Name ________________________ **Class:** ___________ **Reg Number:** _____

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

Chemistry 9647

Paper 3 Free Response **17 Sep 2013**

2 hours

Additional Materials: *Data Booklet*
Writing Paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer 4 out of 5 questions in this paper.

Begin each question on a fresh page of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1 & 2** and **Cover Page for Questions 3, 4 & 5** respectively.

Hand in Questions 1 & 2 and 3, 4 & 5 separately.

You are advised to spend about 30 min per question only.

INFORMATION FOR CANDIDATES

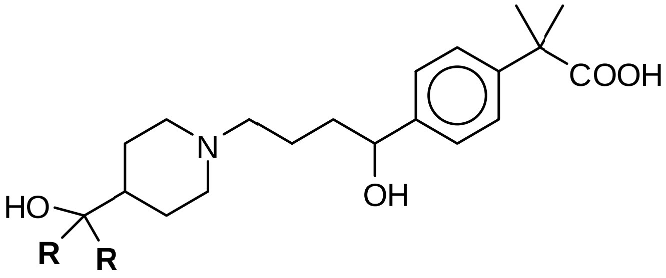
The number of marks is given in brackets [ ] at the end of each question or part question.

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

This document consists of **18** printed pages and **4** blank pages

Answer any 4 out of 5 questions in this paper.
Begin each question on a ***fresh sheet*** *of writing paper.*

1 Antihistamines are consumed to reduce the effects of allergic reactions in the body. The drug *fexofenadine* is used to treat sneezing, runny nose and itchy eyes experienced by hay fever sufferers, without causing drowsiness.



Fexofenadine

***R** is common organic hydrocarbon group*

(a) A sample of 1 g of *fexofenadine* was completely burnt in excess oxygen and 57.6 cm^3 of NO_2 gas was produced. All volumes were measured at 80 ^oC and 1 atm.

(i) Calculate the M_r of fexofenadine, to the nearest whole number, using the above information.

(ii) The actual M_r of *fexofenadine* is 501. Explain why there is a discrepancy between the calculated M_r in **(a)(i)** and the actual M_r.

(iii) Hence, suggest the structural formula of the common organic group **R** in *fexofenadine*, $\mathbf{R}_2C_{20}H_{29}O_4N$.

[5]

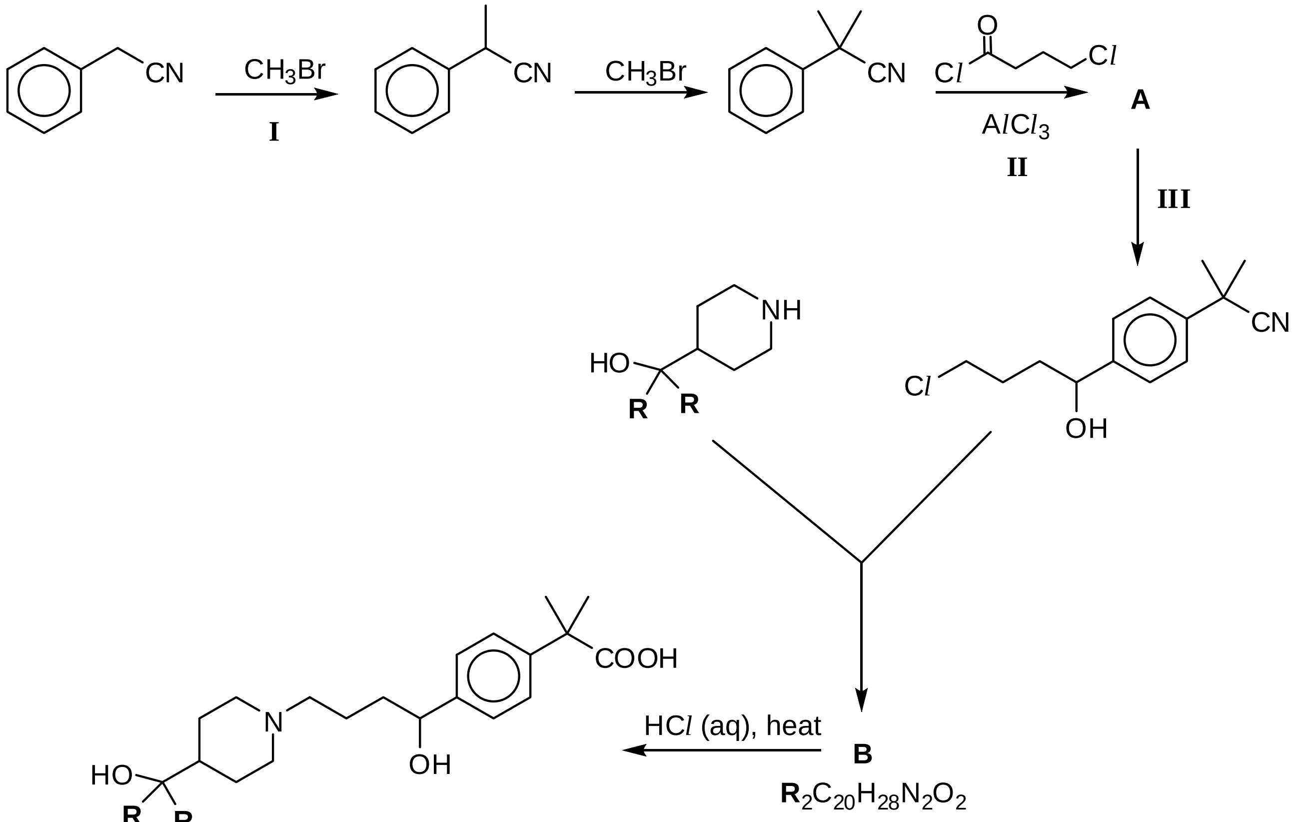
(b) *Fexofenadine* is sold as the hydrochloride salt in tablet form. Each tablet contains 120 mg of the hydrochloride salt. The maximum dosage is 490 mg per intake and twice daily for an average 65 kg adult.

