which compound would yield a solution with a lower pH value.

[2]

(d) Sulphuryl chloride is a very good source of Cl_2. Propene undergoes free radical substitution with sulphuryl chloride to give 3-chloroprop-1-ene.

$$CH_2{=}C_xHCH_3 + SO_2Cl_2 \xrightarrow[\text{Trace of hydrogen peroxide}]{\text{475 K, uv light}} CH_2{=}CHCH_2Cl + SO_2 + HCl$$

(i) Name the type of hybridisation that is present in the carbon atom, C_x, of propene as shown above. Sketch the shape of the hybrid orbitals of C_x.

[2]

(ii) The initiation stage of this mechanism is unique as it consists of two steps:

Step 1 *Homolytic fission* of hydrogen peroxide results in the formation of two hydroxyl radicals.

Step 2 The hydroxyl radical will then combine with one of the C*l* atoms of the sulphuryl chloride to form two stable compounds and a chlorine radical.

1 Define the term *homolytic fission*.

2 Using the information given, deduce the equation for *Step 2* of the initiation stage.

[2]

(iii) Compound **A** can be synthesised from 3-chloroprop-1-ene in a 3-step synthesis. Propose a suitable reaction scheme, suggesting suitable reagents, conditions and intermediate products formed, in the synthesis of compound **A**.

$HOOCCH_2CH(OH)CH_2COOH$

Compound **A**

[3]

(iv) The reaction of 3-chloroprop-1-ene and bromine in trichloromethane in the dark produces an equimolar mixture of compounds **B** and **C**.

1 Outline the mechanism that occurs for the formation of either **B** or **C.**

2 Hence, account for the formation of the equimolar mixture of **B** and **C**. Include the structural formula of isomers **B** and **C** in your answer.

[5]

[Total: 20]

2 Chlorine was identified as an element in 1810 by Sir Humphry Davy. Bromine was discovered by Antoine Balard in 1825 when he found bromide salts in ashes of sea weeds. Iodine was accidently discovered by Bernard Courtois in 1811 while he was isolating sodium carbonate from sea weed. The reactions of halogen-containing compounds span all fields of chemistry.

(a) On an industrial site, an unfortunate accident involving a chemical leak occurred when contractors accidentally poured cold bleach, NaC*l*O, into a drum filled with dilute hydrochloric acid. The reaction between the two chemicals created pressure in the drum, causing the lid to rise, resulting in the release of a choking gas. Civil Defence officers were called to the scene to render assistance.

(i) Name the gas released that created the pressure in the drum and write a balanced equation for its production.

(ii) The Civil Defence officers flushed the plant room with water to dilute the choking gas and bring its concentration down to safety levels.

Using bonding and structure, explain why this action taken by the Civil Defence officers was **not** very successful.

(iii) The gas identified in **(a)(i)** cannot be produced via the reaction between the corresponding halide and excess concentrated sulphuric acid. However, another halogen can be produced via a similar reaction. Explain this observation, including balanced equations in your answer.

(iv) At the scene of the accident, there were three other sealed drums containing gaseous hydrogen astatine, hydrogen bromide and hydrogen iodide respectively.

Using relevant values from the *Data Booklet*, explain the relative thermal stability of the three hydrogen halides.

[9]

(b) Aqueous chloric (III) acid, $HClO_2$, is unstable and decomposes in a variety of ways, two of which are as follows :

Reaction I : $3HClO_2 \longrightarrow 2ClO_3^- + Cl^- + 3H^+$

Reaction II : $5HClO_2 \longrightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O$

(i) Use the following data to calculate E^{θ} cell for each of the reactions above under acidic conditions. Hence, deduce how $HClO_2$ might decompose in acidic solution.

Acidic solution	
couple	E^{θ} / V
$HClO_2$ / Cl^-	+ 1.57
ClO_3^- / $HClO_2$	+ 1.21
ClO_2 / $HClO_2$	+ 1.27

(ii) Similar decomposition reactions can also take place in alkaline medium where chlorate (III) exists as ClO_2^- instead.

