1 Planning (P)

Aqueous chlorine, Cl_2, displaces iodine, I_2, from aqueous potassium iodide. If a solution of chlorine is mixed with an excess of aqueous potassium iodide, iodine is displaced in a 1:1 molar ratio with chlorine.

The concentration of chlorine in the original solution can therefore be calculated from the concentration of the displaced iodine.

$$I_2(aq) + 2Na_2S_2O_3(aq) \rightarrow 2NaI(aq) + Na_2S_4O_6(aq)$$

(a) Write an equation for the reaction between aqueous chlorine, and an excess of aqueous potassium iodide.

$Cl_2(aq) + 2KI(aq) \rightarrow I_2(aq) + 2KCl(aq)$ [1]
[Accept ionic equation, state symbols are optional.]

(b) You are to plan an experiment to determine as accurately as possible the concentration of a saturated aqueous solution of chlorine by titration. The approximate solubility of chlorine is 5 g dm^{-3} at 25 ^oC.

You are provided with the following materials:

- saturated aqueous chlorine;
- solid sodium thiosulfate $Na_2S_2O_3.5H_2O$;
- concentrated aqueous potassium iodide. This will be used in excess.
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- a calculation of the approximate concentration of saturated aqueous chlorine in mol dm^{-3} at 25 ^oC;
  [A_r: Cl, 35.5]
- a detailed description of the method for preparing a solution of aqueous sodium thiosulfate that can be used in the titration. In a titration, it is usual for the titre volume to be approximately equal to that of the volume of solution pipetted. Calculate the mass of sodium thiosulfate, $Na_2S_2O_3.5H_2O$, which will produce a solution suitable for use in this titration. The relevant calculations and reasoning must be shown in full;
  [A_r: H, 1.0; O, 16.0; Na, 23.0; S, 32.1]
- a step–by–step description of how you would carry out sufficient titrations using a suitable indicator to allow an accurate end–point to be obtained;
- an outline calculation to show how the results are to be used to determine the accurate concentration of the aqueous chlorine. Assume that the titre volume used is **w** cm^3.

Approximate concentration of saturated $Cl_2(aq)$

$$= \frac{5}{2 \times 35.5}$$

$= 0.0704$ mol dm^{-3}

Assume 10.0 cm^3 of saturated $Cl_2(aq)$ is pipetted in each titration.

No. of moles of saturated $Cl_2(aq)$ used

$$= 0.0704 \times \frac{10.0}{1000}$$

$= 7.04 \times 10^{-4}$ mol = no. of moles of I_2 formed

No. of moles of $Na_2S_2O_3$ needed for titration
= 2 x 7.04 x 10^{-4}
= 1.41 x 10^{-3} mol

Assume 10.0 cm^3 of $Na_2S_2O_3$ is needed for each titration and 100 cm^3 volumetric flask is used to prepare $Na_2S_2O_3$ solution.

Concentration of $Na_2S_2O_3$ needed
= 1.41 x 10^{-3} ÷ $\frac{10.0}{1000}$
= 0.141 mol dm^{-3}

No. of moles of $Na_2S_2O_3.5H_2O$ needed
= 0.141 x $\frac{100}{1000}$
= 0.0141 mol

Mass of $Na_2S_2O_3.5H_2O$ needed
= 0.0141 x [2(23.0) + 2(32.1) + 3(16.0) + 5(18.0)]
= 3.50 g

[Accept other combinations of pipette and volumetric flask volumes with correct justification.]

Procedure [mass and volumes ecf from above justification]:

Step 1: Accurately weigh 3.50 g of $Na_2S_2O_3.5H_2O$ in a weighing bottle and completely dissolve it in distilled water using a beaker. Pour the solution and the washings into a 100 cm^3 volumetric flask and make up to the mark with distilled water. Shake well to obtain a homogenous solution. Label this solution FA1 and pour it into a burette.

Step 2: Pipette 10.0 cm^3 of saturated aqueous chlorine into a conical flask.

Step 3: Using a measuring cylinder, add 10 cm^3 of concentrated KI(aq) into the conical flask.

Step 4: Titrate the iodine liberated in this solution with FA1. When the colour of the solution turns pale yellow, add about 1 cm^3 of starch indicator. The solution will turn blue–black. Continue the titration and the end–point is reached when the colour just disappears. Record the results.

