

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION **HIGHER 2**

CHEMISTRY	,	96	647/03
CT GROUP	1 3		
CANDIDATE NAME			

9047703

Paper 3 Free Response

24 September 2014

2 hours

Candidates answer on separate paper.

Additional Materials:	Answer Paper
	Graph Paper
	Data Booklet
	Cover Page

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.

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 configuration, explain why

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

 $\begin{array}{l} Cr^{+}: 1s^{2} \ 2s^{2} \ 2p^{6} \ 3s^{2} \ 3p^{6} \ 3d^{5} \\ Mn^{+}: 1s^{2} \ 2s^{2} \ 2p^{6} \ 3s^{2} \ 3p^{6} \ 3d^{5} \ 4s^{1} \end{array}$

The second electron removed from chromium is from an <u>inner 3d subshell</u> which is <u>closer to the nucleus</u> and required a higher energy to remove it.

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

 $Fe^{2+:} 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ Mn^{2+:} 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵

The third electron from Fe experiences <u>inter-electronic repulsion</u> as it is removed from <u>one 3d orbital containing a pair of electrons</u> and required a lower energy to remove it.

[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 HNO₃(aq) and NaOH(aq).

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1. To 2 cm³ of solution in a test tube, add <u>NaOH(aq) until in excess</u> 2. Filter the mixture 3. Add excess HNO₃(aq) to the residue to obtain Fe³⁺(aq) 4. Add excess HNO₃(aq) to the filtrate to obtain Zn²⁺(aq) Precipitation reaction: Fe³⁺(aq) + 3OH⁻(aq) \rightarrow Fe(OH)₃(s) Acid Base reaction: Fe(OH)₃(s) + 3HNO₃(aq) \rightarrow Fe(NO₃)₃(aq) + 3H₂O(*l*)

(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° values from the *Data Booklet*, describe and explain the role of iron(III) ions in the reaction between I⁻ and S₂O₈²⁻. Write equations and calculate the E°_{cell} for the reactions that occur. [4]

[5]

$S_2O_8^{2-}(aq) + 2e^- \implies 2SO_4^{2-}(aq)$	<i>E</i> [⇔] = +2.01V
$Fe^{3+}(aq) + e^{-} \implies Fe^{2+}(aq)$	<i>E</i> [⊖] = +0.77∨
$I_2(aq) + 2e^- \implies 2I^-(aq)$	<i>E</i> [⇔] = +0.54V

Step 1: Formation of intermediate $2Fe^{3^+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2^+}(aq) + I_2(aq)$ $E^{\ominus}_{cell} = +0.77 + (-0.54) = +0.23 V > 0$ Step 2: Regeneration of the catalyst $2Fe^{2^+}(aq) + S_2O_8^{2^-}(aq) \rightarrow 2Fe^{3^+}(aq) + 2SO_4^{2^-}(aq)$ $E^{\ominus}_{cell} = -0.77 + (+2.01) = +1.24 V > 0$

Reaction is energetically feasible.

The ease of interconversion between the +2 and + 3 oxidation states of iron and the reaction of oppositely charged ions (Fe³⁺ and I⁻ as well as Fe²⁺ and S₂O₈²⁻) in the same physical state provide an alternative reaction pathway of lower activation energy.

(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 cm³ of 0.200 mol dm⁻³ of aqueous sodium iodide was mixed with 50.0 cm³ of 2.00 mol dm⁻³ aqueous sodium peroxodisulfate. At various time intervals, 10.0 cm³ of the reaction mixture was withdrawn and quenched with 50 cm³ of ice-cold water. The resultant mixture was titrated against 0.0250 mol dm⁻³ aqueous potassium thiosulfate, K₂S₂O₃, 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 cm³ of aqueous potassium thiosulfate is required to react with 10.0 cm³ of the reaction mixture when the reaction between peroxodisulfate and iodide ions is complete.