Alkaline solution	
couple	E^{θ} / V
ClO_2^- / Cl^-	+ 0.78
ClO_3^- / ClO_2^-	+ 0.33
ClO_2 / ClO_2^-	+ 1.16

Based on the above information, suggest which ion is the weakest reducing agent in alkaline medium.

[4]

(c) Unlike chlorates (VII) and bromates (VII), which contain only the XO_4^- ion (X = C*l* or Br), iodates (VII) can contain the ions IO_5^{3-} and IO_6^{5-} as well as IO_4^- .

(i) Suggest a reason for this difference.

(ii) Draw the dot and cross diagram for IO_6^{5-}.

(iii) Barium iodate (VII), $Ba_5(IO_6)_2$, can be obtained by heating crystals of barium iodate (V), $Ba(IO_3)_2$. Iodine and oxygen are also produced.

1 Construct a balanced equation for this reaction.

2 The variation in the thermal stability of Group II iodate (V) salts parallels that of Group II nitrates. Explain qualitatively whether $Ca(IO_3)_2$ is more or less thermally stable compared to $Ba(IO_3)_2$.

(iv) The purity of iodates (VII) can be estimated by adding an acidified solution of potassium iodide and titrating the iodine produced with aqueous sodium thiosulphate.

In one such analysis, a sample of 0.200 g of sodium iodate (VII), Na_5IO_6, was dissolved in water and treated with an excess of acidified KI to yield iodine as the only product. The iodine liberated required 22.0 cm^3 of 0.100 mol dm^{-3} sodium thiosulphate to reach the end-point.

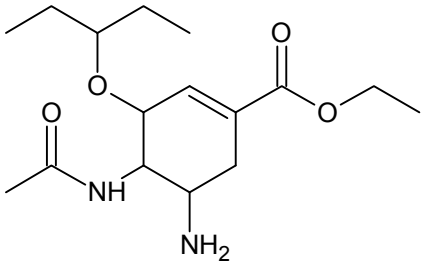
Calculate the purity of the sodium iodate (VII) in the sample.

[Given $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$; M_r of Na_5IO_6 = 338]

[7]

[Total: 20]

3 The 2009 flu pandemic is a global outbreak of a new strain of influenza A virus known as H1N1. *Tamiflu* is an effective drug to combat H1N1 and has been researched in great detail. The structure of *Tamiflu* is shown below:



Tamiflu

(a) Name four functional groups that are present in *Tamiflu*.

[2]

(b) *Tamiflu* is actually sold as the phosphate salt rather than in the form as shown above. Suggest why this is so.

[1]

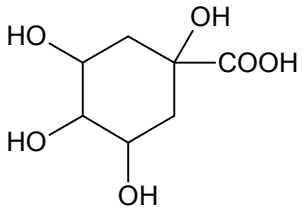
(c) Draw the structural formula of all organic products formed when *Tamiflu* is heated with excess aqueous NaOH.

[2]

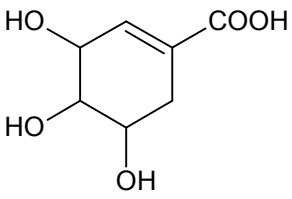
(d) Draw the major organic product formed when excess DBr is added to *Tamiflu* at room temperature and pressure. [D = ^{2}H]

[1]

(e) Two syntheses of *Tamiflu* have been tried and both started from the naturally occurring products quinic acid and shikimic acid.

