



CHEMISTRY
Paper 3 Free Response

9647/03
13th September 2016
2 hours

Candidates answer on separate paper.

Additional materials: Answer paper
 Graph Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Civics Group, Centre number and Index number in the spaces provided on the cover page and on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a HB pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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

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 15 printed pages.

Answer any **four** questions

- 1** Ethanedioic acid is a substance found in many plant foods. Cabbage is among the plant foods with high ethanedioic acid content. However, its anion, $\text{C}_2\text{O}_4^{2-}$ can bind to iron to form iron(II) ethanedioate, which renders much of the iron in cabbage unusable by the body.

(a) 50.0 cm³ sample of iron(II) ethanedioate, FeC_2O_4 was extracted from 300 g of cabbage, diluted in water and the solution made up to 250 cm³. A 25.0 cm³ portion of this solution was acidified and required 26.90 cm³ of 0.0100 mol dm⁻³ potassium manganate(VII) for oxidation of iron(II) to iron(III) and ethanedioate ions to carbon dioxide.

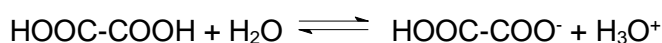
(i) State the change in oxidation number for manganese and carbon in the reaction. [1]

(ii) Write down all the relevant ion-electron half equations and hence the overall redox equation for the reaction between potassium manganate(VII) and iron(II) ethanedioate. [2]

(iii) Calculate the concentration, in mol dm⁻³, of iron(II) ethanedioate in the original sample. [2]

(iv) Calculate the number of moles of iron in each gram of cabbage. [1]

(b) Ethanedioic acid dissociates in water according to the following equation.



The table below compares the K_a values of three organic acids.

	Formula	K_a
Ethanoic acid	CH_3COOH	1.74×10^{-5}
Ethanedioic acid	$\text{HO}_2\text{CCO}_2\text{H}$	6.46×10^{-2}
Oxoethanoic acid	$(\text{CHO})\text{COOH}$	4.79×10^{-4}

With reference to the K_a values, comment on the order of acidity of the three organic acids. [2]

- (c) Compound **A**, with molecular formula C_5H_8O , decolourises aqueous bromine and reacts with PCl_5 giving off white fumes. Upon refluxing **A** with acidified potassium manganate(VII), a symmetrical product **B**, $C_5H_6O_5$, is formed. **B** does not give a red precipitate with Fehling's solution but an orange precipitate is observed with 2,4-dinitrophenylhydrazine. 1 mole of **B** also reacts with 1 mole of Na_2CO_3 with effervescence observed. **B** reacts with $NaBH_4$ to form **C**. Deduce the structures of compounds **A**, **B** and **C**, explaining the chemistry of the reactions involved. [8]
- (d) (i) Describe what you see when separate samples of sodium and sulfur are burned in excess air. Write equations for the reactions that occur. [2]
- (ii) The products resulting from the reactions in (d)(i) both react with water. Write equations for these two reactions and describe the effect of the resulting solutions on Universal Indicator solution. [2]

[Total: 20]

2 Thallium is a Group III element discovered in 1861, and its toxicity was quickly noted. Thallium isotopes and compounds have useful applications, sometimes despite their toxic nature.

(a) Thallium forms compounds similar to aluminium, and thallium(III) chloride and thallium(III) fluoride have very different structures and bonding.

