RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION (II)

CANDIDATE NAME	
CLASS	6
CENTRE NUMBER	S
INDEX NUMBER	

H2 CHEMISTRY 9647/03

Paper 3 Free Response

23 September 2014

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Graph Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of 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.

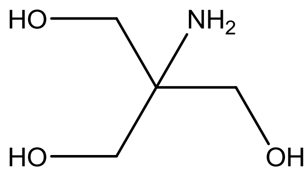
Answer any **four** questions.
Begin each question on a fresh sheet of paper.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

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 **16** printed pages.

Answer any **four** questions.

1 **(a)** TRIS is an organic compound with the formula $(HOCH_2)_3CNH_2$. It is extensively used in biochemistry and molecular biology as a component of *buffer* solutions.



TRIS

The table below summarises key information about TRIS and other amines.

Compound	m.p./°C	b.p./°C	pK_b	Odour
CH_3NH_2	–93	–6	3.43	Fishy
$CH_3CH_2NH_2$	–80	20	3.19	Fishy
$C_6H_5NH_2$	–6	184	9.37	Fishy
TRIS	176	219	5.93	Characteristic

(i) What is meant by the term *buffer*?

(ii) 25.0 cm^3 of 0.10 mol dm^{-3} TRIS is titrated against 0.20 mol dm^{-3} hydrochloric acid.

Calculate the pH of the solution when the following volumes of hydrochloric acid are added.

