TEMASEK
JUNIOR COLLEGE

CHEMISTRY **9729/03**
Paper 3 Free Response **13th September 2017**
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Graph Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

This document consists of **14** printed pages and **2** blank pages.

Section A

Answer **all** the questions in this section.

1 Calcium carbonate is found in rocks and is the main component of pearls and the shells of eggs, snails and many marine organisms. It is the active ingredient in agricultural lime and is also medicinally used as a calcium supplement or as an antacid.

(a) (i) Describe and explain the trend in thermal stability of the Group 2 carbonates.

[3]

- **Down the group, charge of the cation remains constant but ionic radius increases. Hence charge density of the cation decreases.**
- **(CO_3^{2-} ion is a large anion so is easily polarised but) Polarising power of cation decreases resulting in less distortion of the electron cloud of CO_3^{2-} ion, weakening the C-O covalent bond less.**
- **More energy needed to decompose the carbonate, hence down the Group, carbonates become more stable to heat, therefore decomposition temperature increases and thermal stability increases down the group.**

(ii) Determine the minimum temperature for the spontaneous decomposition of calcium carbonate, given that $\Delta H = +178.5$ kJ mol^{-1} and $\Delta S = +163.2$ J K^{-1} mol^{-1}.

[2]

$\Delta G = \Delta H - T\Delta S$
- **$\Delta H - T\Delta S < 0$**

$T > \Delta H / \Delta S$
$T > 178.5 \times 1000 / 163.2$
- **$T > 1090$ K (3 sig fig)**

(b) Limestone is predominantly calcium carbonate, a slightly soluble salt with a K_{sp} value of 3.3×10^{-9}. This rocky material began accumulating in the Earth over 400 million years ago. The Howe Caverns in the USA is a relatively young limestone cave which began forming 800 000 years ago.

(i) Determine the solubility of calcium carbonate.

[1]

Let solubility of $CaCO_3$ be x.
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$
$K_{sp} = x^2$
- **$x = 5.74 \times 10^{-5}$ mol dm^{-3}**

The principal cave-forming process is explained below.

Gaseous CO_2 is in equilibrium with aqueous CO_2 in surface water.

$CO_2(g) \rightleftharpoons CO_2(aq)$ ----- **(1)**

As surface water trickles through cracks in the ground, it meets soil-trapped air which contains higher levels of CO_2 (P_{CO_2} = 100 Pa) and hence [CO_2(aq)] increases.

When this CO_2-rich water contacts limestone, more $CaCO_3$ dissolves. As a result, more rock is carved out, more water flows in and over centuries a cave is formed.

$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$ ----- **(2)**

(ii) Show that the atmospheric partial pressure of CO_2, P_{CO_2}, is 40.5 Pa. You may assume air contains 0.04% by volume CO_2.

[1]

volume of gas α no of mole of gas (Avogadro's Law)

- **P_{CO_2} = 0.04/100 x 101325 = 40.5 Pa**

(iii) State and explain whether CO_2 in the atmosphere or soil-trapped air is behaving less ideally.

[2]

- **CO_2 in soil-trapped air will behave less ideally.**
- **As soil-trapped air will be under higher pressure the total volume occupied by the gas is reduced, the volume of the gas molecules becomes more significant compared with the total volume of the gas.**

Stalactites and stalagmites are rock formations that hang from ceiling of caves and rise from the floor of caves, respectively. They are formed when surface water seeps through rock and drips from the ceiling of a cave.

(iv) With reference to equilibria **(1)** and **(2)**, explain the formation of stalactites and stalagmites in limestone caves.

[3]

- **When the surface water drips from the ceiling, CO_2(g) escape as it comes into contact with the atmosphere, which has a lower P_{CO_2}.**
- **By Le Chatelier's principle, equilibrium (1) shift to the left causing [CO_2(aq)] to decrease. Equilibrium (2) will be be shifted to the left to counter the decrease in [CO_2(aq)]**
- **$CaCO_3$ will then be precipitated out on the ceiling or on the floor resulting in the formation of stalactites and stalagmites.**

(v) Suggest a reason why some of these rock formations can appear reddish brown or bluish green.

[1]

- **It is likely due to the presence of transition metal ions like Fe^{3+} and Cu^{2+}.**

Lakes bounded by limestone-rich soil are less likely to be impacted by acid rain. Limestone dissolves sufficiently in lake water to form a buffer system capable of mitigating the effect of acid rain.

(vi) Suggest, with the aid of an equation, how the buffer system will maintain the pH of the lake water.

[1]

- **CO_3^{2-}(aq) + H^+(aq) → HCO_3^-(aq)**

As the carbonate ions neutralise the H^+ from acid rain, there is negligible change in pH.

Acidification due to acid rain of lakes and rivers poses a serious environmental problem. The concentration of carbonate ions in these water is small due to the high acidity, hence affecting the survivability of some marine organisms.

(vii) Suggest a reason why the survivability of some marine organisms is affected.

[1]

- **Carbonate ions, together with calcium ions, are the building blocks of their shells and skeletons.**

(c) Emission from power stations using coal, which contains sulfur, as fuel has significant environmental consequences. One of the components is sulfur dioxide, which can be oxidised by atmospheric hydroxyl radical to sulfur trioxide.

(i) Write a balanced equation to explain how sulfur trioxide contribute to acid rain.

[1]

- **$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$**

Current power plants are fitted with flue-gas desulfurization devices. These devices heat powdered limestone in air to remove sulfur dioxide from the gases produced during coal combustion. One of the products is calcium sulfate.

(ii) Write a balanced equation for the reaction that had taken place.

[1]

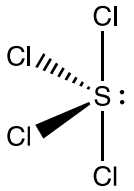
- **$CaCO_3(s) + ½O_2(g) + SO_2(g) \rightarrow CaSO_4(s) + CO_2(g)$**

(d) Sulfur and aluminium can both react with chlorine.

Aluminium chloride is a white solid that sublimes while sulfur tetrachloride, SCl_4, is an unstable pale yellow solid. Both react with water but formed different products.

(i) Predict the shape of sulfur tetrachloride, using a diagram where appropriate. Suggest the bond angle(s) in the molecule.