(i) Suggest why *fexofenadine* is sold as the hydrochloride salt rather than in the *fexofenadine* form.

(ii) Calculate the number of boxes of tablets (refer to the photograph on page 2) a traveller needs to carry for a 5 day journey if he is going to consume it up to the safety limit so as to maximise his runny nose recovery.

[3]

In pharmaceutical companies, *fexofenadine* can be synthesised in the following way.



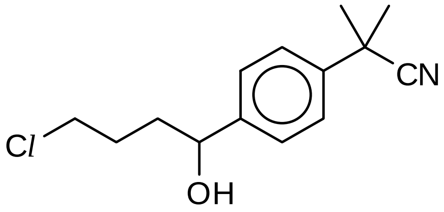
Fexofenadine

(c) **(i)** Draw the structural formula of compounds **A** and **B**.

(ii) State the type of reaction for **II**.

(iii) Suggest the reagent and condition for **III**.

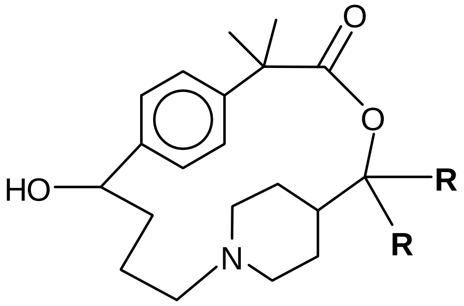
(iv) Draw the structure of the product formed when a sample of the intermediate given below was heated with aqueous $K_2Cr_2O_7$ in D_2SO_4. (D, deuterium = ^2H)

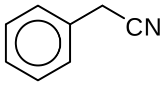
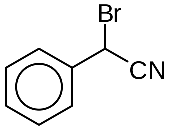


(v) *Fexofenadine* can be converted into a cyclic compound shown below.

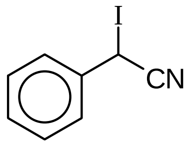
Suggest the reagent and condition for this conversion.

[6]



(d) In a separate experiment, the precursor for the synthesis of *fexofenadine,*  was found to react with one mole of bromine to form 

(i) Outline a mechanism to show how the above product could have been formed.

(ii) Suggest why it is not possible to synthesise the iodo derivative,  from the same precursor when some I_2 is present.