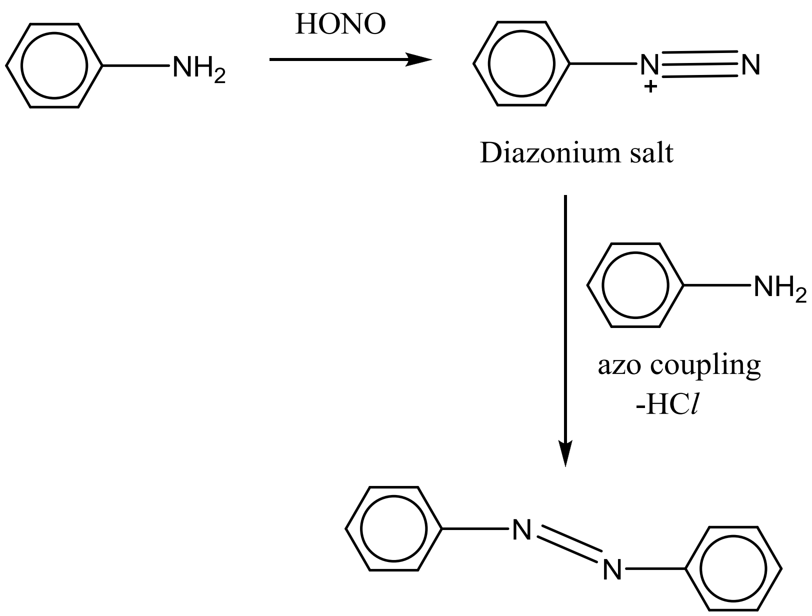
1. 0 cm^3

2. To reach equivalence point

3. 30 cm^3

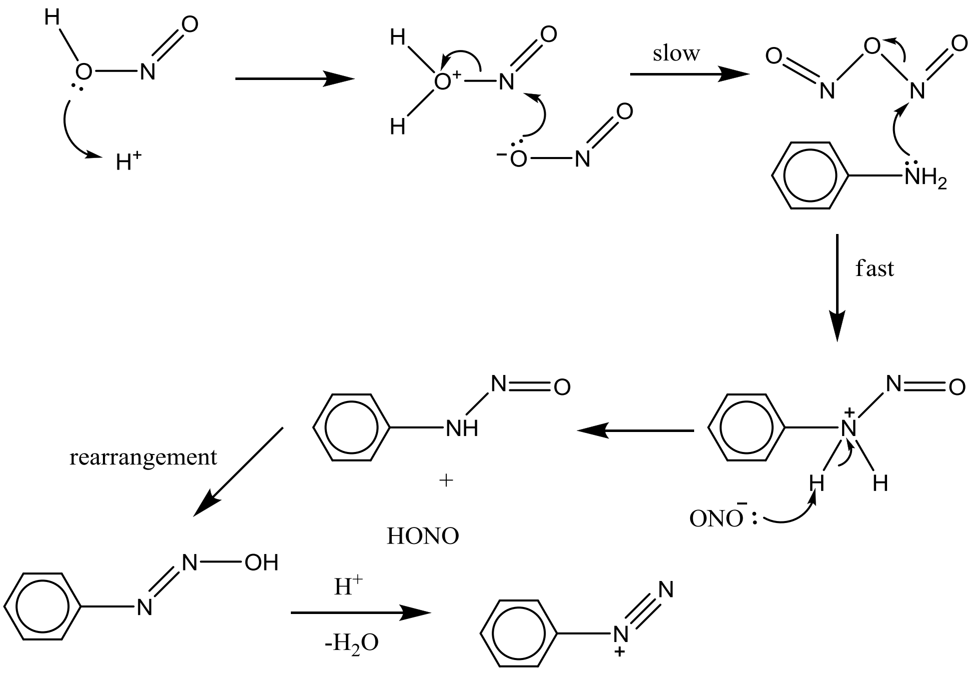
(iii) Apart from its relatively low cost, suggest why TRIS is suitable for use in biochemistry and molecular biology experiments. **[6]**

(b) $C_6H_5NH_2$, also known as aniline, played a key role in the proliferation of synthetic dyes. Many of these compounds involve azo dyes, which contain two aromatic fragments connected by a N=N double bond. Azo dyes are prepared in a two-step reaction, the first being the synthesis of an aromatic diazonium ion from an aniline derivative (note: alkyl diazonium ions are very unstable). The next step is the coupling of the diazonium salt with an aromatic compound. The reaction scheme is shown below.



(i) A student who was interested in studying the rate of reaction of the diazotisation step found the following mechanism on the internet.

$$HONO \rightleftharpoons H^+ + ONO^-$$



Based on the mechanism, state the rate equation for the reaction between $C_6H_5NH_2$ and HONO.

(ii) State the units for the rate constant for this reaction. **[2]**

(c) Compound **G** has the molecular formula $C_{12}H_{15}NO_3$. **G** does not react with PCl_5 to give white steamy fumes.

On boiling **G** with aqueous sodium hydroxide, **H** and a salt of compound **I** are formed. Compound **H** has a fishy smell and does not have a stable reaction with HONO.

Compound **I**, $C_{11}H_{12}O_4$, rotates plane-polarised light and produces a yellow solid on warming with alkaline aqueous iodine. **I** gives a yellow precipitate with 2,4-dinitrophenylhydrazine. On addition of aqueous bromine, compound **J** is formed with the formula, $C_{11}H_{11}O_4Br$.

Suggest structures for compounds **G** to **J** and explain the observations. **[9]**

(d) By means of equations, describe two reactions in which iron or one of its compounds behaves as a catalyst, and state whether the catalyst is homogenous or heterogenous. **[3]**

[Total: 20]

2 Nitrogen is an element that is essential to life on earth. Nitrogen is found in nucleic acids such as DNA and RNA which store genetic information. It is also found in proteins.

In spite of nitrogen's abundance in the atmosphere, the quantity of nitrogen containing compounds that were available for human use was limited. Prior to the 20th century, nitrogenous compounds were either obtained from biological sources such as manure and guano (seabird or bat droppings) or by mining nitrate deposits. Nitrate deposits were very rare and the main deposit that was exploited was in the Atacama Desert, Chile.

The Haber process for the manufacture of ammonia and the Ostwald process for the conversion of ammonia to nitric acid were developed in the early 20th century.