 $n(I^{-}) = (50.0/1000)(0.200) = 0.010 \text{ mol}$ $n(S_2O_8^{2-}) = (50.0/1000)(2.00) = 0.10 \text{ mol}$

 $\begin{array}{l} n(I_2) \mbox{ produced in 100 cm}^3 \mbox{ of reaction mixture } = 0.010 / 2 \\ = 0.00500 \mbox{ mol} \\ n(I_2) \mbox{ in 10.0 cm}^3 = 0.00500 / (100/10.0) \\ = 0.000500 \mbox{ mol} \\ n(S_2O_3^{2-}) = 0.000500 \ x 2 \\ = 0.00100 \mbox{ mol} \\ volume \mbox{ of } S_2O_3^{2-} \mbox{ needed } = 0.00100 / 0.0250 \\ = 0.040 \mbox{ dm}^3 \end{array}$

$$= 40.00 \text{ cm}^{3}$$

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



(iii) The order of reaction with respect to $S_2O_8^{2-}$ 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.

Mix 50.0 cm³ of 0.200 mol dm⁻³ of aqueous sodium iodide with 50.0 cm³ of 4.00 mol dm⁻³ (or any other appropriate concentration) aqueous sodium peroxodisulfate and plot a volume of $S_2O_3^{2-}$ needed against time, the gradient of the graph at time = 0 should be doubled compared to the first experiment if it is first order wrt $S_2O_8^{2-}$. Or

Mix 50.0 cm³ of 0.200 mol dm⁻³ of aqueous sodium peroxodisulfate with 50.0 cm³ of 2.00 mol dm⁻³ aqueous sodium iodide and plot a volume of $S_2O_3^{2-}$ needed against time, the <u>half life should be constant</u> if it is first order wrt $S_2O_8^{2-}$.

[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, R₂, S₂ and T₂, and their respective halides. Aqueous solutions of R₂ and S₂ are brown in colour, while an aqueous solution of T₂ 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	R₂ (aq)	S ⁻(aq)	violet
2	T₂ (aq)	R ⁻(aq)	violet
3	S ₂(aq)	T ⁻(aq)	red-brown

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

Tetrachloromethane acts as an <u>organic solvent</u> to allow the halogen to dissolve in it. This will allow the halogens to be <u>identified by their</u> <u>respective colours</u> when dissolved in an organic solvent.

(ii) Deduce the identities of R_2 , S_2 and T_2 . Explain your reasons clearly.

Oxidising power of halogen decreases down Group VII / Oxidising power: $Cl_2 > Br_2 > I_2$ OR Reducing power of X⁻ increases down the group / Reducing power : I⁻ > Br⁻ > Cl⁻

From Expt 1, iodine is present in the organic layer, which gave the violet colour.

Hence, either R_2 (no reaction between R_2 and S^-) or S^- (R_2 could oxidise S^- into S_2) could be iodine.

From Expt 2, iodine is present in the organic layer. Hence, either T_2 (no reaction between T_2 and R^-) or R^- (T_2 could oxidise R^- into R_2) could be iodine.

Hence, R_2 , the common reagent in both experiments, is iodine.

The remaining unknowns, T_2 and S_2 , are either bromine or chlorine.

Since $Cl_2(aq)$ is pale yellow/colourless, T_2 is chlorine.

The remaining substance, **S**₂, must be bromine.

- [6]
- (b) To determine the standard redox potential of the Br₂/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]

A <u>cream precipitate</u> of AgBr(s) will be formed.

 $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$

This causes a <u>decrease in [Br⁻]</u> in the Br₂/Br⁻ half-cell.

Hence, for the reaction occuring at the Br₂/Br⁻ half-cell, Br₂(aq) + 2e⁻ \implies 2Br⁻(aq) E_{red}

Equilibrium position will shift to the right. $\underline{E_{red}}$ becomes more positive. Hence, $\underline{E_{cell}}$ will become more positive.

(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

 $Br_2 + 2e^- = 2Br^ H_2O_2 = O_2 + 2H^+ + 2e^-$

 $E_{red}^{\Theta} = +1.07V$ $E_{ox}^{\Theta} = -0.68V$

$$Br_2 + H_2O_2 \rightarrow 2Br^- + O_2 + 2H^+$$

 $E_{cell}^{\Theta} = +0.39V > 0$

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Reaction is thermodynamically feasible.