Step 5: Repeat steps 2 to 4 as many times as necessary to obtain consistent results to within ±0.10 cm^3.

Calculations:
Assume 10.0 cm^3 of Cl_2(aq) reacted with exactly **w** cm^3 of FA1 of concentration 0.141 mol dm^{-3}.

No. of moles of FA1 used
= 0.141 x $\frac{\mathbf{w}}{1000}$
= 1.41**w** x 10^{-4} mol

No. of moles of I_2 formed
= 1.41**w** x 10^{-4} ÷ 2
= 7.05**w** x 10^{-5} mol
= no. of moles of Cl_2(aq) used

Concentration of CI_2(aq) used

$= 7.05\mathbf{w} \times 10^{-5} \div \frac{10.0}{1000}$

$= 7.05\mathbf{w} \times 10^{-3}$ mol dm^{-3}

[10]

(c) State one hazard that must be considered when planning the experiment and describe a precaution that should be taken to keep risks from this hazard to a minimum.

Chlorine gas escapes from saturated aqueous chlorine which is poisonous.
Perform the titration in a fume cupboard.

OR

Chlorine gas escapes from saturated aqueous chlorine which causes eye irritation.
Perform the titration in a fume cupboard.

OR

Saturated aqueous chlorine is acidic/oxidising.
Wear safety gloves when performing the titration.

[1]

[Total: 12]

2 **(a)** On Planet Uranus, it is postulated that the number of subshells associated with each principal quantum number and the respective energy levels of the subshells are similar to that on Earth. Each orbital contains a maximum of two electrons. However, the number of orbitals that make up a subshell may or may not be identical to that on Earth.

Figure 1 represents the sketch of the successive ionisation energies of **all** the electrons of an element **T** on Planet Uranus.

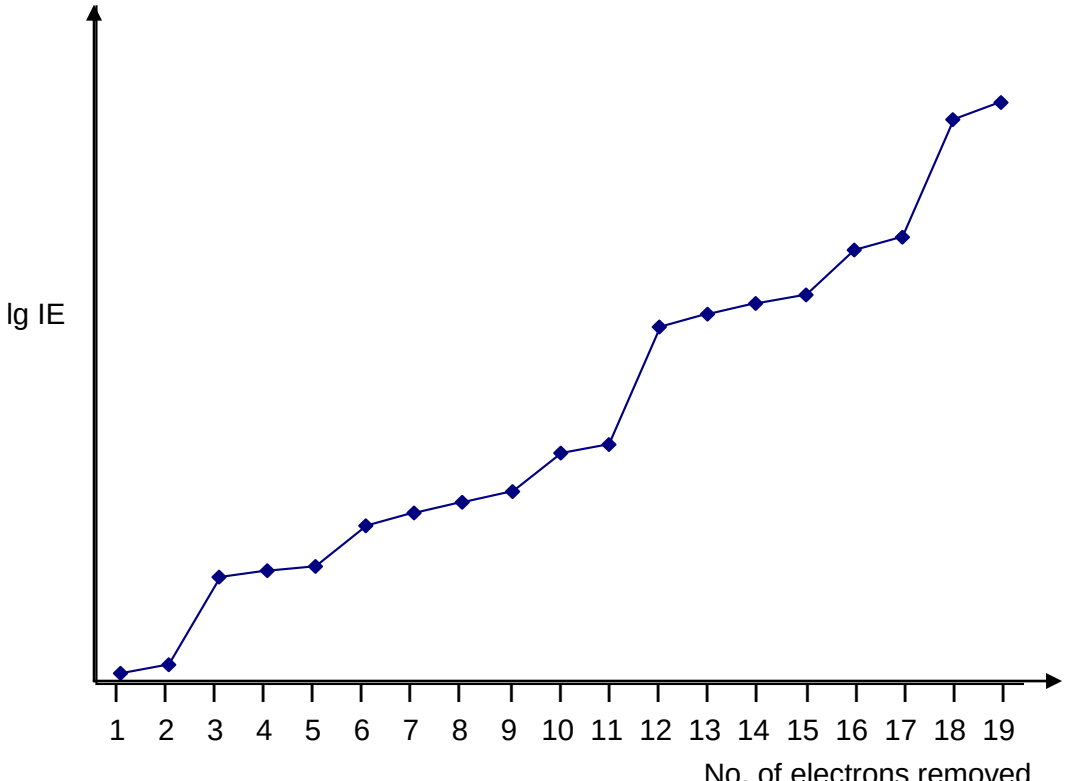


Figure 1

(i) By interpreting figure 1, suggest with reasoning, which period of the Periodic Table element **T** belongs to.