[2]

- **See-saw, < 90° and < 120°**
- 

(ii) Describe and explain, with the aid of equations, the reaction of aluminium chloride with water. Suggest the pH of the resulting solution.

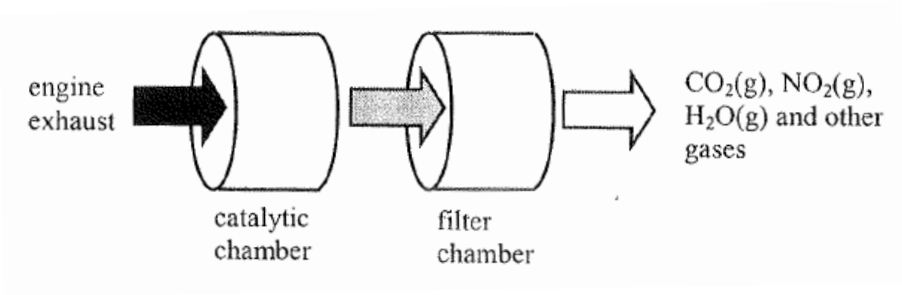
[3]

- **Hydration: $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$**
  Hydrolysis: $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$
- **Hydrolysis is possible because Al^{3+} has a high charge density (small in size and highly charged) hence a high polarising power. It draws electrons away from its surrounding water molecules and weakens the O-H bond. It is easier for a H^+ ion to leave the water molecule.**
- **pH = 3**

[Total: 22]

2 The exhaust of heavy-duty diesel engines contains a significant amount of particulate matter (PM) and harmful gases such as nitrogen oxides. A Continuous Regenerating Trap (CRT) is a device which is designed for use in exhaust systems of buses and lorries running on diesel to remove PM and some of the harmful gases. A second catalytic converter is usually installed to remove the oxides of nitrogen.

The diagram below shows how a CRT works:



(a) (i) Explain, with the aid of equations, why oxides of nitrogen are present in the engine exhaust.

[2]

- **Under the high temperature condition of the internal combustion engine, atmospheric nitrogen reacts with oxygen to from oxides of nitrogen.**
- **$N_2(g) + O_2(g) \rightarrow 2NO(g)$**
  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

(ii) State one harmful effect of nitrogen oxides on the environment.

[1]

- **Acid rain OR photochemical smog**

(iii) State two harmful gases that are also present in the engine exhaust. Use chemical equations to show how these two gases can be removed in the catalytic chamber of a CRT.

[2]

- **CO and hydrocarbons**
- **$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$**
  $C_xH_y(g) + (x + y/4)\ O_2(g) \rightarrow xCO_2(g) + y/2\ H_2O(l)$

A CRT is an automated, self-regenerating device which does not require cleaning of the filter. In a CRT, the carbon, which is the most abundant element in PM, is trapped onto the filter and is then removed by one of the harmful gases.

(iv) Explain, with the aid of an equation, how the carbon trapped on the filter of a CRT can be removed. Hence explain why the filter need not be cleaned.

[2]

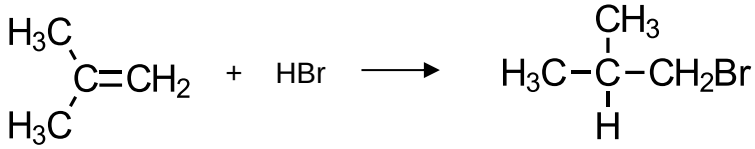
- **$C(s) + 2NO_2(g) \rightarrow CO_2(g) + 2NO(g)$ OR**
  $C(s) + 2NO(g) \rightarrow CO_2(g) + N_2(g)$ OR
  $2C(s) + 2NO_2(g) \rightarrow 2CO_2(g) + N_2(g)$
- **The carbon on the filter is oxidised by the oxides of nitrogen to form gaseous CO_2 and thus the filter need not be cleaned.**

(v) Suggest why buses and lorries equipped with CRT should not run on diesel with high sulfur content.

[1]

- **The sulfur will poison the catalyst rendering it ineffective.**

(b) In the reaction of HBr to alkenes such as methylpropene, scientists discovered that impurities such as peroxides, R-O-O-R, greatly increased the amount of anti-Markovnikov addition product as shown below.

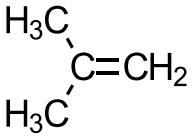


methylpropene 1-bromo-2-methylpropane

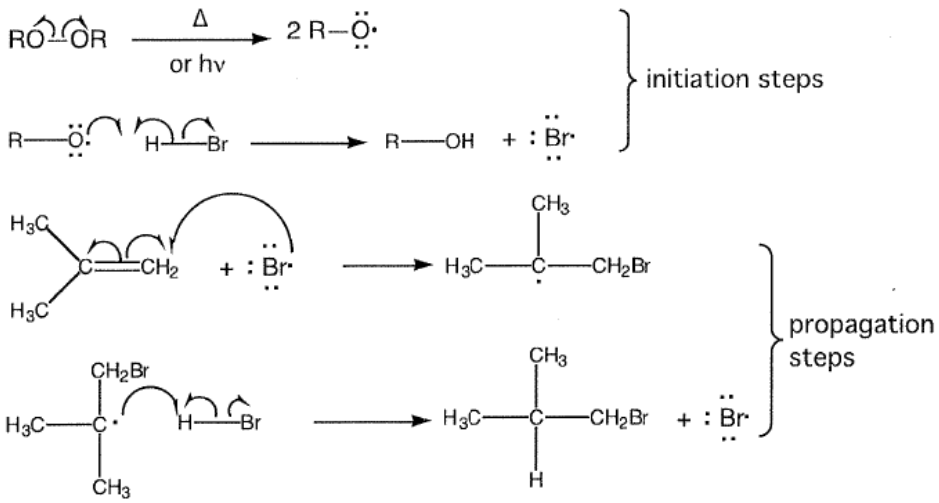
The above reaction is explained by the 4 step free radical addition mechanism as described below.

Step 1: The reaction is initiated by the formation of RO• radicals.
Step 2: This is followed by the reaction of the RO• radical with HBr to give bromine radical.
Step 3: The bromine radical adds to the alkene via the cleaving of the pi bond.
Step 4: The radical obtained from Step 3 reacts with HBr to form the anti-Markovnikov product.