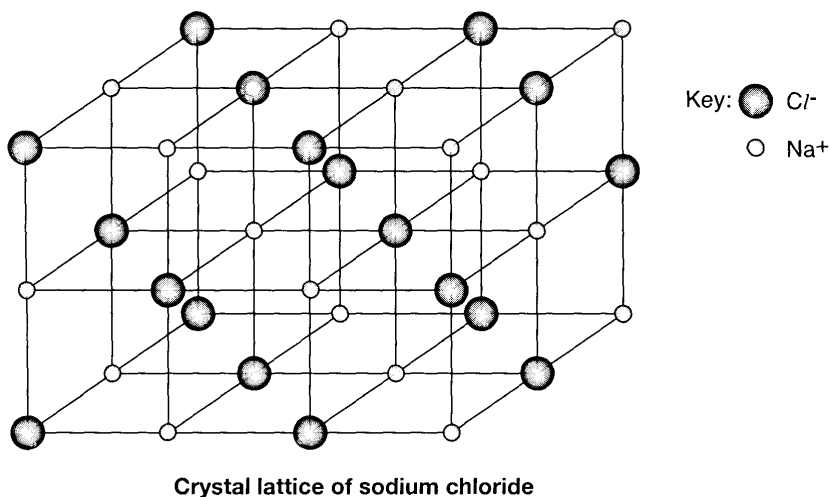
(i) Draw and state the shape of thallium(III) chloride, $TlCl_3$. [1]

(ii) In gaseous phase, thallium(III) chloride is able to form a compound with a M_r of 621. Draw a dot-and-cross diagram of this compound, and state the $Cl-Tl-Cl$ bond angle. [2]

(iii) Explain, in terms of structure and bonding, why thallium(III) fluoride has a high melting point of $550^\circ C$. [2]

(iv) Thallium is also able to form thallium(I) chloride, which is crystalline in nature.

In the crystal lattice of sodium and potassium chlorides, the co-ordination number of each ion is 6. In the crystal lattice of thallium(I) chloride, $TlCl$, the co-ordination number has a different value.



Suggest an explanation for the co-ordination number in the $TlCl$ lattice being different from those in $NaCl$ and KCl . [1]

- (b) Thallium(III) chloride, $TlCl_3$, reacts with hot water to produce thallium(III) oxide precipitate and hydrochloric acid.

(i) Write a balanced equation for the above reaction. [1]

- (ii) In an experiment, a 15 g impure sample of thallium(III) chloride ($M_r = 310.5$) was mixed with hot water, and filtered. Water was then added to the filtrate to make a standard solution in a 250 cm^3 volumetric flask. A 25.0 cm^3 aliquot was titrated against 0.5 mol dm^{-3} aqueous sodium hydroxide, requiring a titre of 22.00 cm^3 . Determine the percentage purity of the sample.

You may assume that the impurities are insoluble in water and are inert. [2]

- (c) Thallium(I) sulfate ($M_r = 504.1$) was often employed as a rodenticide and is highly poisonous. The lethal dosage is 16 ppm of the rat's mass. Assuming a typical rat has a mass of 230 g, determine the number of moles of thallium(I) sulfate needed to kill a rat.

[2]

- (d) Thallium(III) ethanoate, $Tl(CH_3CO_2)_3$, is able to react with an alkene through addition. When cyclohexene reacts with thallium(III) ethanoate, a compound with the molecular formula $C_{10}H_{16}O_4$ is formed. Suggest the structural formula of this compound, and state the number of stereoisomers that this compound has.

[2]

- (e) ^{201}Tl is an isotope of thallium that is often used in medical diagnostics due to its radioactive decay by electron capture with emission of gamma rays. The electronic configuration of the Tl atom is $[Xe]4f^{14}5d^{10}6s^26p^1$.

Electron capture is a process in which a proton-rich nucleus of an atom absorbs one electron from the first or second quantum shell to change one proton into a neutron.

