PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP					
	1	3			

INDEX NUMBER				

CHEMISTRY

9647/03

Paper 3 Free Response

24 September 2014

2 hours

Candidates answer on separate paper.

Additional Materials:	Answer Paper Graph Paper Data Booklet Cover Page

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READ THESE INSTRUCTIONS FIRST

Write your name, CT group and index number 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.

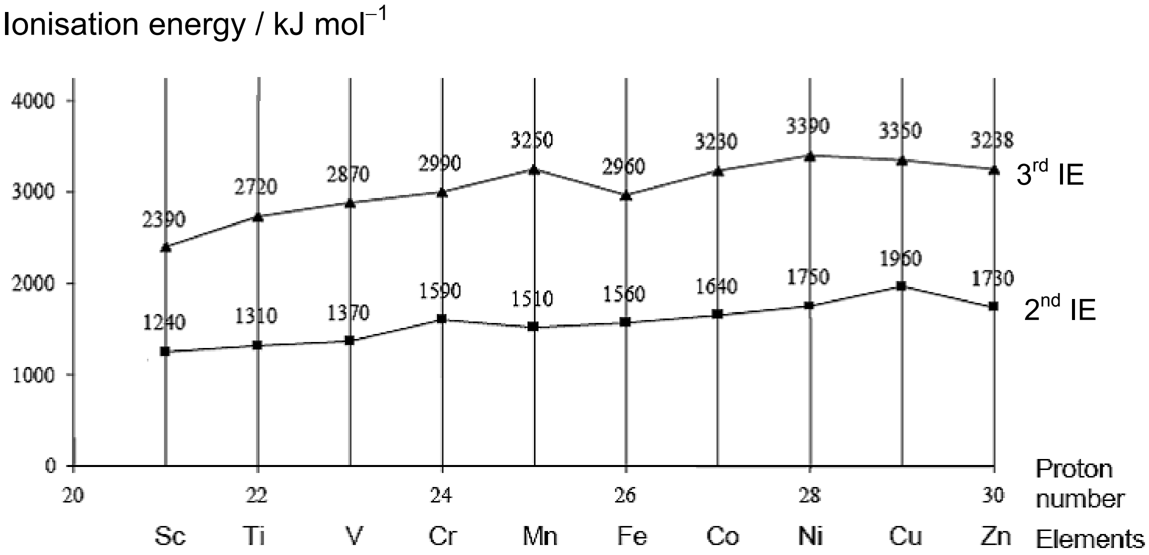
Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

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

This document consists of **12** printed pages.

Answer any **four** questions.

1 **(a)** The graph below shows the second and third ionisation energies for the first d-block elements scandium to zinc.



By writing relevant electronic configurations, explain why

(i) the second ionisation energy of chromium is higher than that of manganese.

(ii) the third ionisation energy of iron is lower than that of manganese.

[4]

(b) An aqueous solution contains a mixture of iron(III) and zinc ions.

(i) Draw a diagram to show the bonding in the hexaaquairon(III) complex ion.

(ii) Describe, in a sequence of steps, how you would separate the two cations so that they are obtained as Fe^{3+}(aq) and Zn^{2+}(aq). Write equations for all the reactions that iron(III) ion and its compound have undergone.

You are only provided with HNO_3(aq) and NaOH(aq).

[5]

(c) An aqueous iron(III) solution can be used as a homogeneous catalyst for the reaction between iodide ions and peroxodisulfate ions, $S_2O_8^{2-}$.

By considering relevant $E^\ominus$ values from the *Data Booklet*, describe and explain the role of iron(III) ions in the reaction between I^- and $S_2O_8^{2-}$. Write equations and calculate the $E^\ominus_{cell}$ for the reactions that occur. [4]

(d) The kinetics of the uncatalysed reaction between peroxodisulfate ions and iodide ions can be investigated experimentally.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

To find the rate equation: rate = $k[S_2O_8^{2-}(aq)]^a[I^-(aq)]^b$ for this reaction, a continuous method with sampling is used.