(i) Use the information given above to draw out the full mechanism for the reaction. You are advised to use structural formulae for all species, such as



for methylpropene, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot and use  to represent movement of an electron. [4]

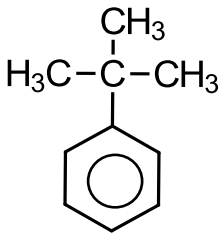


(ii) Unlike HBr, HC*l* does not undergo free radical addition to alkenes, even in the presence of peroxides. Explain this observation by quoting relevant values from the Data Booklet to substantiate your answer.

[2]

- **B.E H-Cl = 431 kJ mol^{-1}**
  B.E H-Br = 366 kJ mol^{-1}
- **The H—Cl bond is a stronger bond with better orbital overlap between H and Cl atoms. More energy is required to break the bond compared to HBr as shown by the bond energy values.**

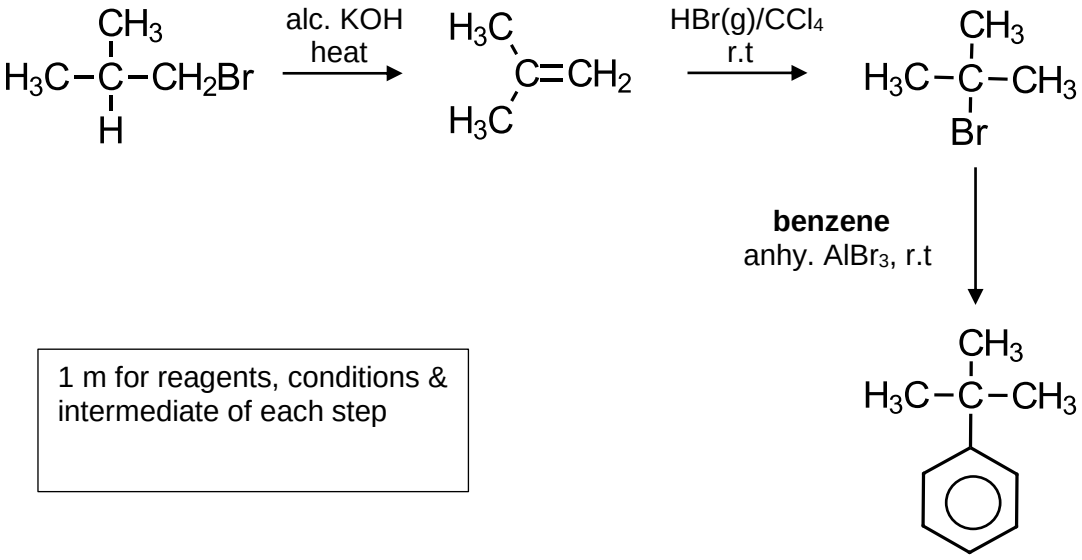
Tertiary butylbenzene is a colourless liquid widely used as a solvent for organic synthesis and also as a polymer linking agent.



t-butylbenzene

(iii) Using 1-bromo-2-methylpropane as the starting material, suggest a 3-stage synthesis of t-butylbenzene. You should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds.

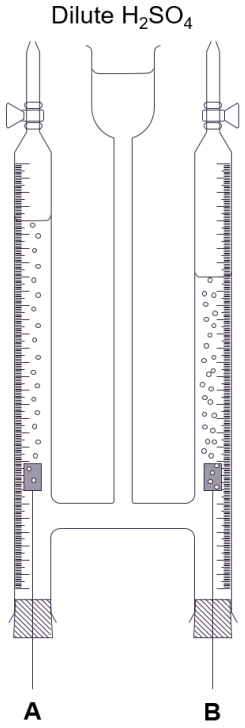
[3]



1 m for reagents, conditions & intermediate of each step

[Total: 17]

3 The following setup was carried out for the electrolysis of dilute sulfuric acid under room conditions, using platinum electrodes. A steady current of 2 A was applied for 1 minute through the circuit. The ratio of volume of gas produced at electrodes **A** and **B** is 1:2.



(a) **(i)** Write the half-equations for the reactions occurring at **A** and **B**. Label the polarity of each electrode clearly.

[2]

- **Anode is A:** **$2H_2O \rightarrow O_2 + 4H^+ + 4e$** **Polarity of electrode: +**
- **Cathode is B:** **$2H^+ + 2e \rightarrow H_2$** **Polarity of electrode: -**

(ii) Calculate the volume of gas produced at **A** after 1 minute.

[1]

Number of moles of electrons = It/F = 2x60/96500 = 1.24×10^{-3} mol
O_2 gas is produced at A. Since 4e ≡ O_2, amount of O_2 gas produced

= $1.24 \times 10^{-3} / 4 = 3.11 \times 10^{-4}$ mol
- **Volume of O_2 gas = $3.11 \times 10^{-4} \times 24000$ = <u>7.46 cm^3</u>**

(iii) A student repeated the same experiment above, but using a copper electrode at **A** this time.

Suggest the volume of gas produced at **A** and explain your answer.

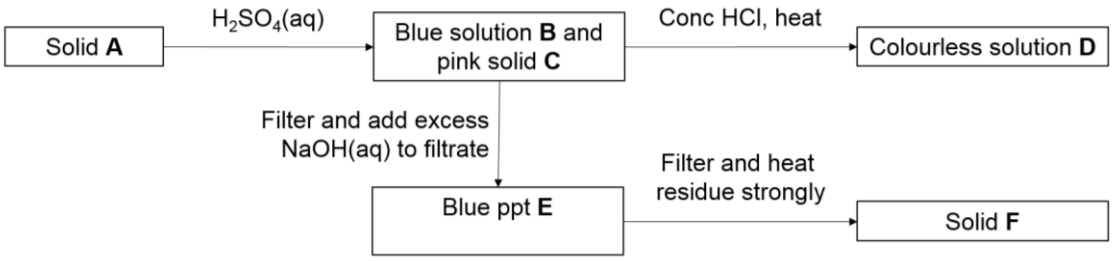
[2]

- **Volume of gas at A = <u>0 cm^3</u>.**

$E^{\ominus}_{Cu^{2+}/Cu} = +0.34$ V

$E^{\ominus}_{O2/H2O} = +1.23$ V
Since the • <u>standard reduction potential of Cu^{2+}/Cu is less positive than O_2/H_2O</u>, the copper electrode would be <u>preferentially oxidised</u> instead of water. Hence, no gas is produced at A.