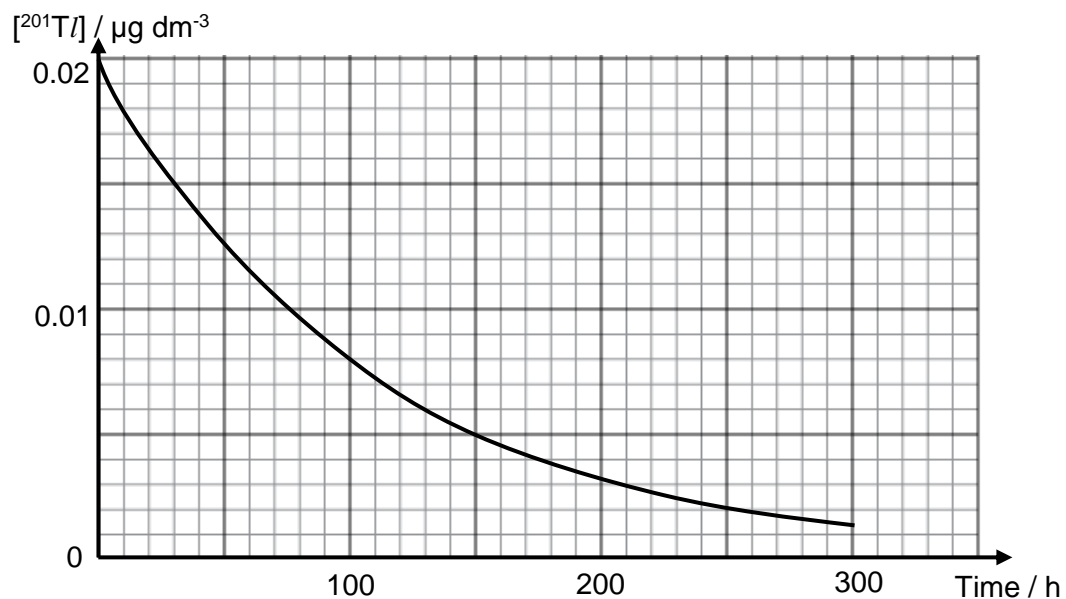
- (i) Suggest the species formed, including the nucleon number, when ^{201}Tl undergoes electron capture. [1]

- (ii) The species formed immediately after electron capture is known to be in excited state, before returning to ground state by emitting gamma rays.

Name the orbital where the excited electron is most likely located in, and explain why **high energy** gamma rays are emitted when the species return to ground state.

[2]

- (iii) A patient is typically injected with $0.02 \mu\text{g}$ of thallium for heart diagnosis. The following graph shows the radioactive decay (through electron capture) of a $0.02 \mu\text{g}$ sample of ^{201}Tl dissolved in 1 dm^3 of inert solvent.



Using the graph, deduce the order of reaction for the radioactive decay of ^{201}Tl . [2]

- (iv) Hence, write the rate equation for this reaction and determine the rate constant, stating its units. [2]

[Total: 20 m]

3 The halogens and organic halides are useful laboratory reagents and have many applications.

- (a)** State and explain the difference in the reactions of chlorine and iodine with sodium thiosulfate respectively. Write balanced equations for the reactions. [3]
- (b)** Deduce which gas, fluorine or chlorine, would behave more ideally at low pressure. Explain your answer. [1]

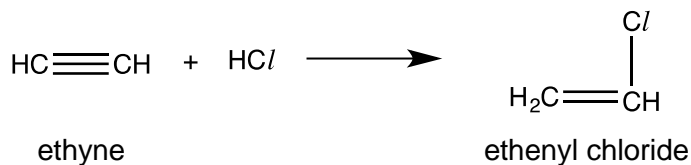
Organic halides are a group of compounds comprising alkyl halides, ethenyl halides and aryl halides.

Alkyl halides are used as solvents for relatively non-polar compounds. They are also used as the starting materials for the synthesis of many compounds.

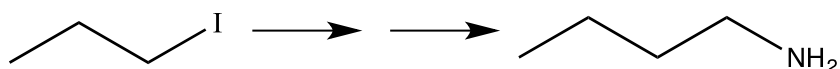
- (c)** Alcohols react with hydrogen halides to produce alkyl halides.
- (i)** Suggest the type of reaction that occur. [1]
- (ii)** 2-iodopropane is formed from propan-2-ol in the presence of sodium iodide and concentrated phosphoric acid.
- Explain, with the aid of an equation, why concentrated sulfuric acid is not used. [2]
- (d)** 2-chloro-2-methylpropane undergoes alkaline hydrolysis to form 2-methylpropan-2-ol.
- (i)** Name and describe the mechanism of the hydrolysis of 2-chloro-2-methylpropane. [3]
- (ii)** With the aid of the *Data Booklet*, explain what will happen to the rate of reaction if 2-bromo-2-methylpropane was used instead. [2]

- (e) Ethenyl chloride is an important industrial chemical mainly used to produce the polymer, PVC.