In an experiment, 50.0 cm^3 of 0.200 mol dm^{-3} of aqueous sodium iodide was mixed with 50.0 cm^3 of 2.00 mol dm^{-3} aqueous sodium peroxodisulfate. At various time intervals, 10.0 cm^3 of the reaction mixture was withdrawn and quenched with 50 cm^3 of ice-cold water. The resultant mixture was titrated against 0.0250 mol dm^{-3} aqueous potassium thiosulfate, using starch as an indicator.

The reaction between thiosulfate and iodine is as follows:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

The results are shown below:

Time / min	0	2	4	6	12	16
Volume of $K_2S_2O_3$ (aq) / cm^3	0	9.50	17.00	22.50	32.25	35.50

(i) Show that 40.00 cm^3 of standard aqueous potassium thiosulfate is required to react with 10.0 cm^3 of the reaction mixture when the reaction between peroxodisulfate and iodide ions is complete.

(ii) By drawing a suitable graph, use it to show that the reaction is first order with respect to iodide ions.

(iii) The order of reaction with respect to peroxodisulfate ions is reported to be one. You are required to conduct a second experiment using the same experimental procedures to confirm the order of reaction.

Suggest suitable concentrations of aqueous sodium iodide and sodium peroxodisulfate to be used and explain how the data obtained could be used to confirm the order of reaction.

[7]

[Total: 20]

2 The halogens are an important class of inorganic elements that forms a large variety of halogen-containing products, many of which are useful to us. Three members of the series, namely chlorine, bromine and iodine, were discovered in the 19th century by Humphry Davy, Antoine-Jérôme Balard and Bernard Courtois respectively.

(a) A student carried out a series of redox reactions on three unknown halogens, $\mathbf{R_2}$, $\mathbf{S_2}$ and $\mathbf{T_2}$, and their respective halides. Aqueous solutions of $\mathbf{R_2}$ and $\mathbf{S_2}$ are brown in colour, while an aqueous solution of $\mathbf{T_2}$ is colourless.

For each experiment, an unknown halogen was added to a solution containing an unknown halide. This was followed by the addition of tetrachloromethane to the resultant solution.

The following table shows the results and observations obtained from the experiments.

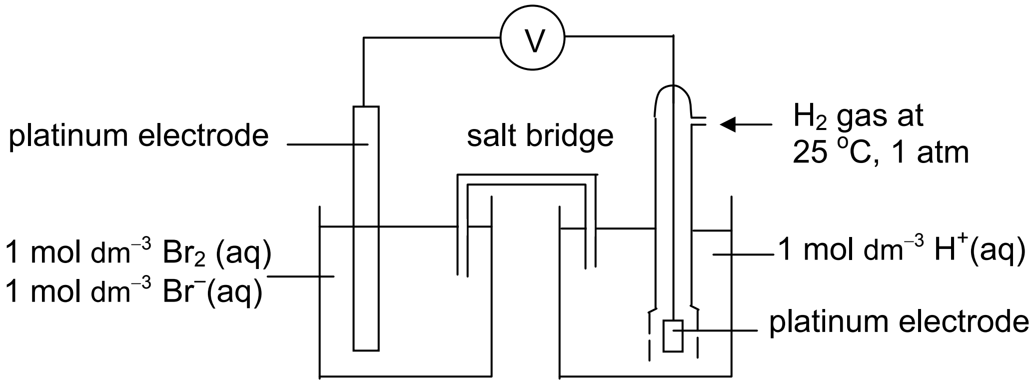
Experiment Number	*Reagent 1*	*Reagent 2*	*Colour of the organic layer after adding and shaking with tetrachloromethane*
1	$\mathbf{R_2}$(aq)	$\mathbf{S}^-$(aq)	violet
2	$\mathbf{T_2}$(aq)	$\mathbf{R}^-$(aq)	violet
3	$\mathbf{S_2}$(aq)	$\mathbf{T}^-$(aq)	red-brown

(i) Explain the role of tetrachloromethane in the series of experiments.