(b) Solid **A,** which is formed when a copper complex reacts with an aldehyde, is subjected to the following reactions.



Suggest the identities of **A** to **F**. [6]

A: Cu_2O
B: $[Cu(H_2O)_6^{2+}](aq)$
C: Cu
D: $[CuCl_2]^-$
E: $Cu(OH)_2(s)$ OR $Cu(OH_2)(H_2O)_4$
F: CuO

(c) Compounds **V** and **W** are gaseous hydrocarbons of empirical formulae CH_2 and CH_3 respectively. When 10 cm^3 of **V** and 10 cm^3 of **W** were completely burnt in 150 cm^3 of oxygen, the total gaseous volume decreased by 55 cm^3. After shaking the residual gases with aqueous sodium hydroxide, the total gaseous volume decreased by another 60 cm^3. When compound **V** is heated with acidified potassium manganate(VII), compound **X**, C_3H_6O, is formed.

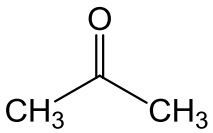
(i) Suggest the molecular formula of **W**. [1]

- **C_2H_6**

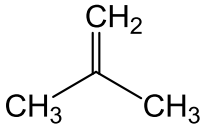
(ii) Suggest the structures of compounds **V** and **X**. Explain your answers. [4]

- **Since the total gaseous volume decreased by 60 cm^3 when shaken with NaOH, the volume of CO_2(g) is 60 cm^3. Compounds V and W contain a total of 6 carbon atoms.**
- **Since W is ethane, CH_3CH_3, V contains 4 carbons and is an alkene that undergoes strong oxidation with $KMnO_4$ to form X (C_3H_6O) and CO_2.**

- **X is**



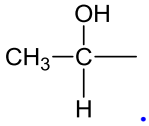
- **V is**

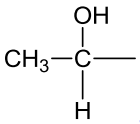


(d) Compounds **Y** and **Z** are isomers of molecular formula $C_4H_7O_2Cl$. When **Y** and **Z** are added to separate portions of water, solutions are formed with pH values of 0.5 and 2.5 respectively. White precipitate is observed when aqueous silver nitrate is added to **Y**, but not **Z**. Both **Y** and **Z** gives yellow precipitate when warmed with aqueous sodium hydroxide and iodine.

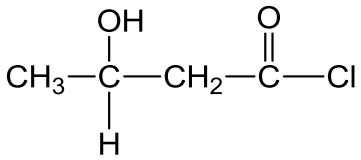
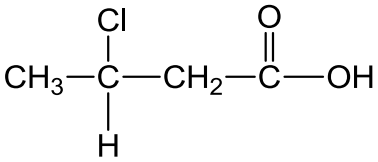
Suggest the structures of compounds **Y** and **Z**. Explain your answers.

[5]

- **Compound Y is an acyl chloride that undergoes hydrolysis in water, giving a solution of lower pH value since HCl is formed.**
- **Compound Z is a carboxylic acid as it gives an acidic solution upon partial dissociation of H^+ ions in water.**
- **Since white precipitate of AgCl is formed when Y is added to aqueous silver nitrate, Y is an acyl chloride.**
- **When warmed with alkaline medium, chloroalkane Z undergoes nucleophilic substitution to form**  **.**



- **Y undergoes oxidation with alkaline aqueous iodine and contains** **.**

- **Y is** 
- **Z is** 

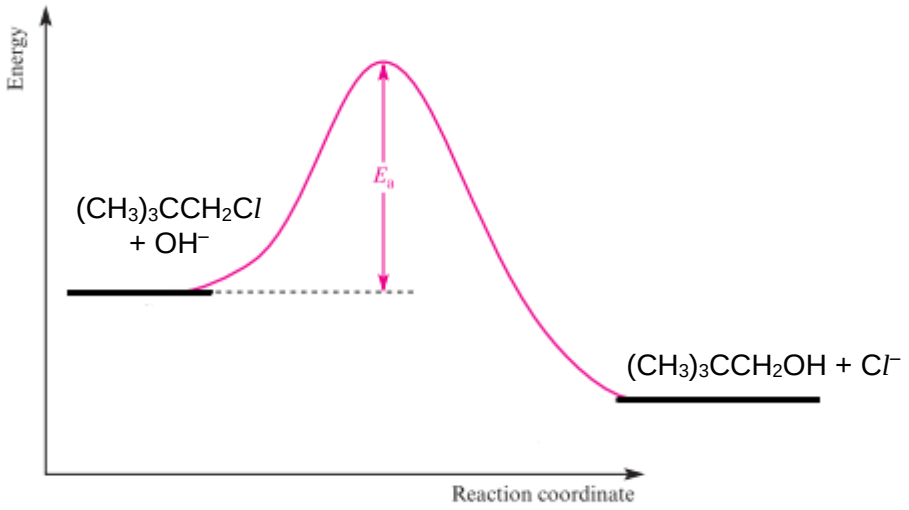
[7 marking points, maximum 5 marks]

[Total: 21]

Section B
Answer **one** question from this section.

4 **(a)** Halogenoalkanes commonly undergo nucleophilic substitution reactions. On the basis of experimental observations developed over a 70-year period, two mechanisms for nucleophilic substitutions have been proposed.