Observation:

Orange / Red-Brown solution decolourises. Effervescence observed, colourless gas rekindles glowing splint.

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

 $2Cl^{-} \stackrel{\longrightarrow}{\longrightarrow} Cl_{2} + 2e^{-} \qquad E^{\Theta}_{ox} = -1.36V$ Fe³⁺ + e⁻ $\stackrel{\longrightarrow}{\longrightarrow}$ Fe²⁺ $E^{\Theta}_{red} = +0.77V$

 $2Cl^{-} + 2Fe^{3+} \rightarrow Cl_2 + 2Fe^{2+}$ $E^{\Theta}_{cell} = -0.59V < 0$ Reaction is NOT thermodynamically feasible.

Observation: Solution <u>remains pale yellow</u>.

[4]

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

Organic Compound	Boiling Point (°C)
CH ₃ C <i>l</i>	-24
CH ₃ CH ₂ F	-37
CH ₃ CH ₂ Cl	12

Explain the difference in boiling points between

- CH₃C*l* and CH₃CH₂C*l*
- CH₃Cl and CH₃CH₂F
- CH_3Cl and CH_3CH_2Cl

Both compounds have simple molecular structures with weak permanent dipole-dipole interactions between their molecules.

 CH_3CH_2Cl has a <u>larger electron cloud</u> as compared to CH_3Cl . The electron cloud of CH_3CH_2Cl is <u>more polarisable</u>, leading to <u>stronger</u> instantaneous dipole / van der Waals' forces.

Hence, <u>more energy is required</u> to overcome the stronger intermolecular forces between the molecules of CH_3CH_2Cl , leading to a higher boiling point.

• CH₃Cl and CH₃CH₂F

Both compounds have simple molecular structures with weak permanent dipole-dipole interactions between their molecules.

 CH_3CH_2F has an <u>electron-donating $-CH_3$ group</u>, which <u>decreases</u> the partial positive charge on the carbon atom of the C-F. This makes the <u>C-F bond less polar</u> than expected, although F is very electronegative.

This results in <u>weaker permanent dipole-dipole interactions</u> between the CH₃CH₂F molecules. Less energy is required to overcome the intermolecular forces, resulting in lower boiling point.

- (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.

$\mathsf{NH}_3 + \mathsf{2HF} \to [\mathsf{NH}_4^+][\mathsf{HF}_2^-]$

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

[F-HIMIF] Covalent Hydrogen bond bond

[7]

[Total: 20]

- 3 (a) Aluminium and phosphorus form the chlorides $A_lC_{l_3}$ and PC_{l_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.

$$2Al^{3+}(aq) + 3CO_3^{2-}(aq) + 3H_2O(l) \rightarrow 2Al(OH)_3(s) + 3CO_2(g)$$

OR
 $2[Al(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow 2Al(H_2O)_3(OH)_3(s) + 3CO_2(g) + 3H_2O$

The <u>high charge density of Al^{3+} </u> polarises and weakens the O-H bonds of the coordinated water molecules, <u>causing H⁺ to be released</u> which reacts with CO_3^{2-} to form CO_2 .

 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 cm³ in volumetric flask. 25.0 cm³ of this solution is titrated with 0.200 mol dm⁻³ of NaOH and required 18.20 cm³ 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 .

Amount of H⁺ in 25.0 cm³ of solution = $(18.20 / 1000) \times 0.200$ = 3.64 x 10⁻³ mol

Total amount of H^+ produced = 3.64 x 10⁻³ x 10 = 3.64 x 10⁻² mol

Amount of PC l_3 dissolved = 1.00 / [31.0 + 3(35.5)] = 7.27 x 10⁻³ mol

Amount of H_3PO_3 produced = 7.27 x 10^{-3} mol

Amount of HCl produced = $7.27 \times 10^{-3} \times 3$ = 0.0218 mol = amount of H⁺ produced by HCl

Amount H^+ produced by $H_3PO_3 = 3.64 \times 10^{-2} - 0.0218$ = 0.0146 mol

7.27 x 10^{-3} mol of H₃PO₃ ≡ 0.0146 mol of H⁺ 1 mol of H₃PO₃ ≡ 2 mol of H⁺

H₃PO₃ is a dibasic acid.