(ii) Deduce the identities of $\mathbf{R_2}$, $\mathbf{S_2}$ and $\mathbf{T_2}$. Explain your reasons clearly.

[6]

(b) To determine the standard redox potential of the $Br_2|Br^-$ system, a student set up the apparatus as shown in the diagram below.



However, she accidentally spilled a few drops of aqueous silver nitrate to the $Br_2|Br^-$ half-cell.

Explain how the E_{cell} of the system would be affected. State what would be observed and write an equation for any reaction that occurred. [3]

(c) Halogens can function as oxidising agents, while their halides can function as reducing agents.

Use the *Data Booklet* to predict what you would expect to observe when the following pairs of solutions are mixed. Write balanced equation for any reaction that occurs.

(i) aqueous bromine and aqueous hydrogen peroxide

(ii) aqueous sodium chloride and aqueous iron(III) nitrate

[4]

(d) **(i)** The following table shows the boiling points of three organic compounds.

Organic Compound	**Boiling Point / °C**
CH_3Cl	–24
CH_3CH_2F	–37
CH_3CH_2Cl	12

Explain the difference in boiling points between

- CH_3Cl and CH_3CH_2Cl
- CH_3Cl and CH_3CH_2F

(ii) Ammonium hydrogen difluoride is a colourless salt that is used as an etchant to allow different designs to be engraved onto glass. It contains one cation and one anion. It is formed by the reaction between ammonia and hydrogen fluoride.

I Write an equation for the formation of ammonium hydrogen difluoride from ammonia and hydrogen fluoride.

II Suggest the structure for the anion and state the types of bonding occurring within it.

[7]

[Total: 20]

3 (a) Aluminium and phosphorus form the chlorides $AlCl_3$ and PCl_3.

(i) When aqueous sodium carbonate is added to aqueous aluminium chloride, a colourless gas is liberated and a white precipitate is formed. Give an ionic equation for the reaction and briefly account for the gas produced.

PCl_3 reacts with water according to the following equation.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

In an experiment, 1.00 g of PCl_3 was dissolved in water. The resulting solution was made up to 250 cm^3 in volumetric flask. 25.0 cm^3 of this solution is titrated with 0.200 mol dm^{-3} of NaOH and required 18.20 cm^3 for neutralisation.

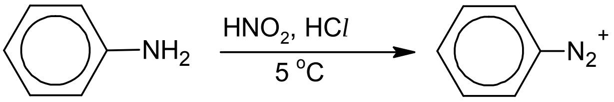
(ii) Calculate the total amount of H^+ that will be formed after the addition of water to PCl_3. Hence, determine the basicity of H_3PO_3.

(iii) Draw the structure of H_3PO_3 and use it to account for the basicity determined in **(a)(ii)**.

(iv) Both PCl_3 and $AlCl_3$ are used in organic synthesis. Explain why anhydrous $AlCl_3$ catalyses the chlorination of benzene, but not PCl_3.

[9]

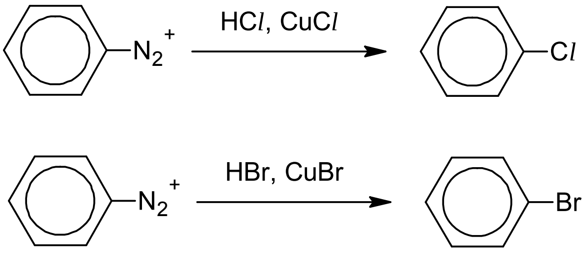
(b) Primary arylamines react with nitrous acid, HNO_2, to yield stable arenediazonium salts.



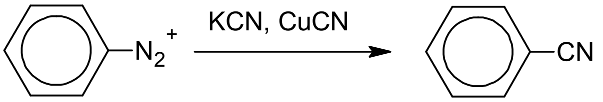
arenediazonium ion

Arenediazonium ions are very useful in the synthesis of many substituted aromatic compounds as the diazonium group ($-N_2^+$) can be replaced with many atoms or groups such as OH, Cl, Br and H.