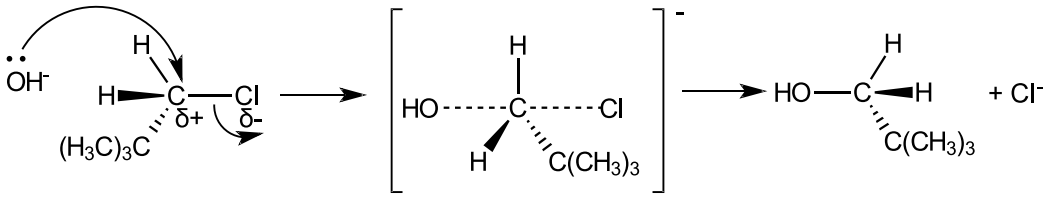
In the kinetics study of the hydrolysis of 1-chloro-2,2-dimethylpropane, $(CH_3)_3CCH_2Cl$, the energy-profile diagram of the reaction was proposed below:



(i) With reference to the energy profile diagram, describe the mechanism of the reaction between 1-chloro-2,2-dimethylpropane and hydroxide ions. The mechanism should include curly arrows to show the movement of electrons and all charges.

[2]

Energy profile diagram indicates S_N2 mechanism



●1m – shows inversion of configuration & correct transition state drawn
●1m – arrows, partial charges

(ii) A student decided to verify the mechanism deduced in **(a)(i)** for the hydrolysis reaction of 1-chloro-2,2-dimethylpropane.

The following results were obtained and you may consider the overall [NaOH(aq)] to remain virtually constant at 0.10 mol dm^{-3} throughout the experiment.

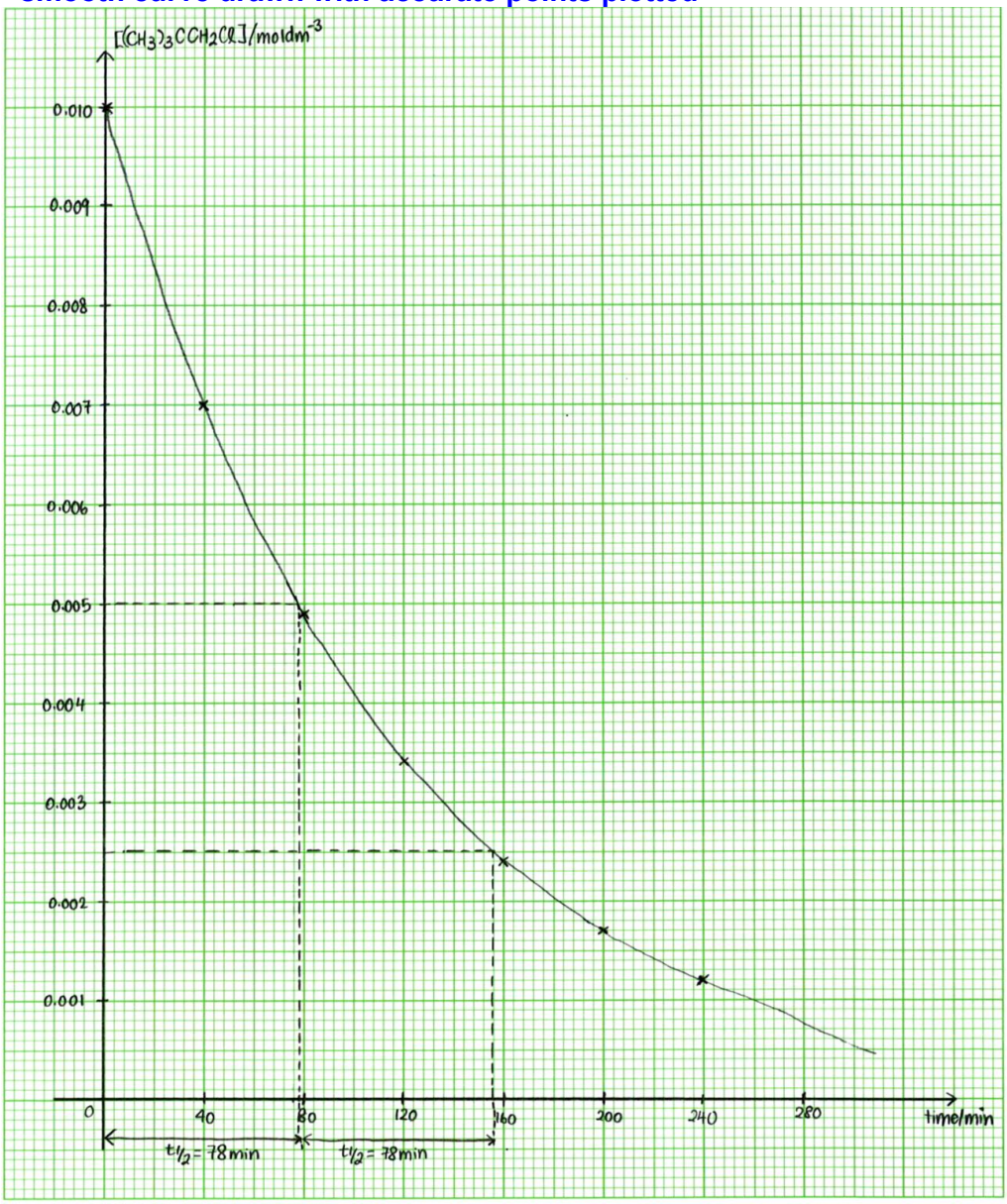
Time/ min	Experiment 1
	$[(CH_3)_3CCH_2Cl]$/ mol dm^{-3}
0	0.0100
40	0.0070
80	0.0049
120	0.0034

160	0.0024
200	0.0017
240	0.0012

Using appropriate axes, plot a graph of $[(CH_3)_3CCH_2Cl]$ against time and use your graphs to deduce the order with respect to the concentration of the 1-chloro-2,2-dimethylpropane, showing your working clearly.

[4]

●appropriate axes
●smooth curve drawn with accurate points plotted



●1st t ½ = 78 min; 2nd t ½ = 78 min (with workings line drawn on graph)
●Since t ½ is a constant, order of reaction is 1st order with respect to $[(CH_3)_3CCH_2Cl]$.

(iii) Given the general rate equation as

$$\text{Rate} = k' [(CH_3)_3CCH_2Cl]^x$$

Using your answer in **(a)(ii),** calculate the rate constant k', stating its units.