Since there are a total of <u>three large increments</u> between successive ionisation energies, this implies that the 3rd, 12th and 18th electrons are removed from different principal quantum shells.
Hence, **T** belongs to the fourth period of the Periodic Table.

(ii) Using figure 1, deduce the number of 2p orbitals present in element **T**.

The 18th and 19th IE belong to 1s subshell.
OR The 16th and 17th IE belong to 2s subshell.
Thus, 12th to 15th IE, i.e. four electrons are removed from a 2p subshell.
Since each orbital can accommodate a maximum of 2 electrons, there are two 2p orbitals.

(iii) State the full electronic configuration of element **T**.

$1s^2\ 2s^2\ 2p^4\ 3s^2\ 3p^4\ 3d^3\ 4s^2$

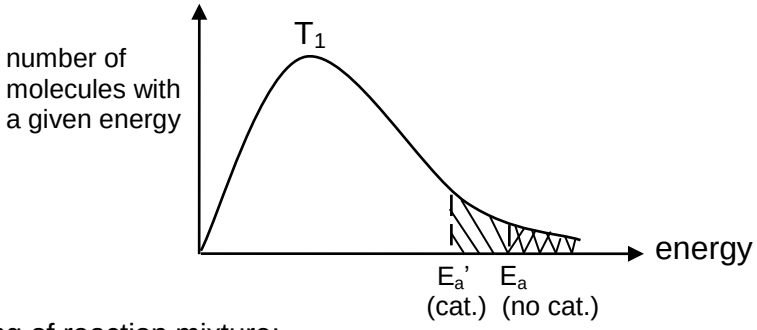
[3]

(b) The hydrolysis of ester to form acid and alcohol is an equilibrium reaction. Using ethyl ethanoate as an example, the reaction for the hydrolysis is shown below.

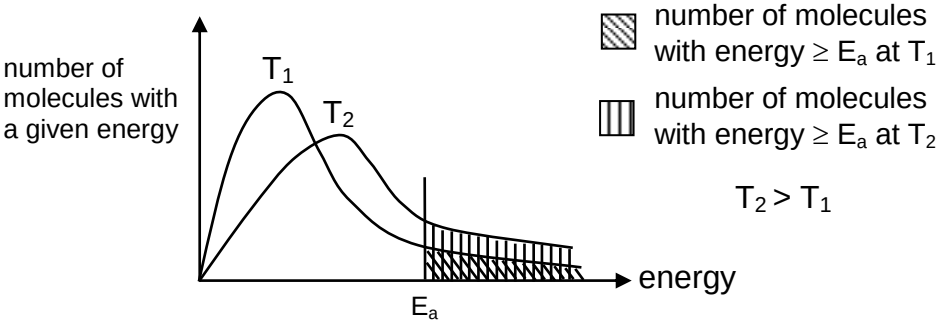
$$CH_3CO_2CH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3CO_2H(l) + CH_3CH_2OH(l)$$

Draw two labelled Maxwell–Boltzmann distribution curves to illustrate clearly how the addition of concentrated sulfuric acid and heating of reaction mixture can increase the rate of hydrolysis. (Written explanation is not required.)

Addition of concentrated sulfuric acid:



Heating of reaction mixture:



Correct axes for both
Correct graph for addition of concentrated sulfuric acid with illustration/shading
Correct graphs for heating of reaction mixture

[3]

(c) The rate of hydrolysis (in mol dm^{-3} s^{-1}) of ethyl ethanoate at 25 ^{o}C is given by the following equation.

$$\text{rate} = (4.0 \times 10^{-6}\ [\text{ester}][H^+]) + (2.5 \times 10^{-1}\ [\text{ester}][OH^-])$$

(i) Calculate the rate of hydrolysis at pH = 1.0 and 13.0 respectively, given [ester] = 0.0100 mol dm^{-3}.

pH 1.0:
rate
$= (4.0 \times 10^{-6})(0.0100)(10^{-1}) + (2.5 \times 10^{-1})(0.0100)(10^{-13})$
$= 4.00 \times 10^{-9}$ mol dm^{-3} s^{-1}

pH 13.0:
rate
$= (4.0 \times 10^{-6})(0.0100)(10^{-13}) + (2.5 \times 10^{-1})(0.0100)(10^{-1})$
$= 2.50 \times 10^{-4}$ mol dm^{-3} s^{-1}