Ethyne reacts with anhydrous hydrogen chloride gas over a mercuric chloride catalyst to give ethenyl chloride.



- (i) With the aid of the *Data Booklet*, determine the enthalpy change of the reaction. [2]
- (ii) Explain why ethenyl chloride does not undergo alkaline hydrolysis readily. [1]
- (f) 1-iodopropane can be converted to butylamine via a two-stage synthesis. Butylamine is then used as an ingredient in the manufacture of pesticide.



- (i) Suggest reagents and conditions for the two stages. Draw the structure of the intermediate compound. [3]
- (ii) Suggest a chemical test to distinguish between 1-iodopropane and 1-chloropropane. [2]

[Total: 20]

- 4 Co-Cr alloys are most commonly used to make artificial joints including knee and hip joints due to high wear-resistance and biocompatibility. However in 2010, faulty Co-Cr alloy hip joints manufactured by DePuy was removed from market due to leakage of toxic chromium and cobalt into the body muscles and blood stream.

(a) State the electronic configurations of

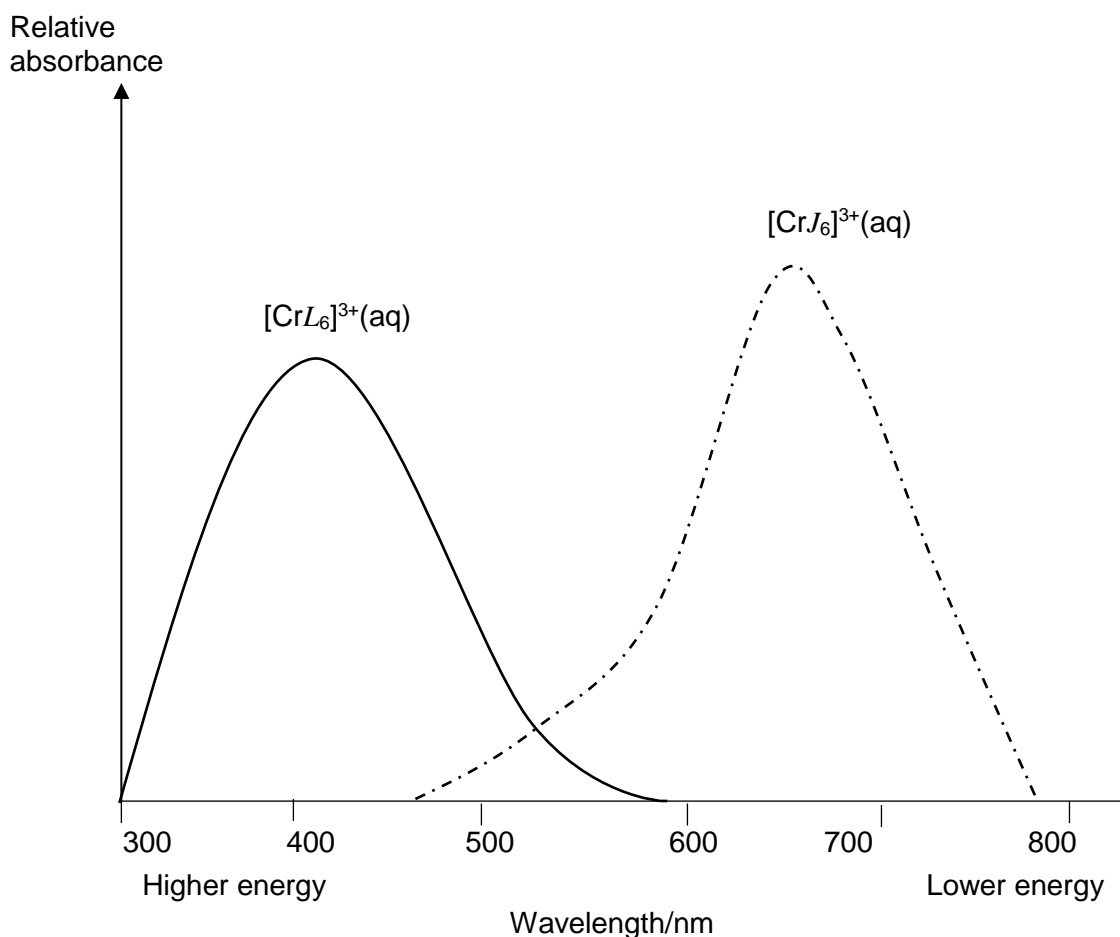
(i) an atom of chromium, [1]