Only the 2 H atoms directly bonded to the electronegative O atoms can be dissociated because the anion formed is stable with the negative charges residing on the two electronegative O atoms.

Or

The O-H bond is more polar than the P-H bond so the hydrogen bonded to the oxygen can be ionised.

(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 .

 $AlCl_3$ is <u>electron deficient</u>. Thus, it is able to accept a lone pair of electron from Cl_2 to form $AlCl_4^-$ and \underline{Cl}^+ , the <u>electrophile</u> for the chlorination of benzene. PCl_3 has a <u>noble gas / octet configuration / not electron</u> <u>deficient</u>. It reacts with Cl_2 to form PCl_5 which is not an electrophile. Thus, it cannot be a catalyst for the reaction.

[9]

(b) Primary arylamines react with nitrous acid, HNO₂, 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, C*l*, 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.

I: CH₃Cl, anhydrous AlCl₃, heat II: concentrated HNO₃, concentrated H₂SO₄, 30 °C **III:** Sn, concentrated HCl, heat followed by NaOH(aq) **IV**: CH₃COC*l* at room temperature

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

The amide group produced in step I reduces the ring activating effect so that only mono-substitution of bromine occurs.

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



Compound Z can be synthesised from 4-methylphenylamine using (v) 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.



- 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.

Nucleophilic substitution (S_N1)



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

Elimination

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

For $CH_3CO_2^-$ ion, the <u>negative charge is delocalised over the two</u> <u>electronegative oxygen atoms</u>, making the <u>lone pair of electron on O less</u> <u>available for protonation</u>.

[6]

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

> Standard enthalpy change of combustion is the heat evolved when one mole of a substance is completely burnt in excess air or oxygen under standard conditions of 298 K and 1 atmospheric pressure.

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

15

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

 ΔH_c of methylethyl ethanoate = \sum mB.E.(reactants) - \sum nB.E.(products) = [3BE(C-C) + 2BE(C-O) + BE(C=O) + 10BE(C-H) + 13/2BE(O=O)] -[10BE(C=O) + 10BE(O-H)]= [3(350) + 2(360) + 740 + 10(410) + 13/2(496)] - [10(740) + 10(460)] $= -2166 \text{ kJ mol}^{-1}$

(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).

The value calculate in (b)(iii) should be for <u>gaseous</u> methyethyl ethanoate and steam, not liquid methylethyl ethanoate and water. This is because bond energy is defined in terms of gaseous reactants and products. Hence, the enthalpy change of vapourisation of methylethyl ethanoate and water should be included in the calculation.

[5]

Compound K is an isomer of methylethyl ethanoate. It does not rotate plane of (c) polarised light and does not give vellow precipitate when warmed with agueous 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]

Information	Deduction	
K does not rotate plane of polarised light.	K contains no chiral carbon.	
K does not undergo oxidation with aqueous alkaline iodine.	K does not contain CH_3CO - or $CH_3CH(OH)$ - group.	
K undergoes <u>elimination</u> with excess concentrated H_2SO_4 to form L .	K contains <u>alcohol g</u> roup.	
L undergoes <u>electrophilic addition</u> with aqueous bromine.	L contains <u>alkene</u> group.	
L undergoes oxidation to form M which undergoes <u>condensation</u> with 2,4-DNPH.	M contains <u>ketone</u> group.	
L undergoes oxidation to form N which undergoes \underline{acid} - \underline{base} reaction with CH_3NH_2 to form O.	L contains <u>aldehyde</u> group. N contains <u>carboxylic acid</u> group. O is an <u>ionic</u> salt.	



[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 p K_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 treated with hydrochloric acid.