[2]

$t_{½} = \frac{ln2}{k'}$ ●k' = $\frac{ln2}{t_{1/2}} = \frac{ln2}{78} = 0.00889\ min^{-1}$ (●correct units)

(iv) When the experiment was repeated at the same temperature, the concentration of NaOH was doubled and the concentration of 1-chloro-2,2-dimethylpropane was monitored against time. The same graph was obtained as Experiment 1.

Deduce the order of reaction with respect to the concentration of hydroxide ion.

[1]

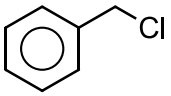
●When [OH^-] doubles, the same graph was plotted means that the initial rate remains the same.
Since initial rate remains the same when concentration doubles, order of reaction is 0^{th} order with respect to [OH^-].

(v) Using your answers in **(a)(ii)** and **(a)(iv)**, explain if the student should agree with the proposed mechanism for the reaction in **(a)(i)**.

[1]

The student ●should not agree with the proposed mechanism as the rate equation is rate = k [$(CH_3)_3CCH_2Cl$], and thus only 1 molecule of $(CH_3)_3CCH_2Cl$ reacts in the rate-determining step.

(b) (Chloromethyl)benzene is a primary alkyl halide.



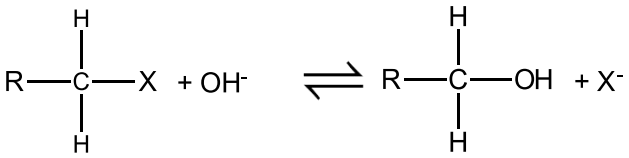
(Chloromethyl)benzene

Suggest a reason why (chloromethyl)benzene undergoes substitution via S_N1 mechanism.

[1]

● (chloromethyl)benzene favours substitution via S_N1 due to resonance stabilisation of the benzyl carbocation.

(c) Different alkyl halides would have different reactivity towards nucleophilic substitution.



where X^- is a leaving group

The difference in reactivity is dependent on the stability of the leaving group. The more stable the halide ion, the better the leaving group. The pK_a values of HX is given below.

Halide (X)	pK_a (HX)
F	+3
Cl	–7
Br	–9
I	–10

(i) Suggest the relationship between pK_a of HX and the stability of the halide ion.

[1]

●The smaller the pK_a of HX, the more stable the halide ion.

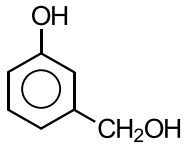
(ii) Iodomethane and chloromethane are separately reacted with hydroxide ions. Using your answer in **(c)(i)**, explain why iodomethane reacts at a faster rate.

[1]

As the pK_a of HI is the smallest, I^- is the most stable halide ion, and thus ●a better leaving group than Cl^-. Thus, iodomethane is more susceptible towards nucleophilic substitution.

(d) Chlorinated phenols have gained an increasing use as fungicides, herbicides, insecticides, and precursors in the synthesis of other pesticides since the early 1930s.

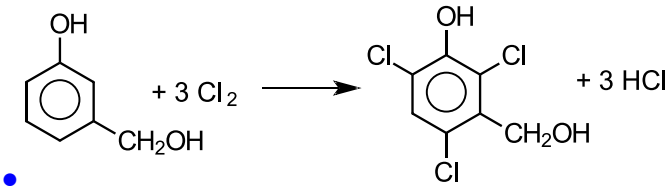
It can be easily synthesised from its precursor **A** using aqueous chlorine.



Precursor **A**

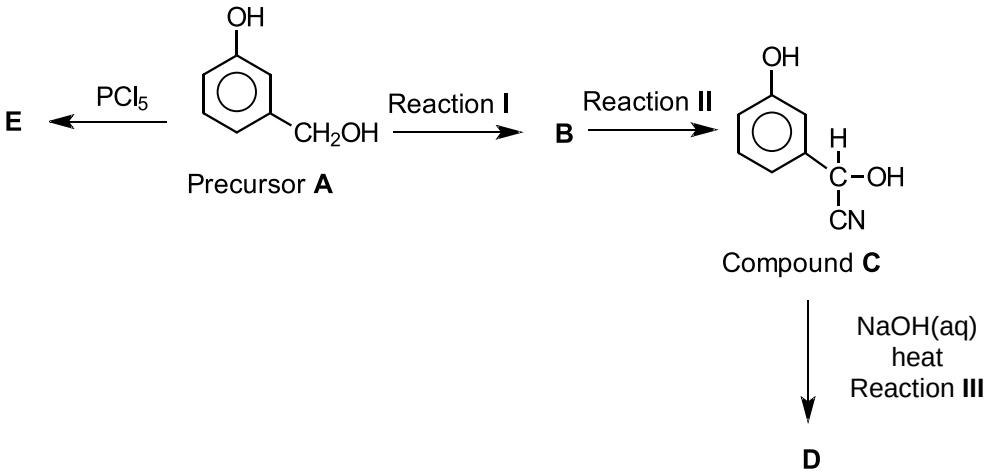
(i) Write a balanced equation for the reaction between precursor **A** and aqueous chlorine.

[1]



●

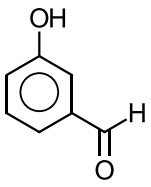
(ii) Precursor **A** undergoes a series of reactions shown in the reaction scheme below.

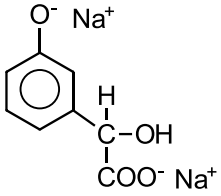


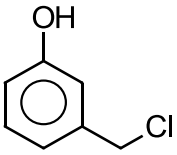
State the reagent and condition for Reaction **I** and **II**, and hence draw the structures of **B**, **D** and **E**.

[5]

•Reaction I: acidified $K_2Cr_2O_7$, warm with immediate distillation
•Reaction II: HCN, in small amount of KCN, 10 – 20 °C

• B: 

• D: 

• E: 

(iii) Reaction **III** can be used as a distinguishing test between compound **C** and precursor **A**. State the observation for this distinguishing test.

[1]

•NH_3 gas will be evolved for compound C. No gas evolved for precursor A.

[Total: 20]

5 **(a)** Describe and explain the relative thermal stabilities of the hydrogen halides down the group.

[2]

• Thermal stability decreases down the group: HF > HC*l* > HBr > HI
• This is because the atomic radius increases down the group, resulting in decreasing degree of effective overlap of orbitals and decreasing covalent bond strength and hence bond energy of HX decreases down the group.