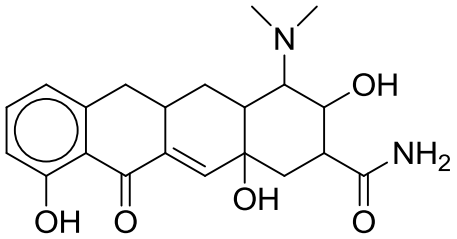
(ii) Comment on your answers in **(c)(i)** by relating to the rate equation.

The rate of hydrolysis of ethyl ethanoate is <u>slower</u> when the pH is <u>low</u>, i.e. at high $[H^+]$, due to the <u>much smaller rate constant</u> associated with $[H^+]$.

OR The rate of hydrolysis of ethyl ethanoate is <u>faster</u> when the pH is <u>high</u>, i.e. at low $[H^+]$, due to the <u>much larger rate constant</u> associated with $[OH^-]$.

[3]

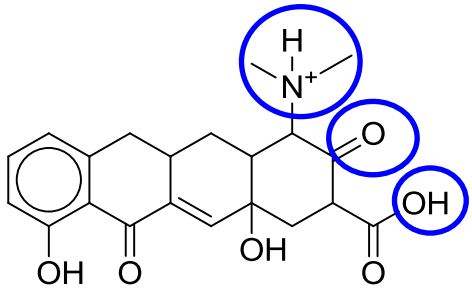
(d) Tetracycline is a broad–spectrum polyketide antibiotic indicated for use against many bacterial infections. It is commonly used to treat acne today. Compound **M**, a derivative of tetracycline, has the structure shown below.



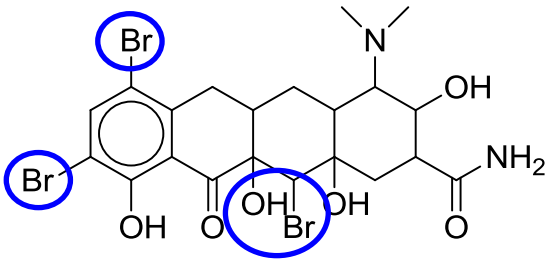
compound **M**

Draw the structures of the organic products formed when compound **M** is treated with

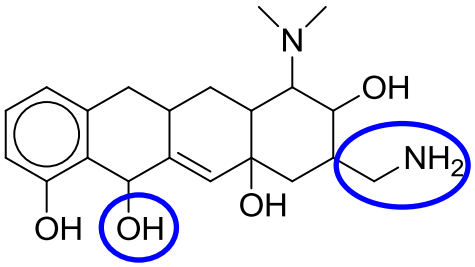
(i) $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat



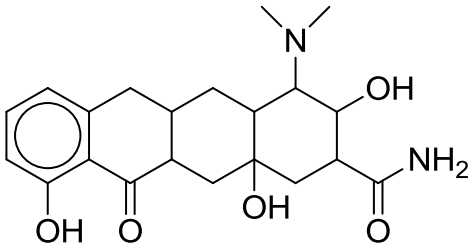
(ii) aqueous bromine, room temperature



(iii) LiA*l*H_4 in dry ether, followed by addition of water



(iv) Suggest a simple chemical test to distinguish between compound **M** and compound **N**. You should state clearly the reagents and conditions used, and the observations you would expect to make with each compound.



compound **N**

Reagents: $KMnO_4$, NaOH(aq) / H_2SO_4(aq)
Condition: cold or room temperature

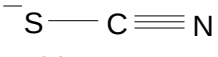
M will decolourise purple $KMnO_4$.
N will not decolourise purple $KMnO_4$.

[6]

[Total: 15]

3 Pseudohalogens are a class of compounds that show chemical reactivity similar to halogens. An example of a pseudohalogen and its anion is $(SCN)_2$ and SCN^- respectively.

thiocyanogen

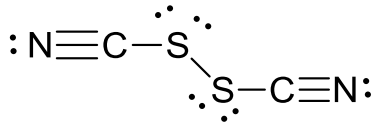


thiocyanate

(a) (i) Draw the shape of the hybrid orbitals around one of the carbon atoms in thiocyanogen.

sp

(ii) Draw a diagram to illustrate the shape of thiocyanogen, indicating clearly the covalent bonds and lone pairs of electrons.