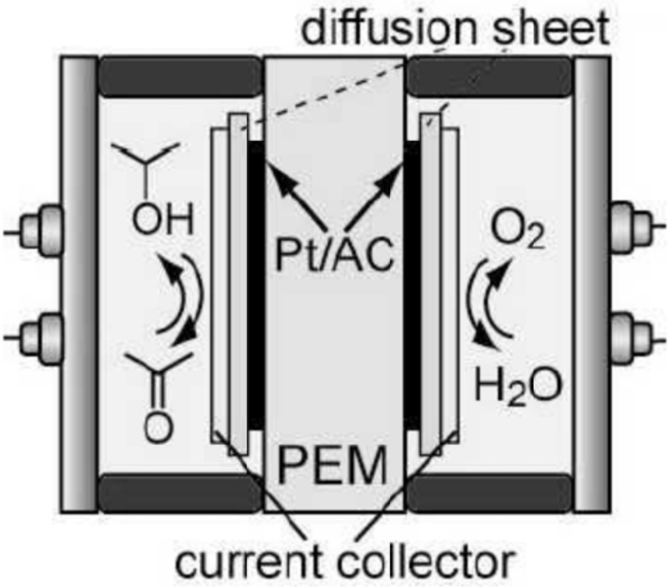
[4]

(e) Compound **B**, with the molecular formula $\mathbf{R}_2C_{20}H_{28}N_2O_2$, contains **two different** nitrogen-containing functional groups. Name and explain which functional group has a higher K_b value.

[2]

[Total: 20]

2 In a direct propan-2-ol fuel cell (D2PFC), the electro-oxidation of propan-2-ol takes place catalytically at temperatures around 80 ^{o}C. The process produces propanone and hydrogen ions. H^+ ions travel through the polymer electrolyte membrane (PEM) to the electrode to react with oxygen to produce water while the electrons travel through the external electrical circuit to the cathode to produce electrical power.



(a) **(i)** Deduce the ion-electron half equation for the anode and hence write the overall cell reaction during discharging.

(ii) A typical D2PFC battery generates about 1.26 volts. Using the *Data Booklet*, calculate the $E^{\theta}{}_{\text{value}}$ involving the propan-2-ol/propanone half-cell.

(iii) Explain qualitatively the change in the overall E^{θ}_{cell} value measured when a small amount of base is added to the propan-2-ol/propanone half-cell.

(iv) Suggest one disadvantage of using this fuel cell.

[6]

(b) One method for the construction of the fuel cell involves electroplating a layer of platinum onto the surface of the PEM. The electrolyte used for this process consists of a solution of $[Pt(NH_3)_4]^{2+}$ and the PEM is the cathode in the electrolyte cell.

(i) Suggest the half-equation including state symbols for the cathode reaction. State an observation.

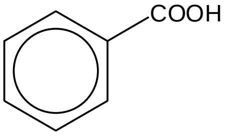
(ii) Calculate the mass of platinum deposited onto a PEM with surface area of 25 cm^2 if a current of 3.5×10^{-3} A cm^{-2} was passed through the circuit for 75 minutes.

[4]

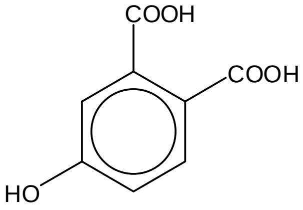
(c) Aromatic compounds **P** and **Q** are alternative fuels used in similar fuel cells that utilise PEM.

(i) The aromatic organic compounds **P** and **Q** are isomers of each other with the molecular formula $C_9H_8O_2$.

P produces effervescence with $NaHCO_3$ but **Q** does not. **P** and **Q** decolourise aqueous chlorine readily to form **R** ($C_9H_9O_3Cl$) and **S** ($C_9H_7O_3Cl_3$) respectively. **Q** reacts with Tollen's reagent but not with Fehling's solution. **P** and **Q** reacts with hot acidified potassium manganate (VII) to form **T** and **U** respectively.



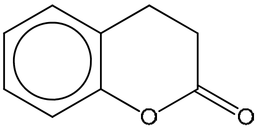
T



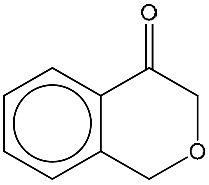
U

Suggest the structures of **P**, **Q**, **R** and **S**, explaining the reactions involved.

(ii) Aromatic compounds **V** and **W** are isomeric to compounds **P** and **Q**.



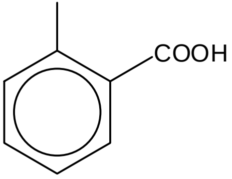
V



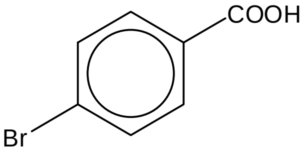
W

Compounds **V** and **W** can be distinguished via the addition of a single reagent. Write a balanced equation to illustrate the positive test.