The First World War began one hundred years ago in July 1914. Almost all explosives contain nitrogen and nitric acid is an essential reagent in their manufacture. The ability to convert atmospheric nitrogen to ammonia and hence other nitrogenous compounds freed Germany and her allies from depending on the Chilean nitrate deposits which had to be transported across the Atlantic by ship. Historians estimate that the First World War would have ended in 1916 instead of 1918 as Germany would have run out of sources of nitrogen.

(a) Ammonium salts and nitrates are sources of nitrogen.

Suggest two reasons why deposits of ammonium and nitrate compounds are rare and found only in deserts. **[2]**

(b) Ammonia is described as a 'real' gas.

State and explain the conditions under which ammonia deviates the most from ideal gas behaviour. Relate your answer to the bonding in ammonia. **[3]**

(c) In an industrial accident, a large quantity of ammonia was released. Ammonia is lethal if the concentration of the gas exceeds 5000 ppm. (1 ppm is equivalent to 1 mg dm^{-3})

Assuming that the pressure of ammonia was 1 atm and that ammonia behaves as an ideal gas, calculate the density of ammonia at 30 °C.

Hence, determine if the concentration of the ammonia was lethal. **[3]**

(d) The Van't Hoff equation relates the equilibrium constant of a reaction with temperature. The linear form of the Van't Hoff equation is given below.

$$\ln K_c = -\frac{\Delta H^{\ominus}}{RT} + \frac{\Delta S^{\ominus}}{R}$$

where R is 8.31 J mol^{-1} K^{-1}

The following table gives equilibrium constant values measured at different temperatures for the Haber process.

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

T / K	K_c / mol^{-1} dm^3	ln K_c	$\frac{1}{T}$ / K^{-1}
300	4.34×10^{-3}	–5.44	3.33×10^{-3}
400	1.64×10^{-4}	–8.72	2.50×10^{-3}

(i) Determine the enthalpy change of the reaction.

(ii) Determine the entropy change of the reaction.

(iii) Hence, determine the temperature at which the reaction becomes spontaneous. **[6]**

(e) Proteins are an important class of biological molecules.

(i) State three functions of proteins.

(ii) Secondary structures are repeated arrangements of amino acids that can be found in proteins. One such structure is termed the β-pleated sheet.

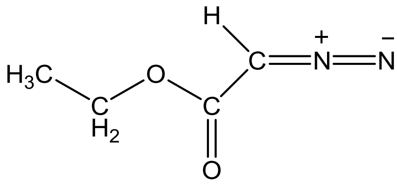
Describe the β-pleated sheet structure of protein. Your answer should include a suitable diagram which shows the bonding between the strands and at least two amino acid residues per strand.

(iii) Globular proteins are a class of water-soluble proteins. Many techniques have been developed to extract proteins from natural sources. One simple technique is termed 'salting-out'. In salting out an inorganic salt such as ammonium sulfate is gradually added to a solution containing proteins. Different proteins will be selectively precipitated out as concentration of the salt in the solution increases.

Using your knowledge of the tertiary structure of proteins, explain why globular proteins can be water soluble and why the addition of ammonium sulfate may cause proteins to be precipitated out. **[6]**

[Total: 20]

3 Ethyl diazoethanoate is an important organic chemistry building block, but its use as an industrial intermediate is limited due in part to the safety concerns associated with its instability and high reactivity.



Ethyl diazoethanoate

(a) At 298 K, ethyl diazoethanoate reacts with water to give ethyl hydroxyethanoate and nitrogen gas.

$$N_2CHCO_2CH_2CH_3(aq) + H_2O(l) \rightarrow HOCH_2CO_2CH_2CH_3(aq) + N_2(g)$$

The rate of the reaction was followed by measuring the volume of nitrogen gas evolved at various time intervals after the start of the reaction. After 50 minutes, when all of the ethyl diazoethanoate had been consumed, the total volume of nitrogen gas produced was 60.0 cm^3. The experimental results are given in the table below:

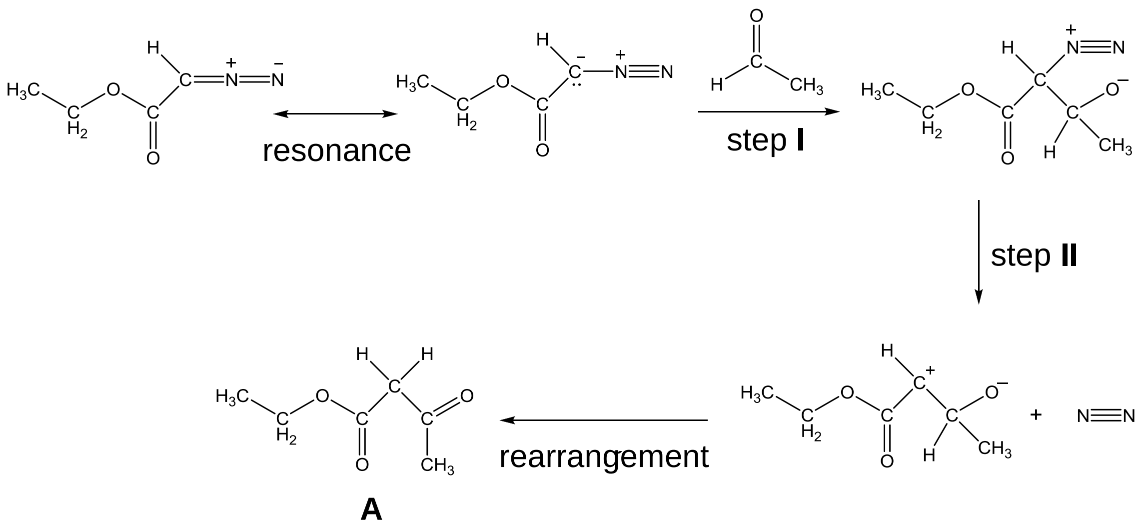
Time / min	**Volume of nitrogen gas / cm^3**
0.0	0.0
10.0	45.0
20.0	55.7
30.0	58.1

(i) Using 2 cm to represent 10.0 min and 10.0 cm^3 on the x-axis and y-axis respectively, plot a graph of volume of nitrogen produced against time.

(ii) Use your graph to determine the order of the reaction with respect to ethyl diazoethanoate and explain how you deduced your answer.