(b) Potassium chlorochromate (VI), $KCrClO_3$, was made using concentrated hydrochloric acid and potassium dichromate(VI).

$$K_2Cr_2O_7 + 2HCl \rightarrow 2KCrClO_3 + H_2O$$

Chlorine gas may be evolved as a side product. It was found that chlorine gas will not be produced if dilute hydrochloric acid was used instead.

Use data from the *Data Booklet* to explain why this is so.

[2]

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^\ominus = +1.33$ V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V
• $E^\ominus_{cell} = +1.33 – (+1.36) = - 0.03$ V
Since $E^\ominus_{cell} < 0$, the reaction is not spontaneous and Cl^- will not be oxidised to form chlorine gas when dilute hydrochloric acid was used.
• When concentrated hydrochloric acid is used, [Cl^-] increases, the position of the above equilibrium shifts to the left by Le Chatelier's Principle and favours oxidation.
$E_{Cl2/Cl-}$ becomes less positive and E_{cell} becomes positive. Hence, the reaction is spontaneous, producing chlorine gas.

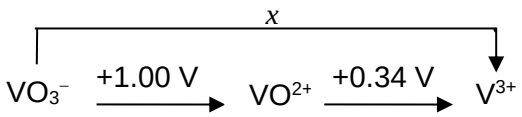
(c) **(i)** Vanadium is a transition element that exhibits variable oxidation states.

Explain why vanadium has the ability to form compounds with different oxidation states.

[1]

• Transition elements can exhibit a variety of oxidation states due to close proximity in energy of the 3d and 4s electrons. Thus both 3d and 4s electrons are available for bond formation (both ionic and covalent).

(ii) A Latimer diagram shown below summarises the standard electrode potential data of vanadium complexes in acidic medium.



x, the standard electrode potential of converting VO_3^- to V^{3+}, is **not** the summation of +1.00 V and +0.34 V. It can be calculated from $\Delta G^{\ominus}$.

Write a half-equation for the conversion of VO_3^- to V^{3+}.

[1]

• $VO_3^- + 6H^+ + 2e^- \rightarrow V^{3+} + 3H_2O$

(iii) Calculate x, given that $\Delta G^{\ominus}$ for the conversion of VO_3^- to V^{3+} is -129000 J mol^{-1}.

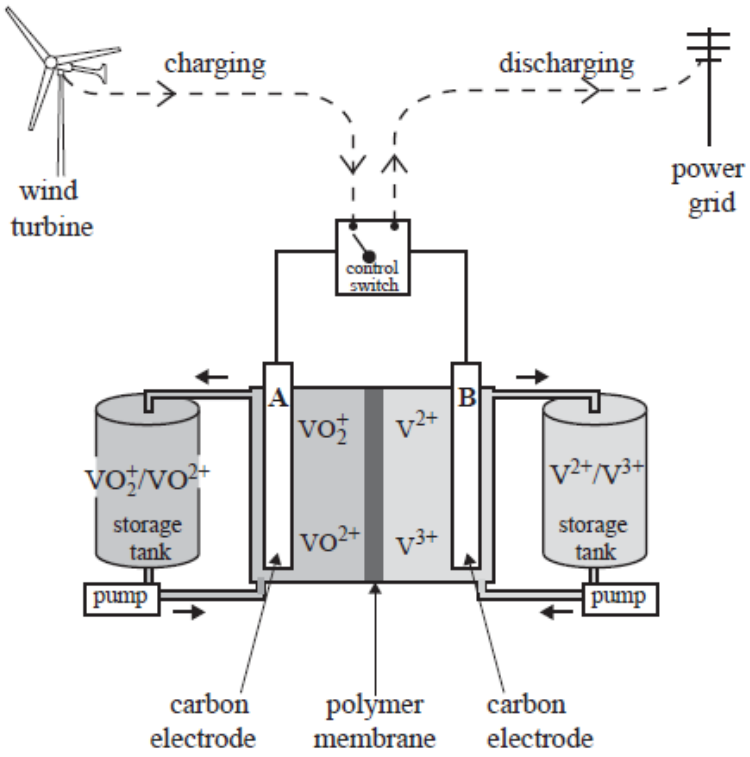
[1]

$\Delta G^{\ominus} = -nFE^{\ominus}$

• $E^{\ominus} = (-129 \times 10^3) / -(2 \times 96500) = +0.67$ V

(d) A vanadium redox battery is used to store electrical energy generated at a wind farm in Tasmania. The battery supplies electricity to the power grid as required through a control switch.

The diagram below shows the structure of a cell in a vanadium redox battery. The reactants are dissolved in an acidic solution, stored in large tanks and pumped through the cell. The cell is recharged using electricity generated by the wind turbines. A polymer membrane allows the movement of particular ions.



(i) State the polarity of electrode **A** when the cell is **discharging.** Explain your answer.

[2]

$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$ $E^\ominus$ = +1.00 V
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$ $E^\ominus$ = – 0.26 V
• When the cell is discharging, it is a galvanic cell. Since $E^\ominus$ VO_2^+/VO^{2+} is more positive than $E^\ominus$ V^{3+}/V^{2+}, VO_2^+ will undergo reduction.
• Therefore, electrode A is the cathode and is positive.

(ii) Write an equation for the reaction that occurs when the cell is being **recharged**.

[1]

• $VO^{2+} + H_2O + V^{3+} \rightarrow VO_2^+ + V^{2+} + 2H^+$

(e) Nitrogen containing compounds such as ammonia and amines are common ligands found in transition metal complexes.

(i) Explain the relative basicities of ammonia, methylamine, dimethylamine and trimethylamine in the gaseous phase.

[2]

● Basicity increases in the order of ammonia, methylamine, dimethylamine and trimethylamine.
●The greater the number of electron donating methyl group, the more available the lone pair on N for dative bonding with a proton.

(ii) Amides, such as ethanamide, are nitrogen containing compounds that do not exhibit basic properties like amines.

Explain why amides are neutral.