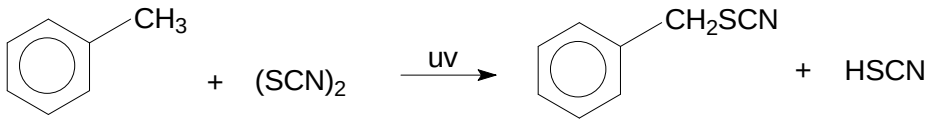
bent shape at sulphur (bond angle of 105^o)
linear at CN
Lone pairs on N
Lone pairs on S

(iii) Thiocyanogen can be synthesised by reacting sodium thiocyanate, NaSCN, with chlorine gas. Write an equation for the formation of thiocyanogen.

$2NaSCN + Cl_2 \rightarrow (SCN)_2 + 2NaCl$

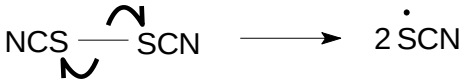
[4]

(b) Thiocyanogen can react with hydrocarbons such as methylbenzene via free radical substitution.

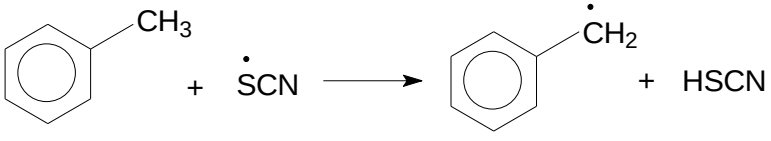


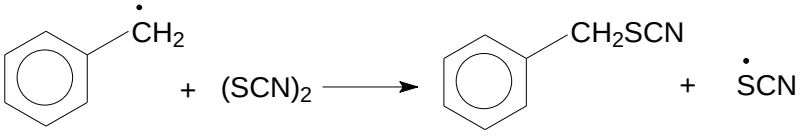
(i) Write equations that describe the following steps.

Initiation

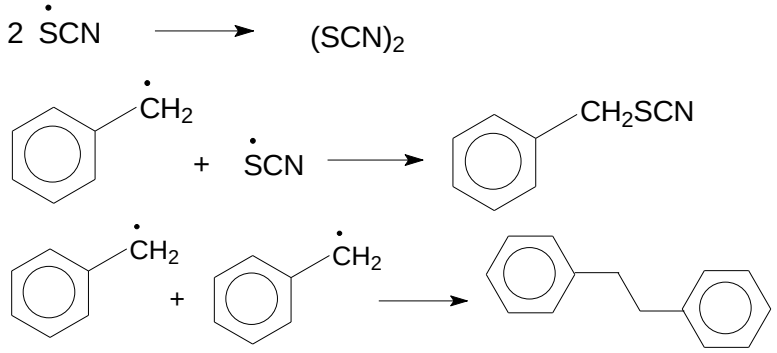


Propagation

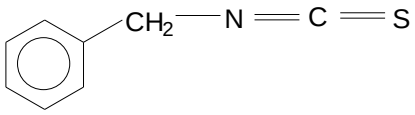


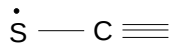
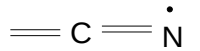


Termination (Write down all the possible termination steps.)



(ii) An isomer of the product shown below was also isolated. Suggest a reason for the formation of this isomer.



Delocalisation of electrons in  produced at the initiation step allows  to be formed, resulting in such a side product.

[4]

(c) The standard reduction potential of $(SCN)_2$ is given as

$\frac{1}{2}(SCN)_2 + e^- \rightleftharpoons SCN^-$ $\quad E^\ominus = +0.43$ V

With the aid of the *Data Booklet*, predict the reactions, if any, that might occur when the following reagents are mixed. Write a balanced equation for the reaction that occurs.

(i) $Na_2S_2O_3$ and $(SCN)_2$

$\frac{1}{2}(SCN)_2 + e^- \rightleftharpoons SCN^-$ $\quad E^\ominus = +0.43$ V

$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$ $\quad E^\ominus = +0.09$ V

$E^\ominus_{cell} = 0.43 - 0.09 = +0.34$ V > 0. Hence reaction is feasible.
$2S_2O_3^{2-} + (SCN)_2 \rightarrow S_4O_6^{2-} + 2SCN^-$

(ii) acidified $K_2Cr_2O_7$ and $(SCN)_2$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $\quad E^\ominus = +1.33$ V

Both $Cr_2O_7^{2-}$ and $(SCN)_2$ are oxidising agents.
Hence reaction cannot proceed.