(iii) Under appropriate conditions, compound **T** is converted into two isomers **X** and **Y**.



X



Y

Predict and explain which compound **X** or **Y** has a higher acid strength.

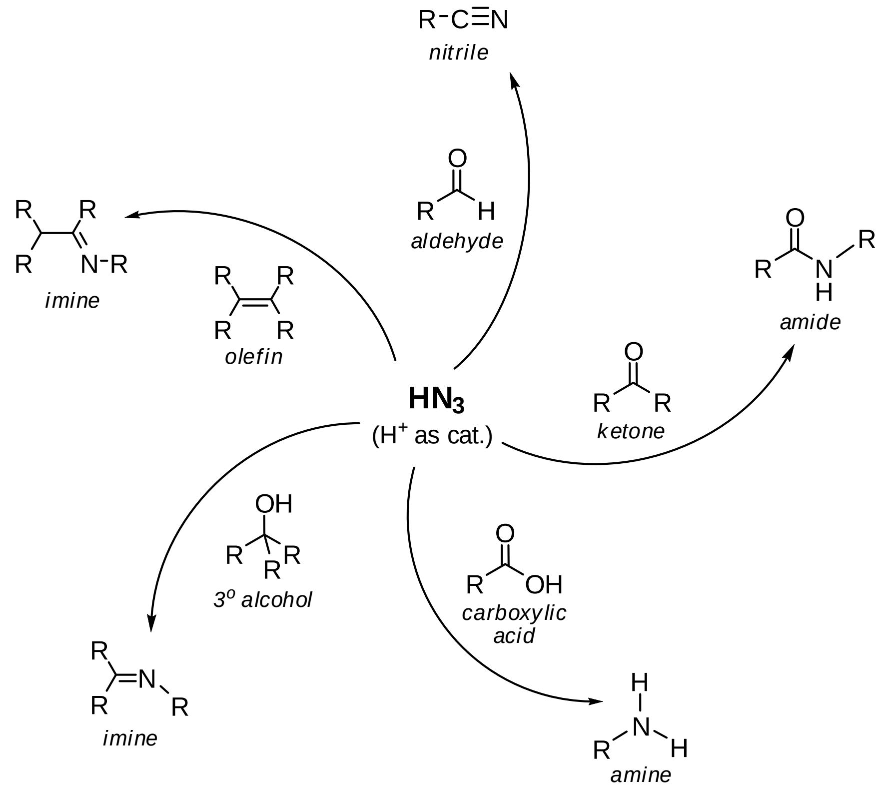
[10]

[Total: 20]

[Turn over

3 Azides are energy-rich molecules with many applications. Sodium azide, for example, is used as a preservative, mutagen, biocide, and assay reagent. Organic azides and hydrogen azides are important starting materials capable of producing a diversity of organic compounds.

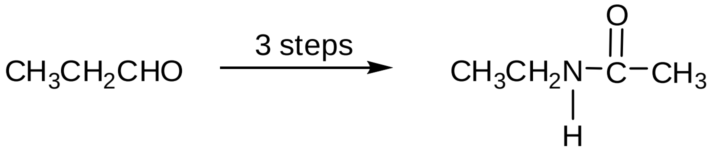
In the Schmidt rearrangement reactions shown below, hydrogen azide, HN_3, can be converted to the following products using acid as a catalyst (cat).



(a) **(i)** Suggest the structure of hydrogen azide, HN_3.

(ii) Draw the structure of the product formed when hydrogen azide, HN_3, reacts with cyclopentanone.

(iii) Outline how you could bring about the following conversion in **three steps**. In your answer, you are to clearly state the reagents and conditions used and draw the intermediates formed. An appropriate reaction from the Schmidt rearrangement is to be used as one of the steps.



$$CH_3CH_2CHO \xrightarrow{\text{3 steps}} CH_3CH_2\underset{\displaystyle H}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{||}{C}}-CH_3$$

[5]

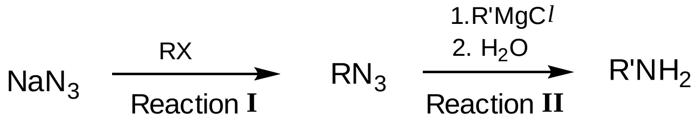
(b) An acid is used as a homogeneous catalyst in the Schmidt reactions to lower the activation energy of the reaction by providing an alternative pathway.