(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.

$$H_3N^+$$
 O_{OH} + H_2O \longrightarrow H_3N^+ O_{O^-} + H_3O^+

 $K_{\rm a}$ = 10^{-2.4} = 3.98 x 10⁻³ mol dm⁻³

Let the concentration of $[C_2H_6NO_2^+]$ dissociated be x

 $\boldsymbol{K}_{a} = \frac{x^{2}}{\left(\left[C_{2}H_{6}NO_{2}^{+}\right] - x\right)}$

Since $[C_2H_6NO_2^+] >> x$, $K_a = \frac{x^2}{[C_2H_6NO_2^+]}$

 $R_a = \left[C_2 H_6 N O_2^+\right]$ x = 0.0200 mol dm⁻³ = [H₃O⁺]

pH = 1.70

(ii) Sketch the pH-volume added curve you would expect to obtain when 30 cm³ of 0.10 mol dm⁻³ NaOH is added to 10 cm³ 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.

Methyl orange, bromothymol blue or any other indicator with a working pH range between 3 to 8.

(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.

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Conjugate acid-base pair: {}^{+}H_3NCH_2CO_2H and {}^{+}H_3NCH_2CO_2^{-}
{}^{+}H_3NCH_2CO_2H + OH^{-} \rightarrow {}^{+}H_3NCH_2CO_2^{-} + H_2O
{}^{+}H_3NCH_2CO_2^{-} + H^{+} \rightarrow {}^{+}H_3NCH_2CO_2H
Or
Conjugate acid-base pair: {}^{+}H_3NCH_2CO_2^{-} and H_2NCH_2CO_2^{-}
{}^{+}H_3NCH_2CO_2^{-} + OH^{-} \rightarrow H_2NCH_2CO_2^{-} + H_2O
H_2NCH_2CO_2^{-} + H^{+} \rightarrow {}^{+}H_3NCH_2CO_2^{-}
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[10]

(b) *TAT* is a gene in the type 1 human immunodeficiency virus. (HIV-1). It is purported that the gene is released into the blood stream to be absorbed by healthy cell. This causes the cell to die and thus assisting in the progression to acquire immunodeficiency syndrome (AIDS).

Amino acid	Abbreviated name	Formula of side chain (R in RCH(NH ₂)CO ₂ H)
isoleucine	lle	-CH(CH ₃)(CH ₂ CH ₃)
arginine	arg	-(CH ₂) ₃ NHC(NH ₂)=NH
lysine	lys	-(CH ₂) ₄ NH ₂
glycine	gly	-H
serine	ser	-CH ₂ OH
glutamine	gln	-(CH ₂) ₂ CONH ₂
threonine	thr	-CH(OH)CH ₃
alanine	ala	-CH ₃

The *TAT* gene produces a protein that consists of a total of 86 amino acids. Eight of the most common amino acids in the tat molecule are listed below.

(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 allows the protein to be soluble in the blood stream.

Any of these: lysine, serine, threonine, arginine, glutamine

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

Positively charged $-NH_3^{\pm}$ groups undergoes acid-base to form uncharged $-NH_2$ (or undergoes <u>deprotonation</u>). This causes the <u>ionic interactions to</u> <u>break</u> and the <u>3D conformation of the protein is disrupted</u>.

(c) The Strecker amino acid synthesis is a series of chemical reactions 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.

$$CH_{3}CH_{2}OH \xrightarrow{K_{2}Cr_{2}O_{7}(aq), H_{2}SO_{4}(aq)}_{heat and distill} \xrightarrow{CH_{3}}H \xrightarrow{KCN}_{NH_{4}Cl} \xrightarrow{NH_{2}}_{CH_{3}} \xrightarrow{H_{2}SO_{4}(aq)}_{heat} \xrightarrow{NH_{2}}_{Hat} \xrightarrow{H_{2}SO_{4}(aq)}_{heat} \xrightarrow{NH_{2}}_{CH_{3}} \xrightarrow{H_{2}SO_{4}(aq)}_{CH_{3}}$$

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

A <u>racemic mixture is obtained from the synthesis</u> whereas a human protein only contains the L-isomer.

[4]

[Total: 20]

End of Paper