(ii) the Co^{3+} ion. [1]

(b) Why are transition metal complexes coloured? [3]

(c) The colour of the complexes can be measured by a spectrometer. The amount of light absorbed is expressed as an absorbance value. The higher the absorbance, the more of a particular wavelength of light is being absorbed.

The spectrum below shows the major absorption peaks for $[\text{CrL}_6]^{3+}(\text{aq})$ and $[\text{CrJ}_6]^{3+}(\text{aq})$.



colour	Wavelength/nm
Violet	400-430
Blue	430-490
Green	490-570
Yellow	570-590
Orange	590-620
red	620-750

- (i) What are the colours of $[\text{CrL}_6]^{3+}(\text{aq})$ and $[\text{CrJ}_6]^{3+}(\text{aq})$? [2]
- (ii) What deduction can be made from the spectra about the size of the d-orbital splitting in the two complexes? [2]

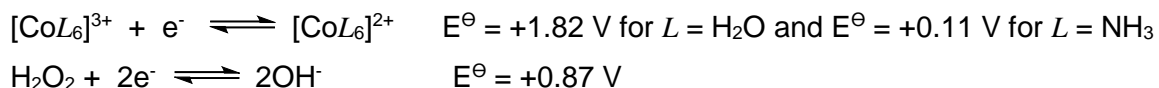
Cobalt forms many complexes with ligands such as H_2O , NH_3 and $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CO}_2^-$. The most common oxidation states of cobalt are +2 and +3.

Cations containing cobalt in these two oxidation states have significantly different colours even when the ligands are the same.

- (d) When H_2O_2 is mixed with pink $\text{Co}^{2+}(\text{aq})$ solution, no significant colour change is observed. When $\text{Co}^{2+}(\text{aq})$ is mixed with excess $\text{NH}_3(\text{aq})$ a slight colour change occurs and cation **Q** is formed.

When cation **Q** is mixed with H_2O_2 , a reddish brown solution is observed.

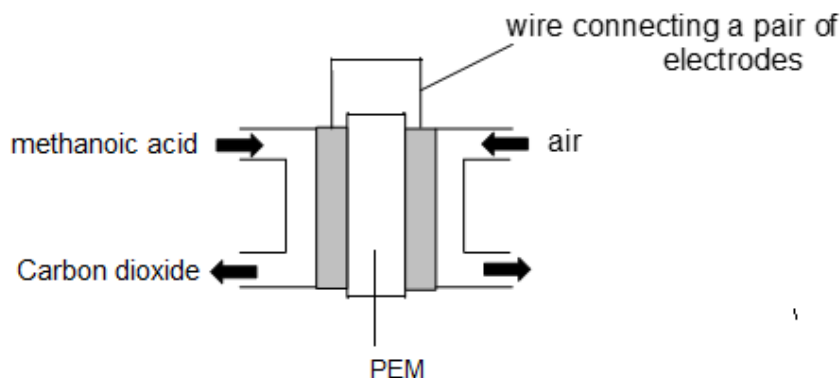
E^\ominus data for the cobalt complex ions and hydrogen peroxide are given below.