Other common homogeneous catalysts are transition element ions. Using the *Data Booklet*, explain how Fe^{2+} ions increases the rate of the following reaction.

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

[3]

Azides, being very versatile, can play the role of either a nucleophile or an electrophile in organic reactions.



$$NaN_3 \xrightarrow[\text{Reaction I}]{RX} RN_3 \xrightarrow[\text{Reaction II}]{\text{1.R'MgC}l \text{ 2. } H_2O} R'NH_2$$

(c) Identify the roles of azide in Reaction **I** and Reaction **II**.

[1]

(d) When NaN_3 reacts with $CH_3CH_2CHBrCH_3$ according to Reaction **I**, the product formed, $CH_3CH_2CH(N_3)CH_3$ does **not** rotate plane polarised light.

(i) Name and outline the mechanism in Reaction **I**.

(ii) Explain why the product formed in **(d)(i)** does not rotate plane polarised light.

[4]

(e) $MgCl_2$ reacts with water in a similar way as the Grignard reagent in Reaction **II**, R'MgC*l*.

Using balanced equations, explain how magnesium chloride reacts with water and state the pH of the resultant solution.

[3]

(f) To determine the structure of an organic molecule, it is useful to know the number of double bonds it has using the formula below.

$$\text{Number of double bonds} = C - \frac{H}{2} - \frac{X}{2} + \frac{N}{2} + 1$$

where *C = number of C,*
H = number of H,
X= number of halogen and
N = number of N

Note that a triple bond, eg. in a nitrile, -C≡N is equivalent to 2 double bonds

When compound **A**, $C_5H_{12}O_2$, which contains a chiral carbon, is heated with acidified potassium dichromate under distillation, compound **B**, $C_5H_{10}O_2$, is collected as the distillate. Compound **B** gives a brick red precipitate when warmed with Fehling's solution and white fumes when reacted with $SOCl_2$. Compound **A** reacts with hydrogen azide to give compound **C**, $C_5H_{11}NO$.

(i) Determine the number of double bonds in compounds **A**, **B** and **C**.

(ii) Using your answers in **(f)(i)** and the Schmidt's rearrangement scheme, suggest the structural formula of each of the compounds, **A**, **B** and **C**.

[4]

[Total: 20]

4 A controversial issue in Singapore recently centred upon the demise of American researcher, Dr Shane Todd who worked at the Singapore Institute of Microelectronics on a research project presumably involving gallium nitride, GaN.

Powdered gallium nitride can be made from the reaction of gallium with ammonia.

$$2Ga + 2NH_3 \longrightarrow 2GaN + 3H_2$$

(a) Gallium is a silvery-blue metal that can exist as a liquid at room conditions. Its low melting point of 30^oC is thought to be due to the existence of Ga_2 dimers.

Explain, in terms of structure and bonding, why the melting of point of Ga_2 dimers would be lower than the melting point of aluminium.

[2]

(b) Like gallium nitride, silicon has little electrical conductivity when used in a pure form as a semiconductor. Their electrical properties are altered through a process called 'doping', which involves the mixing of a small amount of impurities into their crystal structure.

In the case of silicon, phosphorus is often used in what is known as *n*-type doping, whereas boron is used in *p*-type doping. Introduction of these elements causes changes to the structure of silicon (illustrated in **Diagram 1**), which increases the conductivity of the material.

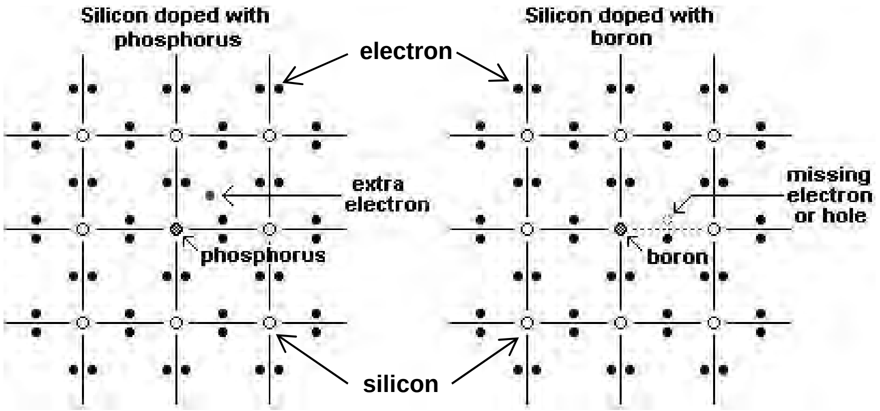


Diagram 1 : Structure in *n*-type (left) and *p*-type doping of silicon

Suggest how the introduction of the following increases electrical conductivity of silicon.