(iii) What is the value of the rate constant for this reaction at 298 K? **[5]**

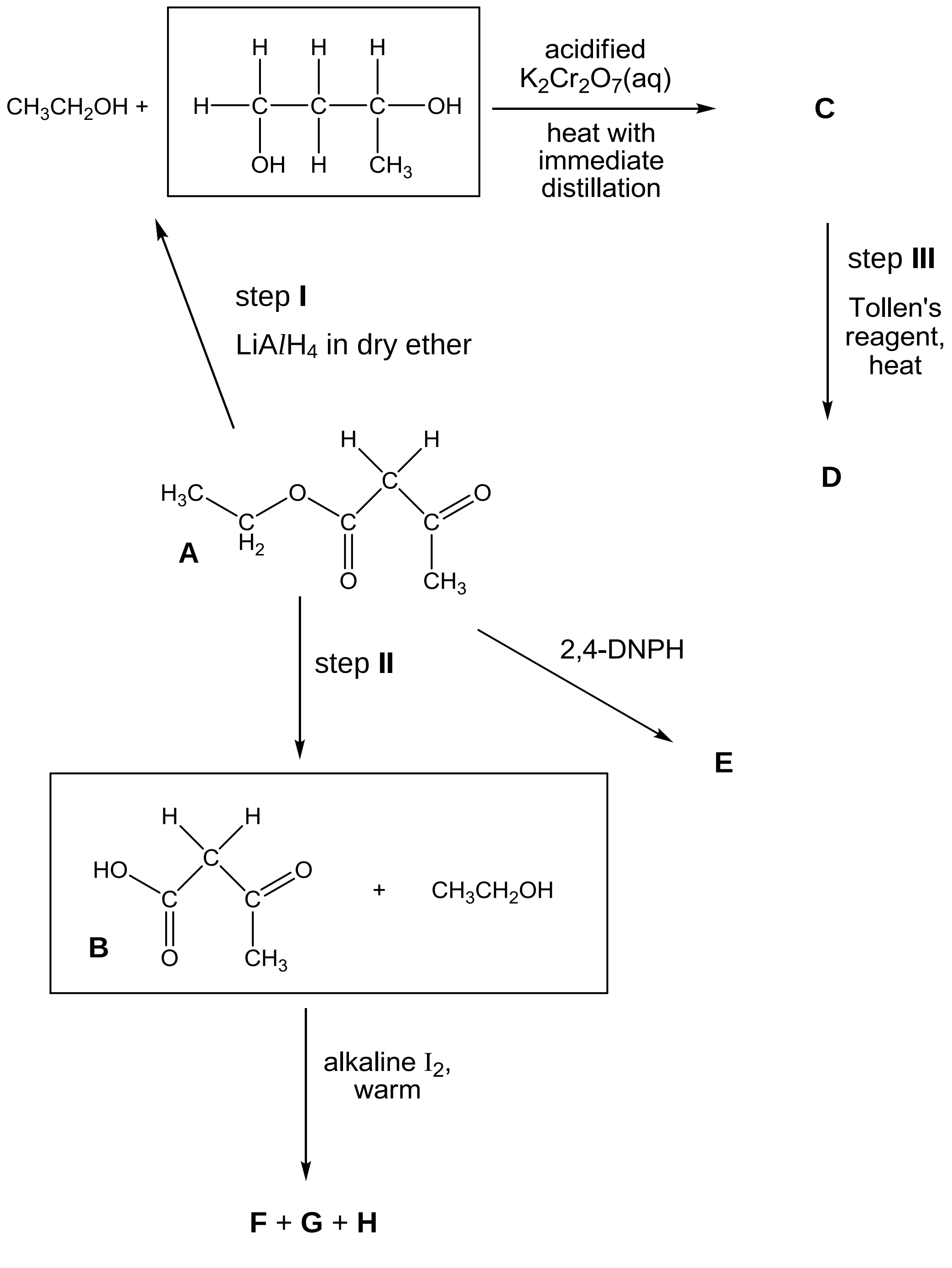
(b) Ethyl diazoethanoate also undergoes the Büchner-Curtius-Schlotterbeck reaction involving the reaction with an aldehyde to form a β-keto ester, **A**. The general reaction scheme is as follows:



(i) State the type of reaction involved in step **I**.

(ii) Suggest why step **II** is spontaneous. **[2]**

(c) The β-keto ester formed, **A**, undergoes reactions in the following scheme. The products formed in the boxes are subjected to further reactions.



(i) State the types of reactions in steps **I** and **III**.

(ii) Give the reagents and conditions required in step **II**.

(iii) Draw the structures of the organic products **C** to **H**. **[9]**

(d) Compound **B**, formed in the above scheme, undergoes condensation reaction with methanol. The reaction is exothermic.

$$CH_3COCH_2CO_2H(l) + CH_3OH(l) \rightleftharpoons CH_3COCH_2CO_2CH_3(l) + H_2O(l)$$

A mixture of 0.25 mol of **B** and 0.34 mol of methanol was allowed to reach equilibrium. The equilibrium mixture was found to contain 0.13 mol of the ester.

(i) Calculate the value of the equilibrium constant, K_c, for the condensation reaction.

(ii) Explain the effects of the following actions on the equilibrium position of the reaction:

- addition of a small amount of concentrated sulfuric acid
- increasing the temperature at which the reaction was carried out **[4]**

[Total: 20]

4 Iron is one of the most abundant element found on earth. It comprises about 5.6% of the earth's crust and almost all of the earth's core. It is also commonly found in both humans and plants.