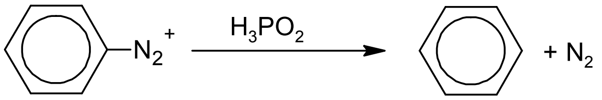
The arenediazonium ion can react with copper(I) chloride or copper(I) bromide to replace the diazonium group with Cl and Br respectively. The reaction of an arenediazonium salt with the corresponding copper(I) halide is known as the Sandmeyer reaction.



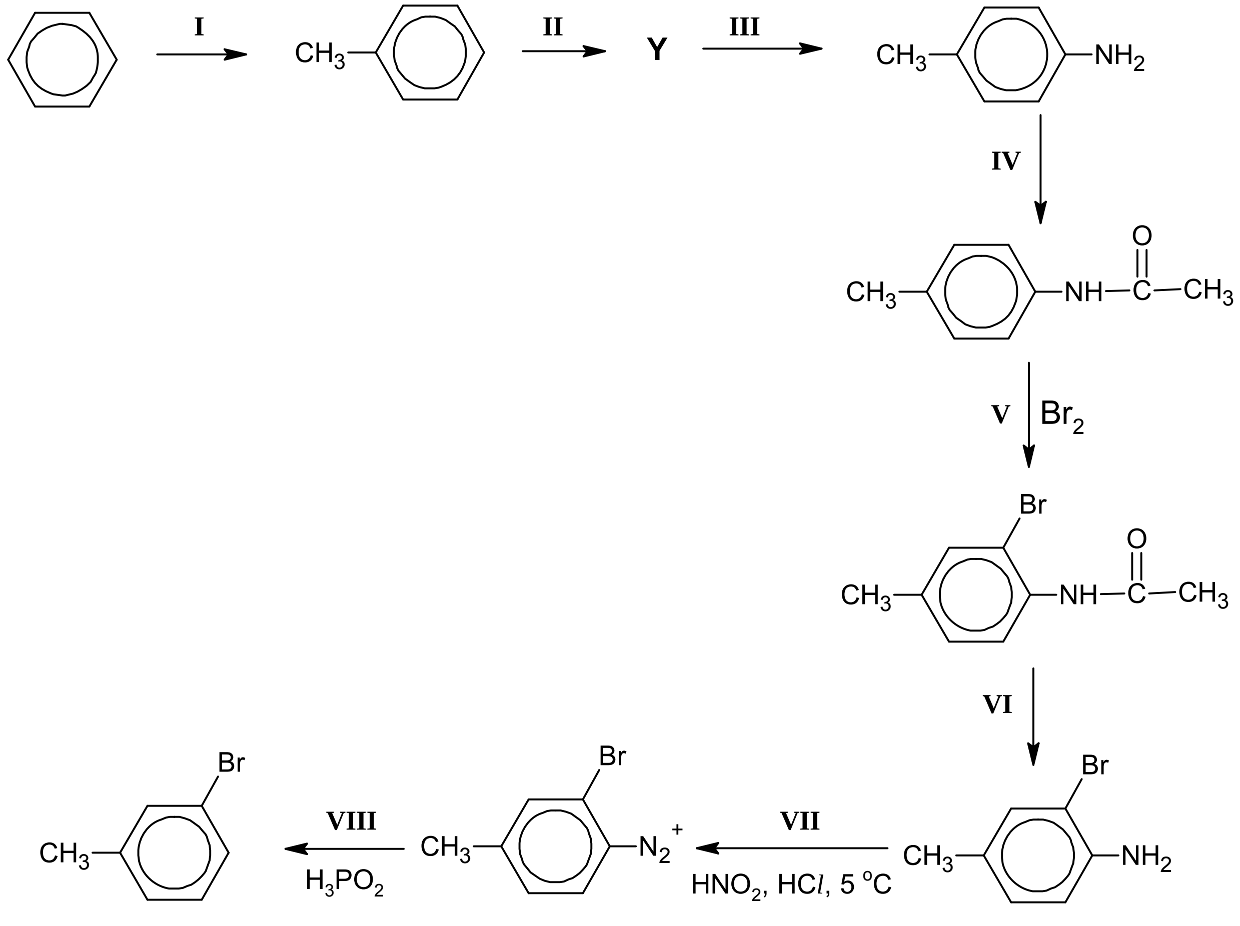
Similar treatment of the arenediazonium ion with copper(I) cyanide yields the arenenitrile.