Suggest an explanation for the above observations, giving equations where appropriate and identify the cation **Q**. [5]

- (e) Explain why the neutral complex formed between a Co^{2+} ion and two $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CO}_2^-$ ions is soluble in cyclohexane. [1]

The direct oxidation of methanoic acid in a fuel cell, DFAFC, shown below represents potentially the most efficient method of obtaining useful energy from a renewable fuel.



- (f) The electrons pass around the external circuit to the cathode. The protons produced migrate across the proton exchange membrane, PEM, to the cathode, where they react with oxygen from air, producing water.

Write the equations for the anode and cathode reactions. Hence construct the equation for the overall reaction. [2]

- (g) One method for the construction of DFAFC, involves electroplating a layer of platinum onto the surface of the proton exchange membrane, PEM. The electrolyte for this process is a solution containing $\text{Pt}(\text{NH}_3)_4^{2+}$ and Cl^- ions. The PEM is the cathode in this electrolytic cell.

- (i) Suggest the half-equation for the cathode reaction that deposits platinum on the PEM. [1]

- (ii) In one such preparation, a PEM with a surface area of 25 cm^2 was immersed in an electrolyte bath and a current of 0.0875 A was passed for 95 minutes.

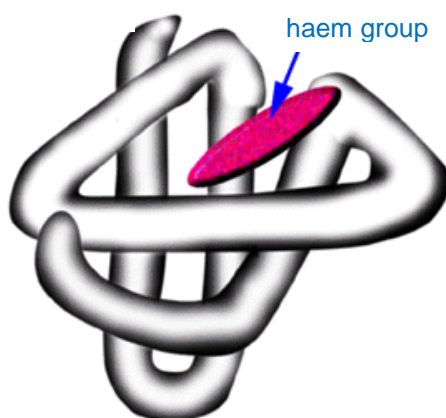
Calculate the mass of platinum deposited onto the surface of PEM. [2]

[Total: 20]

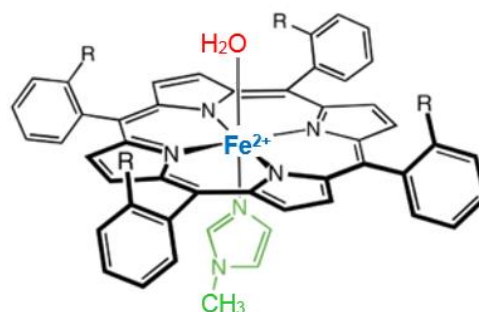
- 5 (a) Myoglobin and haemoglobin are globular proteins that serve to bind and deliver oxygen. The former serves as an intracellular storage site for oxygen in the muscle tissues, while the latter transports oxygen in the bloodstream.

Each myoglobin molecule contains one haem group.

In deoxygenated myoglobin, a water ligand is weakly bound to the Fe^{2+} of the haem group as shown:



Myoglobin



Haem group in deoxygenated myoglobin

- (i) Briefly describe how myoglobin maintains its three-dimensional shape. [2]

- (ii) In the presence of the haem group, the polypeptide chain coalesces into a myoglobin molecule.

With the aid of the equation,

$$\Delta G = \Delta H - T\Delta S$$

and by considering the chemical interactions involved, explain why this is a spontaneous process at low temperatures. [2]

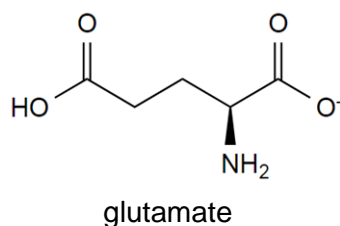
- (iii) Deoxygenated myoglobin is responsible for the dull purplish red muscle colour, observed in the depth of the muscle. When meat is freshly cut, colour change occurs in two stages:

Stage 1: Bright red colour when muscle surface is exposed to air.