Iron is a typical transition element. Transition elements typically form complexes. Complexes having different ligands exhibit different properties even when the central metal ions are the same.

The common oxidation states of iron are +2 and +3. Both iron(II) and iron(III) ions form complexes with H_2O and CN^-.

A solution of Fe^{3+}(aq) contain the ion $[Fe(H_2O)_6]^{3+}$.

(a) The oxidising power of a complex may be deduced from its standard reduction potential, $E^{\ominus}$.

(i) Draw a fully labelled diagram to describe how the standard reduction potential of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system can be measured using a standard hydrogen electrode.

(ii) By quoting $E^{\ominus}$ values from the *Data Booklet*, show that $[Fe(H_2O)_6]^{3+}$ has a stronger oxidising power than $[Fe(CN)_6]^{3-}$.

(iii) Suggest a reason for the difference in oxidising power of the two complexes in **(a)(ii)**. **[6]**

(b) In an octahedral complex such as hexacyanoferrate(II) ions, $[Fe(CN)_6]^{4-}$, the d-orbitals are split into two levels, as shown in *Figure 1* below.

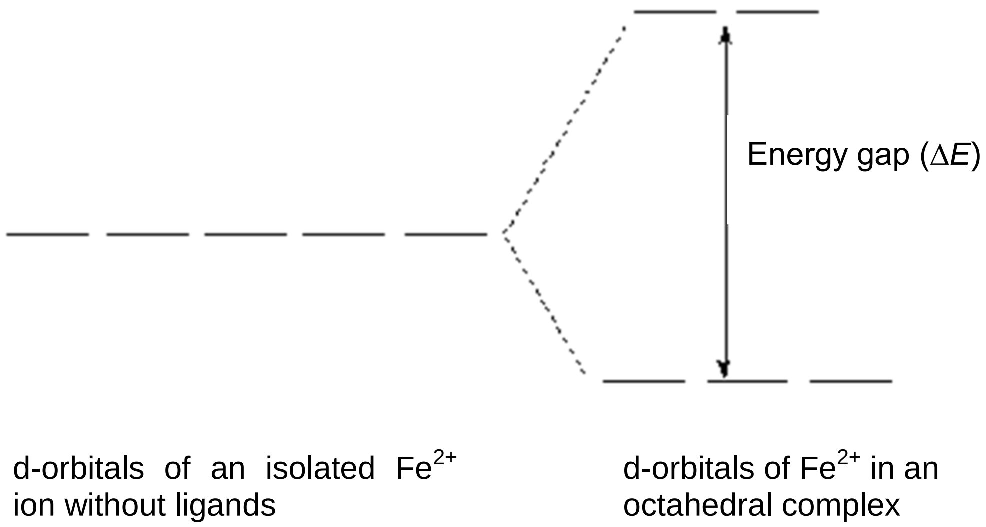


Figure 1

Complexes exist in two spin states.

In a *high spin* state, the electrons of the central metal occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a *low spin* state, the lower energy d-orbitals are filled first, with pairing if necessary, before the higher energy d-orbitals are used.

(i) Write the full electronic configuration of the iron ion in $[Fe(CN)_6]^{4-}$.

(ii) Electrons usually prefer to occupy orbitals singly because of repulsion that would occur between two electrons occupying the same orbital.

In light of this, suggest why a complex might still adopt a *low spin* state.

The value of the energy gap (ΔE) is dependent on the strength of ligand. For a given metal ion, the series below shows how the ligand affects ΔE:

$$CO > CN^- > NO_2^- > NH_3 > edta^{4-} > H_2O > OH^- > F^-$$

larger ΔE smaller ΔE

(iii) Predict whether $[Fe(CN)_6]^{4-}$ will adopt a *high spin* or *low spin* state. Briefly explain your answer.