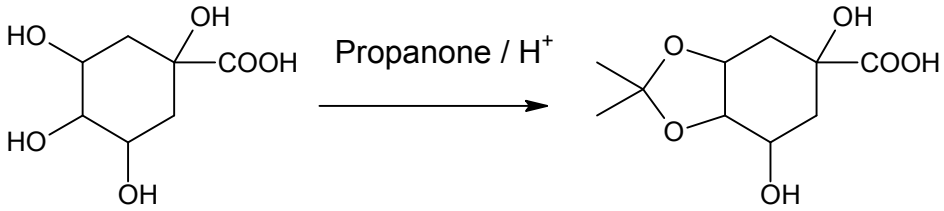


quinic acid



shikimic acid

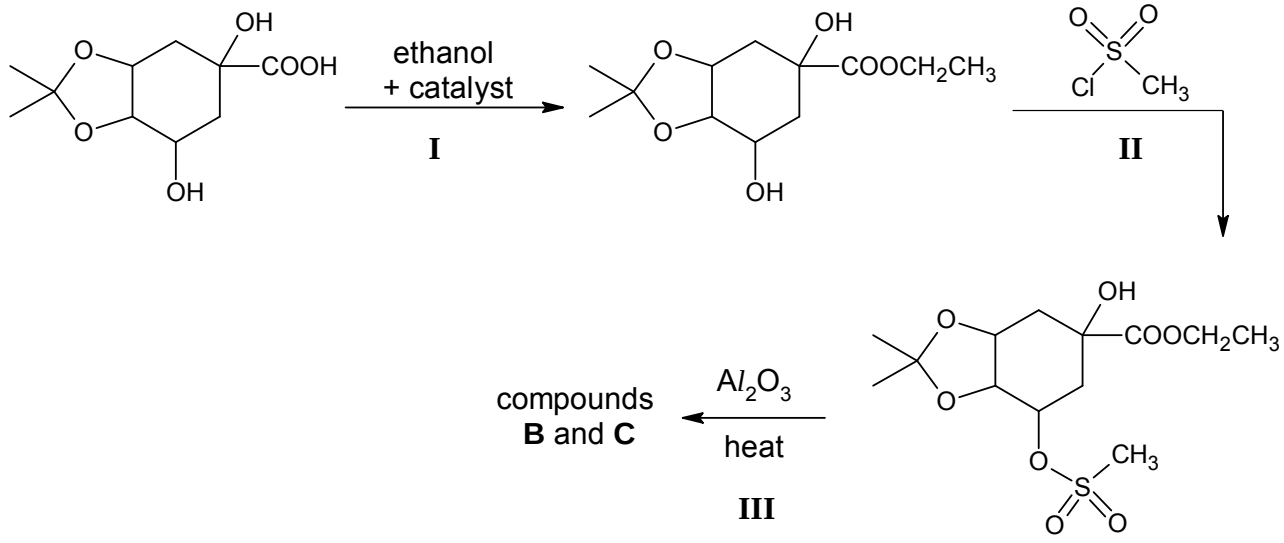
The first step starting from quinic acid is shown below:



Suggest the structural formula of the product formed if pentan-3-one was used instead of propanone.

[1]

(f) The next steps in the synthesis are outlined below. Inorganic by-products are not shown in the scheme.



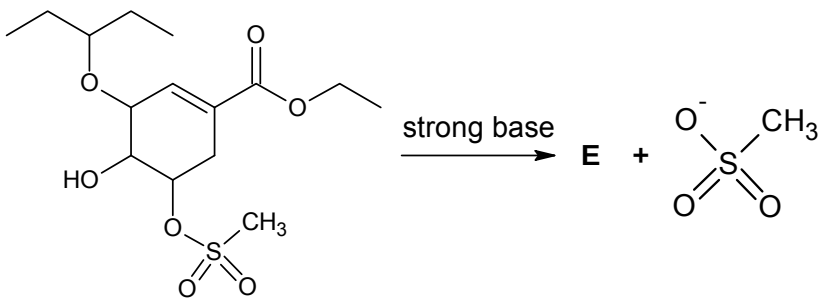
(i) What *type of reaction* is reaction **II**?

(ii) Compounds **B** and **C** are structural isomers.

Draw a possible structure of *either* compound **B** *or* **C**.

[2]

(g) In a later step of the synthesis of *Tamiflu*, compound **D** cyclises to give **E** which contains a 3-membered ring.