[3]

(d) SCN^- acts as a ligand in the formation of complex ions. The formation of a complex ion from the hydrated metal ion is shown in the following equilibrium:

$$[M(H_2O)_6]^{m+}(aq) + nL^-(aq) \rightleftharpoons [M(H_2O)_{6-n}L_n]^{(m-n)+}(aq) + nH_2O(l)$$

where *m* and *n* are whole numbers.

The equilibrium constant is called the stability constant, K_{stab}. The table below provides information for the formation of two complexes.

Complex ion	M^{m+}	L^-	*n*	K_{stab}	Colour
Iron(III) thiocyanate	Fe^{3+}	SCN^-	1	90	Red
Cobalt(II) thiocyanate	Co^{2+}	SCN^-	4	100	Blue

(i) Write an equation for the formation of cobalt(II) thiocyanate and hence write an expression for its equilibrium constant, K_{stab} and state its units.

$$[Co(H_2O)_6]^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons [Co(H_2O)_2(SCN)_4]^{2-}(aq) + 4H_2O(l)$$

$$K_{stab} = \frac{[[Co(H_2O)_2(SCN)_4]^{2-}]}{[Co(H_2O)_6^{2+}][SCN^-]^4}$$

Units : $mol^{-4}\ dm^{12}$

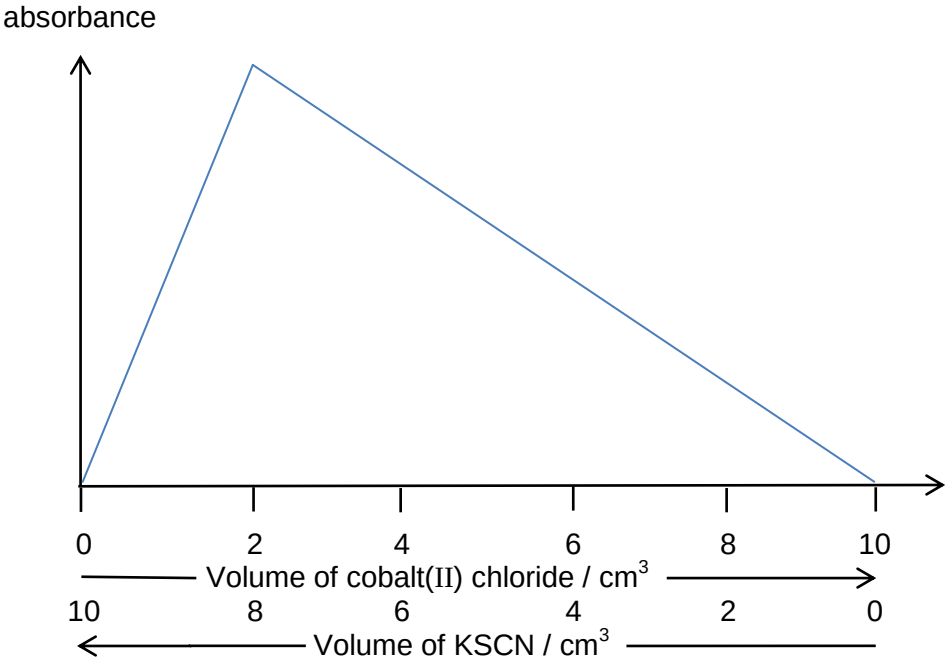
(ii) Calculate the concentration of the complex ion formed when 0.0050 mol of solid cobalt(II) chloride was added to a 2 dm^3 solution of 0.95 mol dm^{-3} KSCN solution.