A paramagnetic substance is one that will be attracted by an externally applied magnetic field. Chemical species with at least one unpaired electrons will be paramagnetic.

(iv) By using your answers to **(b)(i)** and **(b)(iii)**, deduce whether $[Fe(CN)_6]^{4-}$ will be paramagnetic. Explain your answer. You may find it useful to include a diagram in your answer. **[7]**

(c) Iron also exists in other oxidation states.

An oxoanion of iron has the formula FeO_x^{2-}. In acidic conditions, FeO_x^{2-} is a strong oxidising agent and is reduced to Fe^{3+}. In an experiment, a 10 cm^3 of 0.200 mol dm^{-3} of FeO_x^{2-} completely oxidised 30 cm^3 of 0.200 mol dm^{-3} of Fe^{2+} to Fe^{3+}.

Determine the value of x. **[3]**

(d) Iron(III) chloride can be used in qualitative analysis for both inorganic and organic chemistry.

(i) A label has fallen off a bottle containing a colourless solution suspected to be either NH_4SCN or NH_4NO_3.

Outline how a solution of iron(III) chloride can be used to determine the identity of the solution.

A neutral solution of iron(III) chloride can be used to test for a particular organic functional group.

(ii) Describe the appearance of a positive result of this test.

(iii) Draw the structure of **one** compound with the molecular formula C_7H_8O that would show a positive result in this test, and the structure of **one** compound with the same molecular formula that would not. Label your structures clearly. **[4]**

[Total: 20]

5 Chlorine was identified as an element in 1810 by the English Chemist Sir Humphry Davy. The reactions of chlorine and chlorine-containing compounds span all fields of chemistry.

(a) When concentrated sulfuric acid is warmed with solid sodium chloride, white fumes are produced. However, when concentrated sulfuric acid is warmed with solid sodium iodide, purple fumes are produced.

(i) Identify the fumes that are produced.

(ii) Write equations for the reactions that occurred for NaI.

(iii) Briefly explain the differences in the reactions of solid sodium chloride and sodium iodide with concentrated sulfuric acid. **[4]**

(b) **(i)** Halogens can also act as oxidising agents.

Describe and explain the trend in oxidising power of the halogens down the group.

(ii) Describe and explain how the thermal stabilities of the hydrogen halides vary down the group. **[5]**

(c) Methylmalonic acid, MMA, is a compound that reacts with vitamin B12 to produce coenzyme A (CoA). Coenzyme A is essential to normal cellular function. When vitamin B12 deficiencies occur, MMA levels increase. Measurement of MMA levels can provide the doctor with information about an existing vitamin B12 deficiency.

The following table compares the pK_a values of methylmalonic acid with malonic acid.

$$HO_2C\text{-}(CH_2)_n\text{-}COOH \xrightarrow{pK_1} HO_2C\text{-}(CH_2)_n\text{-}COO^- \xrightarrow{pK_2} {}^-O_2C\text{-}(CH_2)_n\text{-}COO^-$$

Acid	Formula	pK_1	pK_2
Malonic acid	HO_2CCH_2COOH	2.85	5.70
Methylmalonic acid	$HO_2CCH(CH_3)COOH$	3.07	5.76

(i) Suggest a reason why the pK_1 value of methylmalonic acid is higher than that of malonic acid.

(ii) Suggest a reason why the pK_2 values of methylmalonic acid and malonic acid are higher than their corresponding pK_1 values.

(iii) High concentration of calcium malonate, $C_3H_2O_4Ca$, is found in beetroot juice. A cup of 100 cm^3 of beetroot juice is found to have a pH of 8.

Given that calcium malonate is the only component in beetroot juice, calculate

1. the concentration of OH^- in the beetroot juice;
2. the initial concentration of calcium malonate.

You may use X^{2-} to represent the malonate ion in this calculation. **[7]**

(d) State and explain how the acidities of phenol, ethanoic acid and propan-1-ol compare with each other. **[4]**

[Total: 20]

- End of Paper -