D

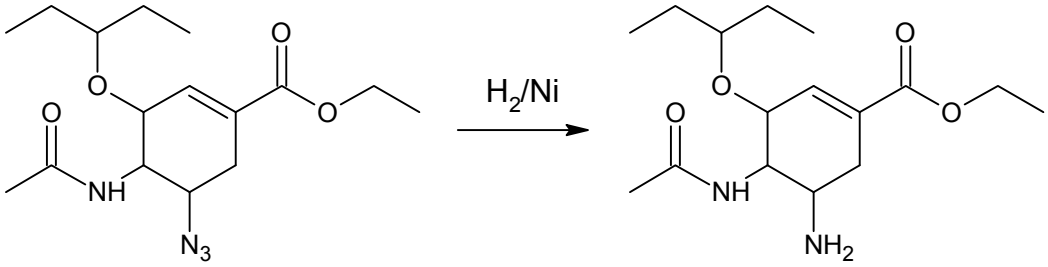
The alkoxide ion was formed from **D** before compound **E** was produced.

(i) Suggest a structural formula for compound **E**.

(ii) Suggest a mechanism for the reaction. Show all relevant curly arrows and dipole moments in your answer.

[2]

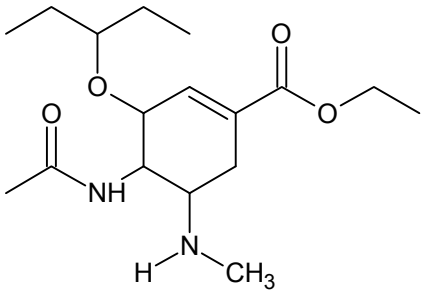
(h) The final step of the synthesis of *Tamiflu* involves the step below. State the type of reaction and suggest what is unusual about this reaction.



[1]

(i) *Tamiflu* can react to form the following compound **F**. State the reagents and conditions required and explain whether *Tamiflu* or compound **F** is more basic.

[3]



compound **F**

(j) In order to determine the base strength of *Tamiflu*, 25 cm^3 of 1 mol dm^{-3} H_2SO_4 was added to 45 cm^3 of 1 mol dm^{-3} *Tamiflu* in a polystyrene cup.

The changes in temperature were recorded and plotted in Figure 1.