[1]

• Amides are neutral because the lone pair of electrons on nitrogen atom in amides is in a *p* orbital, and can overlap with the π orbital of the adjacent carbonyl group. Hence, not available for donation to a proton.

(f) In 1893, Alfred Werner proposed the octahedral configuration of transition metal complexes. He was able to interpret isomeric properties using extensive studies on the octahedral cobalt complexes.

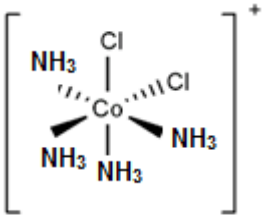
The following table gave information of two cobalt complexes **A** and **B** which are isomers of each other.

	Complex	Colour of solid	Does the complex have a dipole moment
A	$CoCl_2(NH_3)_4^+$	Violet	Yes
B	$CoCl_2(NH_3)_4^+$	Green	No

(i) Suggest structures for the cobalt complexes **A** and **B**.

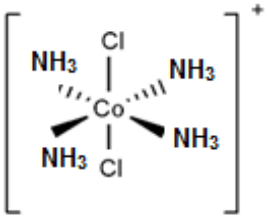
[2]

A



cis isomer

B



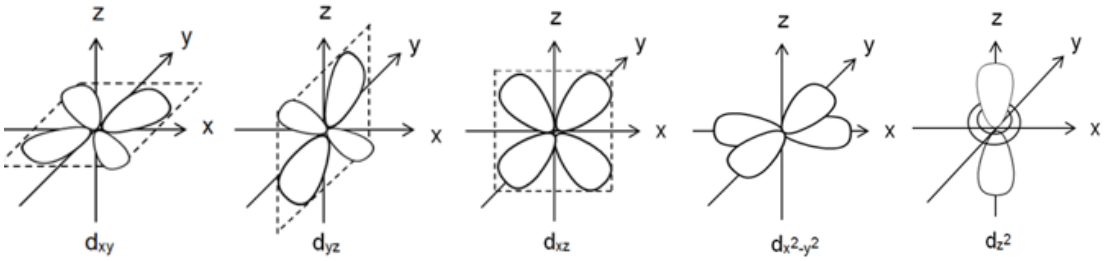
trans isomer hence no net dipole

(ii) The crystal field theory can be used to explain colour of transition metal complexes.

Describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes.

[3]

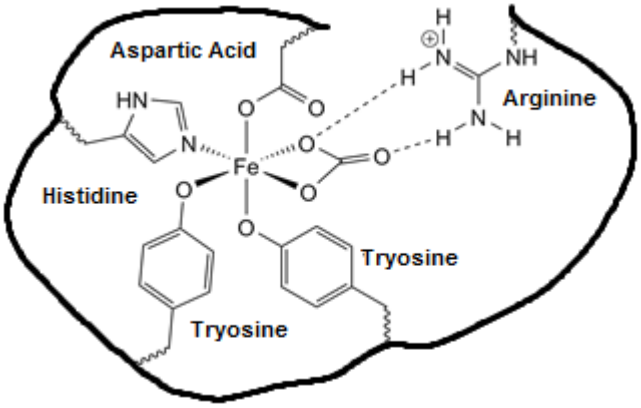
•



• d_{z^2} and $d_{x^2-y^2}$ orbitals experience stronger electronic repulsion with the negative charges as the orbital lobes are in the region of the negative charges. Due to these stronger electronic repulsion, the d_{z^2} and $d_{x^2-y^2}$ orbitals are at a higher energy level and the degenerate d orbitals split into 2 different energy levels.

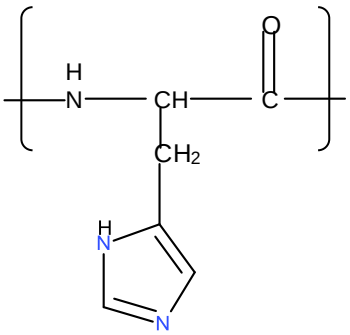
• the d_{xy}, d_{yz} and d_{xz} orbitals have lobes that project between the charges hence are at a lower energy level.

(g) R-groups on amino acids residues on protein act as ligands in biological systems. *Transferrin* is a protein in the blood that transports iron from food to the rest of the body.

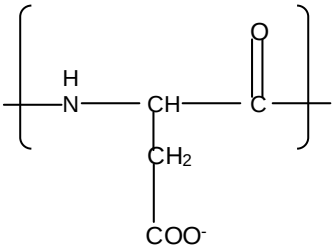


binding sites of *Transferrin*

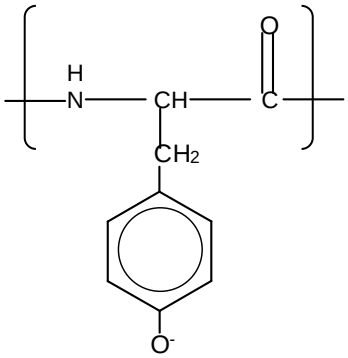
Transferrin binds to iron(III) via tryosine, histidine and aspartic acid residues as shown below.



Histidine residue
Side chain pK_a = 6.00



Aspartic acid residue
Side chain pK_a = 3.65

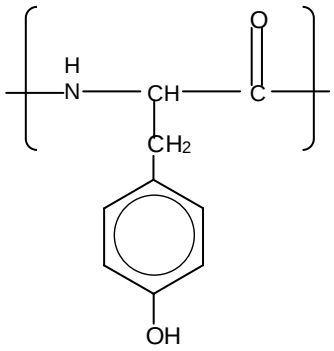


Tyrosine residue
Side chain pK_a = 10.07

The key to controlling uptake and release iron(III) is the change in pH. At pH 7.4, free transferrin binds to iron(III) to form the iron-transferrin complex. When the pH is lowered from 7.4 to 5.5, free iron(III) ions will be released from the protein binding site.

(i) Draw the structural formula of the tyrosine residue at its most stable state at pH 5.5.

[1]



● tyrosine residue pronotated

(ii) Suggest how the decrease in pH releases iron(III) from the protein complex.

[1]

● When pH decreases, tryrosine and histidine are protonated, it reduces the protein affinity to/ can no longer form dative bonds with Fe(III) thus releasing the free Fe(III).

[Total: 20]