To get the arene, deamination of the arenediazonium ion can be carried out using phosphinic acid, H_3PO_2.



An application of the Sandmeyer reaction and deamination can be seen in the synthesis of 3-bromomethylbenzene which cannot be carried by the direct bromination of methylbenzene or by Friedel Crafts alkylation of bromobenzene. The following reaction scheme shows how 3-bromomethylbenzene can be obtained in high yield.



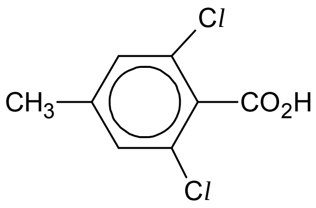
(i) Give the structure of compound **Y**.

(ii) State the reagents and conditions for steps **I**, **II**, **III** and **IV**.

(iii) Explain the significance of step **IV** before bromination takes place in step **V**.

(iv) By means of a half-equation, show that deamination in step **VIII** is a reduction.

(v) Compound **Z** can be synthesised from 4-methylphenylamine using arenediazonium ion as an intermediate at some stage of each synthesis. In no more than 4 steps, suggest the reagents and conditions required for the transformation. Give the structures of the intermediate compounds formed.



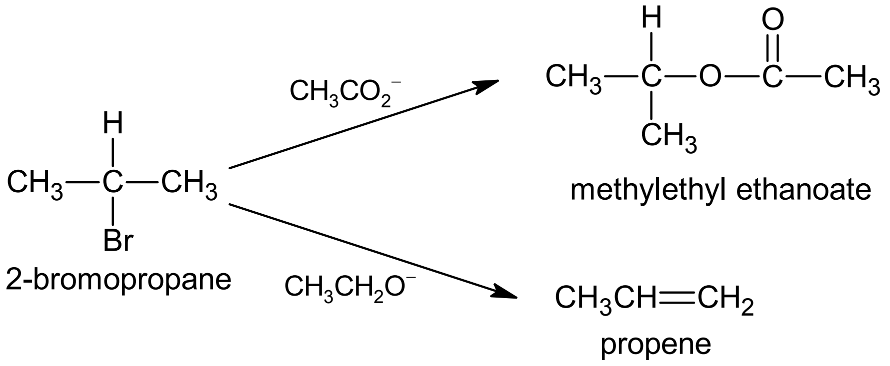
Compound **Z**

[11]

[Total: 20]

4 Methylethyl ethanoate is a colourless liquid with a characteristic fruity odour.

(a) Methylethyl ethanoate can be produced from 2-bromopropane using $CH_3CO_2^-$. However, in the presence of $CH_3CH_2O^-$, a stronger base, propene is obtained.



(i) A student determined experimentally the rate equation of the reaction between 2-bromopropane and $CH_3CO_2^-$ to be rate = k[2-bromopropane].

Name and suggest a mechanism for the reaction. In your answer show any relevant charges, dipoles or lone pairs of electrons you consider important in this mechanism.

(ii) Name the type of reaction between 2-bromopropane and $CH_3CH_2O^-$.

(iii) Explain why $CH_3CO_2^-$ is a weaker base than $CH_3CH_2O^-$.

[6]

(b) **(i)** Define the term *standard enthalpy change of combustion*.

(ii) Write an equation to represent the standard enthalpy change of combustion of methylethyl ethanoate.

(iii) Using bond energy data from the *Data Booklet*, calculate a value of standard enthalpy change of combustion of methylethyl ethanoate.

(iv) The actual standard enthalpy change of combustion of methylethyl ethanoate is –2230 kJ mol^{-1}. With reference to the definition of bond energy, account for the discrepancy between this value and that calculated in **(b)(iii)**.