	$[Co(H_2O)_6]^{2+}(aq)$	+ $4SCN^-(aq)$	⇌	$[Co(H_2O)_2(SCN)_4]^{2-}(aq)$	+ $4H_2O(l)$
Initial	0.0050/2	0.95			
Change	– z	– 4z		+ z	
Eqm	0.0025 – z	0.95 – 4z		z	

$$[Co(H_2O)_2(SCN)_4]^{2-} = 100 \times (0.95 - 4z)^4 \times (0.0025 - z)$$
$$z = 100 \times 0.8145 \times (0.0025 - z) \quad \text{since } 0.95 >> 4(0.0025)$$
$$z = 0.2036 - 81.45\,z$$
$$82.45\,z = 0.2036$$
$$z = 2.47 \times 10^{-3}\ mol\ dm^{-3}$$

(iii) In an experiment to study the stoichiometry of cobalt(II) thiocyanate, a solution of 1.0×10^{-3} mol dm^{-3} cobalt(II) chloride is mixed with different proportions of a solution of 1.0×10^{-3} mol dm^{-3} KSCN(aq) such that the total volume of each mixture is kept constant at 10 cm^3. The absorbance due to the complex ion in each mixture is measured with a colorimeter. The absorbance is directly proportional to the concentration of the complex.

In the grid below, sketch the graph you would expect to obtain.



Inverted V-shape
Point : 0 cm^3 of cobalt(II) chloride and 10 cm^3 of KSCN
Point : 10 cm^3 of cobalt(II) chloride and 0 cm^3 of KSCN
Max absorbance at 2.0 cm^3 of $CoCl_2$ and 8.0 cm^3 of KSCN

[6]

(e) KSCN is used to standardise a solution of silver nitrate. A white precipitate of AgSCN (K_{sp} = 1.1 x 10^{-12} $mol^2\ dm^{-6}$) is formed during the titration. The indicator used in the titration is yellow aqueous iron(III) solution.

$$Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)$$

In an experiment, 5 cm^3 of 5 mol dm^{-3} nitric acid, 25 cm^3 of water and 1 cm^3 of iron(III) solution are added to 25.0 cm^3 of silver nitrate solution in a conical flask. End-point of titration is reached when 15.00 cm^3 of 0.100 mol dm^{-3} KSCN solution is added.

(i) Calculate the concentration of the original silver nitrate solution.

No of moles of KSCN = 0.100 x 15.00/1000 = 1.50 x 10^{-3} mol
No of moles of Ag^+ = 1.50 x 10^{-3} mol
$[Ag^+]$ = 1.50 x 10^{-3} ÷ 25.0/1000 = 6.00 x 10^{-2} mol dm^{-3}

(ii) Calculate the concentration of $Ag^+(aq)$ in the solution at the equivalence point.

K_{sp} = $[Ag^+][SCN^-]$
Since $[Ag^+]$ = $[SCN^-]$
$[Ag^+]$ = $\sqrt{1.1 \times 10^{-12}}$ = 1.05 x 10^{-6} mol dm^{-3}

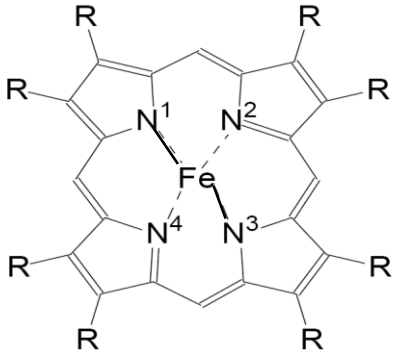
(iii) With reference to the table given in **(d)**, explain why iron(III) solution can be used as an indicator and state the observation at the end-point of the titration.

Additional SCN^- added just after the end-point will react with Fe^{3+} to form $Fe(H_2O)_5(SCN)^{2+}$ which will produce a red coloration.

[4]

[Total: 21]

4 (a) Haemoglobin is an important protein present in the red blood cell, which is responsible for transport of oxygen in the body. It contains a haem group and a metal centre as shown below. The four N atoms and the Fe atom are planar.



(i) State the types of hybridisation at N^1 and N^2, and the nature of the bonding around Fe atom.

Hybridisation at N^1: sp^2
Hybridisation at N^2: sp^2
Type of bond between Fe atom and N^1: covalent bond
Type of bond between Fe atom and N^2: dative bond / co-ordinate bond

(ii) One molecule of haemoglobin (Hb) binds up to four oxygen molecules to form oxyhaemoglobin ($Hb(O_2)_4$), as shown in the following equation.

$$Hb(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq) \qquad (I)$$

By applying *Le Chatelier's Principle,* explain how oxygen molecules are transported from the lungs to the body tissues.

In the lungs, the concentration of O_2 is high.
Thus equilibrium position <u>shifts to the right</u>
to form oxyhaemoglobin. OR Oxygen is transported in the body as oxyhaemoglobin.