(i) phosphorus in *n*-type doping.

(ii) boron in *p*-type doping.

[2]

[Turn over

(c) Gallium forms many halogen-containing compounds such as gallium (III) chloride which is a reagent for organic synthesis.

(i) Construct a labelled Born-Haber cycle for the formation of gallium (III) chloride, from its elements. Use the cycle to determine the standard enthalpy change of formation of gallium (III) chloride.

Incorporate data from the table below as well as relevant data from the *Data Booklet*.

Enthalpy term	**ΔH / kJ mol^{-1}**
Lattice energy of $GaCl_3$	-5645
Standard enthalpy change of atomisation of gallium	+277
First electron affinity for chlorine	-364

(ii) The numerical values of lattice energies for the gallium (III) halides are listed in the table below. Two sets of data for the lattice energies are available, as one is determined experimentally, while the other is theoretically calculated.

Compound	**experimental value / kJ mol^{-1}**	**theoretical value / kJ mol^{-1}**
$GaCl_3$	5645	5217
$GaBr_3$	5552	4966
GaI_3	5476	4611

Table: Lattice Energies of Gallium (III) Halides

Account for the differences in agreement between the experimental and theoretical values of the lattice energies of the gallium (III) halides from $GaCl_3$ to GaI_3.

[6]

(iii) Gallium(III) chloride has a melting point of only 78°C. Conversely, gallium (III) fluoride, GaF_3, is a white solid that melts above 1000°C. Under room conditions, the molar mass of gallium chloride is 352.4 g mol^{-1}.(A_r of Ga = 69.7, A_r of Cl = 35.5)

1 Draw the dot-and-cross diagrams of gallium (III) fluoride and gallium (III) chloride.

2 Deduce with reasoning, the shape and bond angle around gallium in gallium (III) chloride.

[4]

(d) When heated at very high temperatures, gallium (III) chloride reacts with elemental gallium to form the respective gallium (I) chloride. Cooling the mixture favours the reverse disproportionation reaction.

$$2Ga\ (s)\ +\ GaCl_3\ (g) \rightleftharpoons 3GaCl\ (g)$$

When a 3: 2 mole ratio of $GaCl_3$ and $GaCl$ respectively at 3 atmospheres is passed over gallium at a certain high temperature, the partial pressure of $GaCl$ at equilibrium is found to be 1.8 atm.

(i) Calculate K_p, stating the units.

(ii) Explain with reasons, whether the formation of gallium(I) chloride is favoured by high or low pressure.

(iii) Deduce how the entropy of the forward reaction will change. Hence, determine how the value of the free energy of this reaction will change with temperature and what consequences would it have on the conditions required for the formation of gallium (I) chloride.

[6]

[Total: 20]

5 Transport proteins serve the function of moving other materials within an organism. They are vital to the growth and life of all living things. Hemoglobin is an iron-containing oxygen-transport protein found in the red blood cells of all vertebrates.