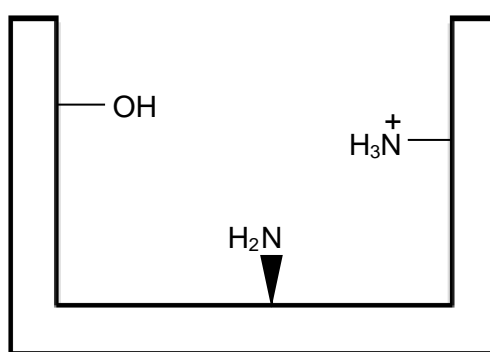
Stage 2: With time, the bright red colour slowly changes to an unattractive, dull brown colour associated with stale and spoiled meat.

With reference to the structure of the haem group and the reaction that occurs in each stage, explain the colour changes involved. [2]

- (b) One of the isolated compounds that is primarily responsible for the umami (savory) flavor is glutamate, which is a salt formed from glutamic acid that is commonly found in meat.



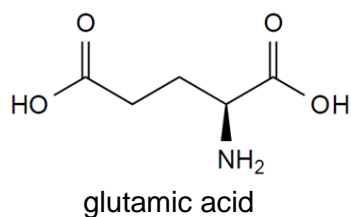
It is thought that glutamate stimulates a specific receptor site located in the taste buds on the tongue, which is essentially a protein molecule. A simplified diagram of the receptor site is shown below:



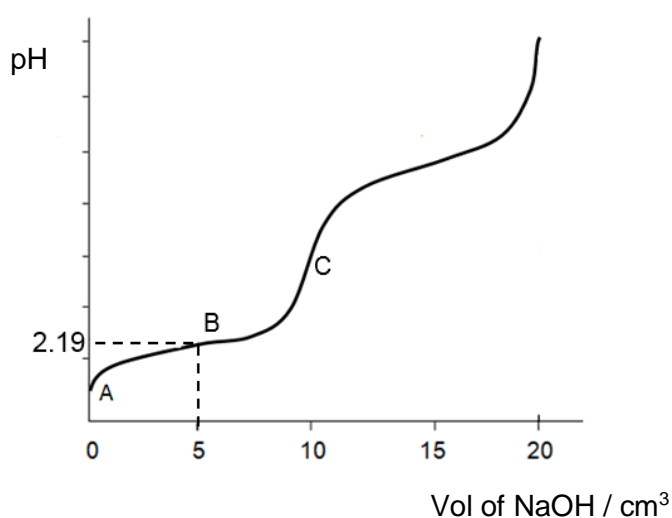
- (i) State **two** different types of interactions that can be formed between glutamate and the receptor protein. Illustrate your answer with labelled diagram(s). [2]
- (ii) To enhance the flavor of food, many retailers in the food industry use monosodium glutamate (MSG) as a food additive, which can be easily synthesized in the laboratory.

Given that laboratory synthesis gives a racemic mixture, explain why 50% of the glutamate synthesized in the laboratory is unable to bind precisely with the correct orientation to the receptor protein. [1]

The structure of glutamic acid is shown below:



10 cm³ of the fully protonated glutamic acid is titrated with 20 cm³ of 1.00 mol dm⁻³ sodium hydroxide solution. Its titration curve is shown below:



(iii) Show that the concentration of glutamic acid is 1.0 mol dm⁻³ at **A**. [1]

(iv) Hence, calculate the pH of the solution at **A**. [1]

(v) Identify the specie(s) present at **B**.

With the help of an equation, explain how the solution at **B** can resist a change in pH when a small amount of base is added. [2]

(vi) In a separate experiment, the solution at **B** was reacted with 10.0 cm³ of 0.05 mol dm⁻³ sodium hydroxide.

Calculate the pH of the mixture after the reaction.

You may find it useful to represent the fully protonated glutamic acid as HA. [2]

(c) Compound **P**, $\text{C}_9\text{H}_{11}\text{NO}_2$, rotates the plane of polarised light and reacts with the following reagents:

- aqueous bromine to give compound **Q**, $\text{C}_9\text{H}_9\text{NO}_2\text{Br}_2$
- sodium carbonate to give a salt
- PCl_5 to give a 5-membered cyclic compound **R**

Deduce the structural formulae of compounds **P**, **Q** and **R**.

[5]

[Total: 20]