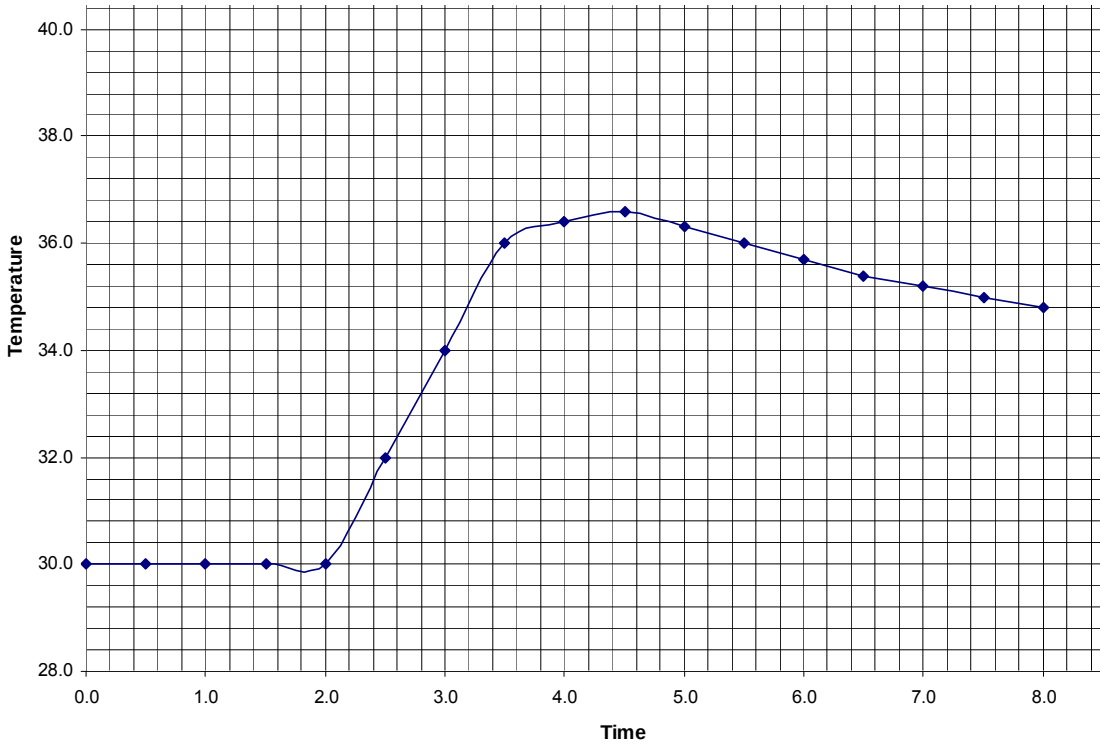


Figure 1

With reference to the above graph, calculate the enthalpy change of neutralization of *Tamiflu* and H_2SO_4.

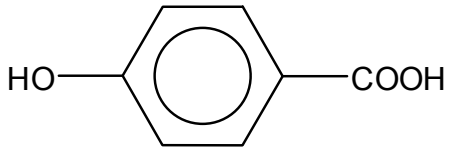
Hence, deduce and explain if *Tamiflu* is a strong or weak base.

(You may assume the density of the solutions is 1.00 g cm^{-3} and their specific heat capacity is 4.18 J g^{-1} K^{-1}.)

[5]

[Total: 20]

4(a) 4-hydroxybenzoic acid is primarily used as the basis for the preparation of its esters, known as parabens. Parabens are a class of chemicals widely used as preservatives in the cosmetic and pharmaceutical industries.



4-hydroxybenzoic

4-hydroxybenzoic acid is a weak dibasic acid with Ka_1 = 6.31 x 10^{-5} mol dm^{-3} and Ka_2 = 1.58 x 10^{-10} mol dm^{-3}.

In an experiment, 25.0 cm^3 of 0.05 mol dm^{-3} 4-hydroxybenzoic acid was titrated against 12.5 cm^3 of 0.10 mol dm^{-3} NaOH.

(i) Explain why Ka_1 is much bigger than Ka_2.

(ii) Calculate the initial pH of 0.05 mol dm^{-3} 4-hydroxybenzoic acid, stating any assumption made.

(iii) Calculate the pH of each of the resultant solutions when 6.25 cm^3 and 12.50 cm^3 of 0.10 mol dm^{-3} NaOH were added respectively.

(iv) Sketch a graph to show the changes in pH when the above titration was performed. Label the appropriate pH values you have calculated in **(a)(ii)** and **(iii)** on your graph.

[10]

(b) Observations from kinetics studies often allow scientists to deduce the mechanisms of organic reactions.

When $(CD_3)_3CBr$ was treated with sodium phenoxide under suitable conditions, the product formed was $(CD_3)_3COC_6H_5$. The reaction was found to be first order with respect to $(CD_3)_3CBr$ and zero order with respect to sodium phenoxide. The half–life for the reaction was determined to be 10 minutes.

(i) Write the rate equation for the above reaction.

(ii) Suggest a mechanism that is consistent with the above rate equation, and indicate which step in the mechanism is the rate determining step. Show all relevant curly arrows and dipole moments in your answer.

(iii) If the initial concentration of $(CD_3)_3CBr$ used is 0.64 mol dm^{-3}, sketch a fully labelled graph of the concentration of $(CD_3)_3CBr$ against time to show the time taken for the concentration of the reactant to decrease to 12.5 % of its original concentration.

[5]

(c) Alkene **W**, C_8H_{16}, reacts with cold alkaline $KMnO_4$, to form an optically inactive diol. When **W** is treated with chlorine in ultraviolet light, it produces a mixture of chlorinated compounds, including **X**, $C_8H_{14}Cl_2$, which are optically inactive. When **X** is reacted with ethanolic NaOH, compound **Y**, C_8H_{12} is the only product formed. Compound **Y** produces two compounds, CO_2 and $CH_3COCOOH$ in equimolar amounts when it is oxidised by hot acidified $KMnO_4$.

(i) Suggest the structural formula for compounds **W**, **X** and **Y**.

(ii) There are other possible isomers of $C_8H_{14}Cl_2$ that could give **Y** on dehydrochlorination. Draw the structural formula of **one** of them.