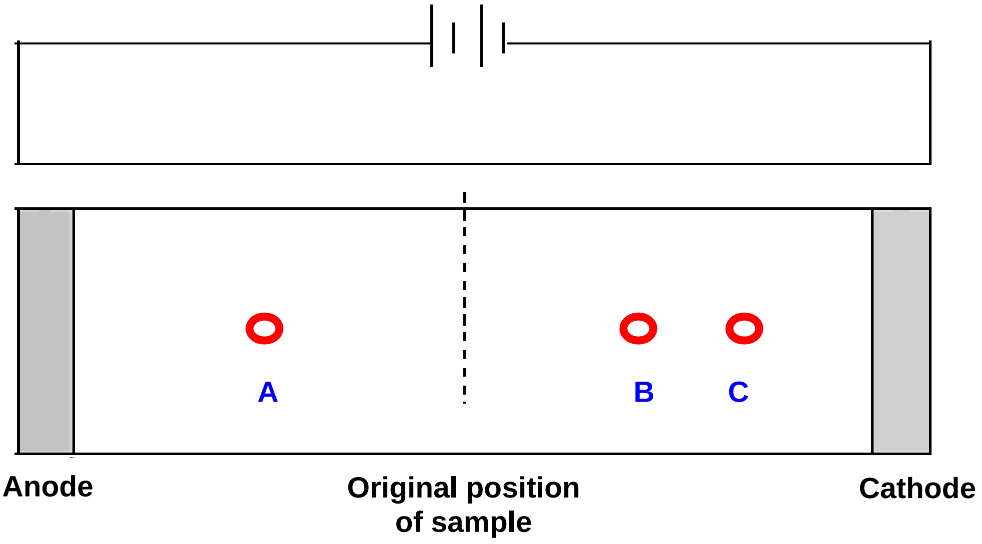
(a) State the type of bonding or interactions involved in the *primary*, *secondary*, *tertiary* and *quaternary* structures of proteins like hemoglobin.

[2]

(b) The following amino acids are some of the amino acids present in the primary sequence of hemoglobin.

Amino Acids	**Formula of side chain (R' in R'CH(NH_2)CO_2H)**	**Isoelectric Point**
Valine	$-CH(CH_3)_2$	6.00
Glutamic acid	$-CH_2CH_2COOH$	3.15
Asparagine	$-CH_2CONH_2$	5.41

An electrophoresis experiment is run on a solution containing the above three amino acids at pH 5.00. The relative positions of the amino acids are shown in the diagram below.

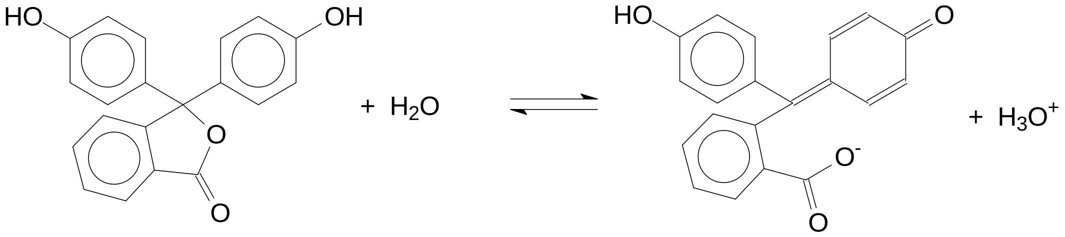


Suggest the identities of amino acid **A**, **B** and **C**.

[1]

(c) Haemoglobin is able to exhibit peroxidase-like activity to catalyse the oxidation of colourless phenolphthalein into its bright pink conjugate base. This reaction is often used to test for the presence of blood at a crime scene.

Phenolphthalein is a *weak acid* which dissociates in water according to the following equation:



Phenolphthalein
colourless

Conjugate base of phenolphthalein
pink

The K_a of phenolphthalein is 3.00×10^{-10} mol dm^{-3}.

Distinct colour change for phenolphthalein occurs when half of the indicator is phenolphthalein and the other half is its conjugate base.

(i) Determine the pH at which phenolphthalein shows distinct colour change.

(ii) The change of colour for phenolphthalein occurs over a limited range of pH and falls between ±1.00 of the pK_a value.

In an experiment, a 25.0 cm^3 sample of the hydroxylammonium chloride, $NH_3OH^+Cl^-$, solution was titrated against a solution of 0.100 mol dm^{-3} sodium hydroxide. 14.40 cm^3 of sodium hydroxide was needed for complete neutralisation as shown by the equation below:

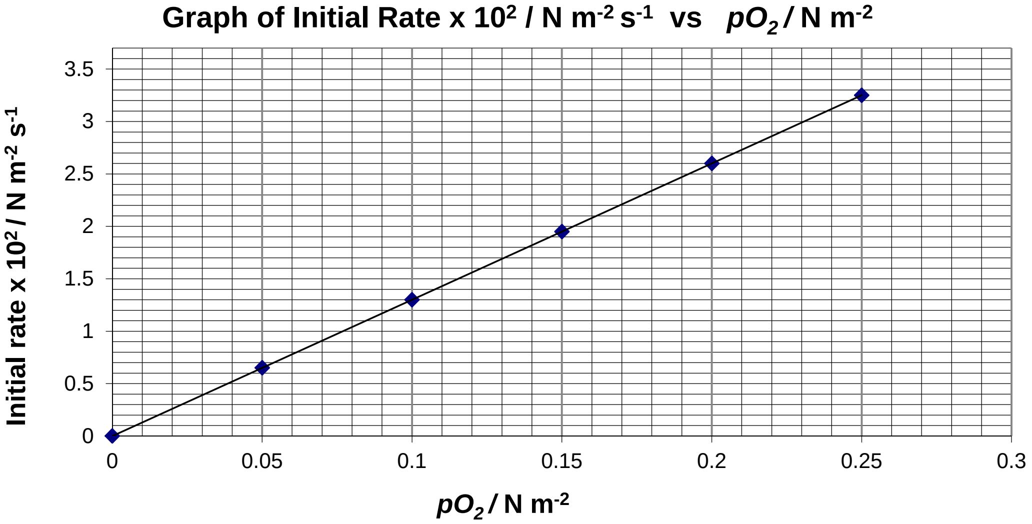
$$NH_3OH^+Cl^- + NaOH \rightarrow NH_2OH + NaCl + H_2O$$

Given that K_a value of NH_3OH^+ is 9.09×10^{-7} mol dm^{-3}, determine the pH of resulting solution. Hence, explain if phenolphthalein is a suitable indicator for this titration.

[4]

(d) The reaction kinetics of oxygen binding to hemoglobin in human red blood cell suspensions is studied. This is done by measuring the rates of uptake of oxygen by hemoglobin at different partial pressures of oxygen.

The graph of initial rate against partial pressure of oxygen was plotted below.



Graph of Initial Rate x 10^2 / N m^{-2} s^{-1} vs pO_2 / N m^{-2}

(i) Using the graph above, state the order of reaction with respect to oxygen.

(ii) The concentration of hemoglobin was halved and a new series of experiments was conducted at the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from the above graph.

Deduce the order of reaction with respect to hemoglobin? Explain your answer.

(iii) Construct the rate equation for the reaction between hemoglobin and oxygen.

Air oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at 1.6 x 10^{-6} mol dm^{-3} by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to 8.0 x10^{-6} mol dm^{-3}.

(iv) Calculate the rate of oxyhemoglobin formation if the rate constant is k = 2.1 x 10^6 dm^3 $mol^{-1}s^{-1}$ at 37 °C.

[4]

(e) Another type of protein that transports oxygen throughout the bodies of invertebrates is *hemocyanin*, which contains two copper atoms that reversibly bind a single oxygen molecule.

(i) *Hemocyanin* exhibits catalytic activity to catalyse the hydroxylation of monophenols to diphenols.

Using an appropriate sketch of the Maxwell-Boltzmann distribution, explain how the presence of *hemocyanin* increases the rate of hydroxylation of monophenols.

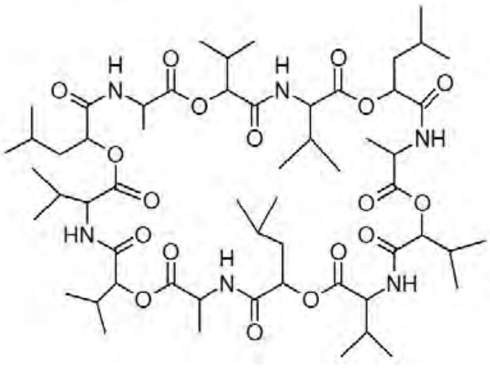
(ii) Partial *denaturation* actually improves *hemocyanin*'s catalytic ability by providing greater access to the active site.

1 What is meant by the term *denaturation*?

2 Suggest how a weak acid might interact with *hemocyanin* to bring about denaturation.

[6]

(f) *Cereulide* is another example of a transport protein. As a natural dodecadepsipeptide ionophore, *cereulide* acts as potassium transporters, where potassium, K^+, plays a vital role in bacterial physiology.



Cereulide

(i) Apart from the peptide group, name another functional group that is present in the molecule?

When treated with a peptidase enzyme, the peptides bonds in the ring are hydrolysed. Only three different products are formed.

(ii) Out of the three products formed, two of the amino acid residues are present **more than once** in the protein. Draw the structural formula of the two amino acid residues.

[3]
[Total: 20]

End of Paper 3