[5]

(c) Compound **K** is an isomer of methylethyl ethanoate. It does not rotate plane of polarised light and does not give yellow precipitate when warmed with aqueous alkaline iodine.

Upon heating with excess concentrated sulfuric acid, **K** forms compound **L** which decolourises aqueous bromine readily. On oxidation with acidified potassium manganate(VII), **L** produces compound **M**, of molecular formula C_3H_6O, as the only organic product. **M** gives orange precipitate when reacted with 2,4-dinitrophenylhydrazine.

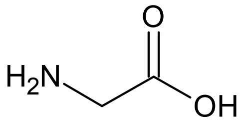
On oxidation with acidified potassium dichromate(VI), **L** produces compound **N**. When **N** is added to methylamine, compound **O** with molecular formula $C_6H_{13}O_2N$ is formed.

Give the structures of compounds **K**, **L**, **M** and **O**. Explain the chemistry of the reactions.

[9]

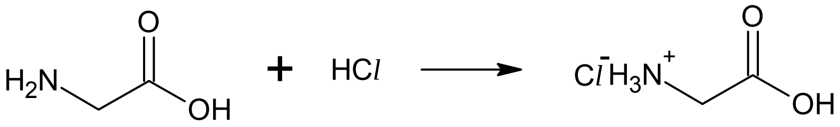
[Total: 20]

5 **(a)** Glycine is a non-essential amino acid. It is frequently used to enhance the flavour of savoury foods. The structure of glycine is shown below.



The pK_a values of the α-carboxyl and the protonated α-amino groups of glycine are 2.4 and 9.8 respectively.

Glycine hydrochloride is produced when glycine is reacted with hydrochloric acid as shown below.



(i) Calculate the pH of a 0.100 mol dm^{-3} solution of glycine hydrochloride.

Ignore the effect of pK_a of the protonated amino group on the pH.

(ii) Sketch the pH-volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 sample of the solution in **(a)(i)**.

Show the initial pH, pH of the first equivalence point and pK_a values on your curve.

(iii) Suggest a suitable indicator to be used for the first equivalence point.

(iv) Identify a conjugate acid-base pair present in the course of the titration. By means of two equations, show how the conjugate acid-base pair can act as a buffer.

[10]

(b) *Tat* is a regulatory protein that drastically enhances the HIV viral transcription. It consists of a total of 86 amino acids. Eight of the most common amino acids in the *Tat* molecule are listed below.

Amino acid	**Abbreviated name**	**Formula of side chain (R in $RCH(NH_2)CO_2H$)**
isoleucine	ile	$-CH(CH_3)(CH_2CH_3)$
arginine	arg	$-(CH_2)_3NHC(NH_2)=NH$
lysine	lys	$-(CH_2)_4NH_2$
glycine	gly	$-H$
serine	ser	$-CH_2OH$
glutamine	gln	$-(CH_2)_2CONH_2$
threonine	thr	$-CH(OH)CH_3$
alanine	ala	$-CH_3$

(i) A section of the protein has the sequence thr-lys-ala.

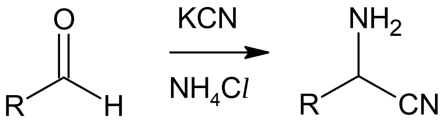
Draw the displayed formula of the section of the protein.

(ii) Suggest **three** amino acids in the above table which allow the protein to interact with water molecules in the bloodstream.

(iii) Suggest how the addition of a base to *Tat* causes denaturation of the protein.

[6]

(c) The Strecker amino acid synthesis is devised by Adolph Strecker to produce amino acids in the laboratory. The first step of the synthesis involves the reaction of an aldehyde with ammonium chloride followed by potassium cyanide.



(i) Using the Strecker amino acid synthesis, suggest, in no more than 3 steps, how the amino acid, alanine (R = $-CH_3$) can be synthesised from ethanol.

(ii) Briefly explain why alanine prepared by the Strecker amino acid synthesis does not show optical activity but that found in protein does.

[4]

[Total: 20]

End of Paper