(iii) Suggest, with a reason, the number of stereoisomers for compound **Y**.

[5]

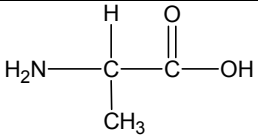
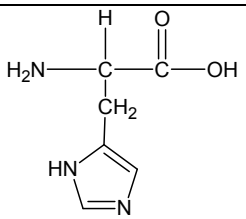
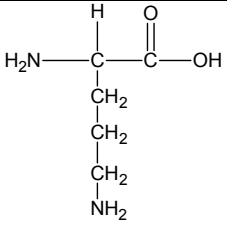
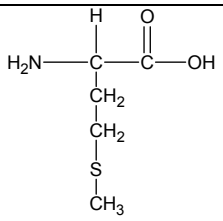
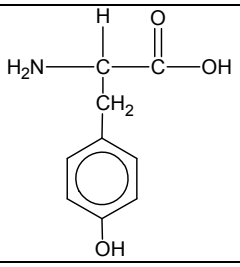
[Total: 20]

5 Haemoglobin is a tetrameric protein consisting of two *α* and two *β* subunits.

Two of the subunits have beta-pleated sheet structures while the other two subunits have alpha-helical structures. Haemoglobin also contains haem, which is an iron-containing molecule which gives haemoglobin its red colour and is responsible for binding the oxygen that haemoglobin transports round the blood stream.

(a) Briefly state the interactions that give rise to the four different levels of protein structures found in haemoglobin. **[2]**

(b) The following amino acids have the structural formulae:

Amino Acids	Structural Formula	Isoelectric Point
Alanine *(ala)*		6.00
Histidine *(his)*		7.47
Lysine *(lys)*		9.59
Methionine *(met)*		5.74
Tyrosine *(tyr)*		5.66

(i) Draw the displayed formulae of residues of a tripeptide, with the sequence *his-lys-tyr*, indicating the peptide linkage clearly, showing the form it would exist at pH 7.

(ii) Amino acids can act as buffers in solutions. Explain, with the aid of relevant equations, how alanine can act as a buffer on separate small additions of the following reagents :

- dilute HC*l*
- dilute KOH

[5]

(c) Hemochromatosis is an autosomal recessive genetic disease that results in deregulated iron absorption resulting in iron overload in specific organs such as the liver and heart. Excess iron deposition is associated with numerous clinical complications including liver disease such as liver cancer.

(i) Suggest the type of intermolecular interactions that arise when a methionine molecule replaces a lysine molecule on two polypeptide chains in haemoglobin. **[1]**

(ii) Human haemoglobin undergoes denaturation in a strongly basic medium. With respect to the globular protein subunit, explain why denaturation takes place. **[1]**

(iii) A patient is suspected to inherit hemochromatosis due to his frequent complaints of fatigue, acute chest pains and the onset of jaundice. Blood tests can determine whether the amount of iron stored in the body is too high hence diagnose if a patient is suffering from hemochromatosis.

Describe in outline the **practical** details you would need to follow in order to use a standard solution of potassium manganate (VII), to determine the percentage of iron in a processed blood sample containing iron (II) ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$.

You would like to note the following in your plan:

- The end point of the titration is sharpened markedly if phosphoric acid is present, because Fe^{3+} ion produced in the titration forms an essentially colourless complex with the acid.
- Dilution is not required as the concentration of iron is minimal.

You should include an ionic equation for the titration reaction, and name any other chemicals and apparatus you would use. Do **not** include any details of the calculation. **[4]**

(iv) Using relevant E^{θ} values from the *Data Booklet,* suggest why **both** aqueous HC*l* and aqueous HNO_3 are not preferred choices for the acidification process in your plan in **(c)(iii)**. **[3]**

(v) The increase in liver enzymes is classified as one of the possible early symptoms of hemochromatosis. Using the concept of activation energy together with an appropriate sketch of the Maxwell-Boltzmann distribution, explain how the presence of such enzymes aggravates the condition of a patient diagnosed with hemochromatosis. **[4]**

[Total: 20]