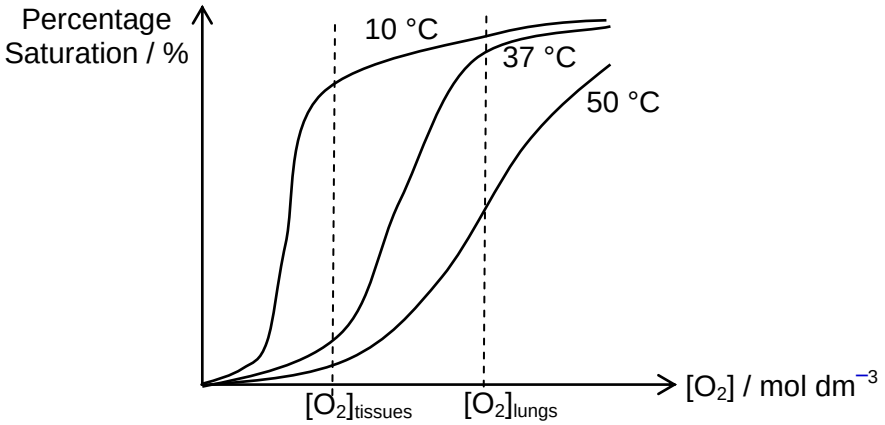
In the tissues, the concentration of O_2 is low.
Thus equilibrium position <u>shifts to the left</u> and
oxyhaemoglobin starts to dissociate to release oxygen.

(iii) The percentage saturation of haemoglobin is defined as the percentage of haemoglobin present in the blood that has been converted to oxyhaemoglobin.

With reference to equilibrium (I), state and explain how the percentage saturation of haemoglobin changes when temperature increases.

The forward reaction of the above equilibrium is <u>exothermic</u>
due to formation of <u>dative/coordinate bond</u> between the oxygen and Fe atom in the haemoglobin.
When temperature increases, <u>endothermic reaction</u> is favoured OR the <u>backward reaction</u> is favoured so as to remove excess heat.
Oxyhaemoglobin dissociates and the <u>percentage saturation decreases</u>.

(iv) The relationship between the percentage saturation of haemoglobin and concentration of oxygen in blood at different temperatures is shown below.

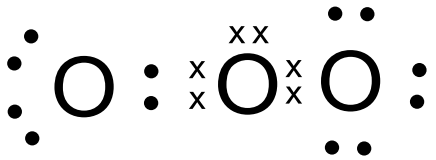


Suggest the optimum temperature at which haemoglobin operates. Explain your answer.

37 °C
Optimum temperature occurs at high percentage saturation at lungs and low percentage saturation at tissues
OR The difference in the percentage saturation at lungs and tissues is the largest.

[8]

(b) (i) Draw the dot-and-cross diagram of ozone, O_3.

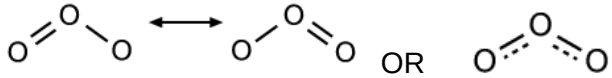


(ii) Oxygen–oxygen bond lengths of 3 species are given in the table below.

Species	Oxygen–oxygen bond length / nm
O_3	0.128
O_2^{2-}	0.149
O_2	0.120

With the aid of suitable structures, explain why the two oxygen-oxygen bonds in the ozone molecule have the same bond length which are very different from the peroxide ion and oxygen molecule.

O_3 forms resonance structures as shown below.



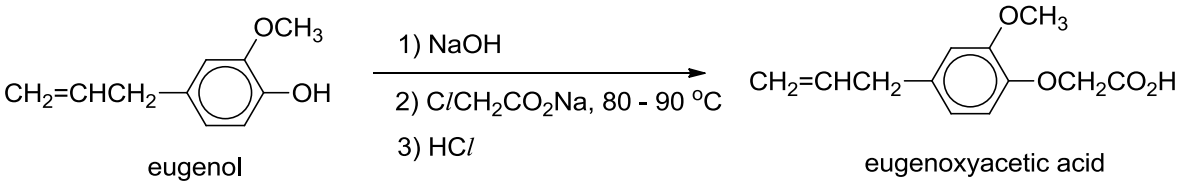
(dative bonds acceptable)
Thus, the two oxygen-oxygen bonds are equivalent, shorter than oxygen-oxygen single bond in O_2^{2-} and longer than oxygen-oxygen double bond in O_2.

[3]

[Total: 11]

5 (a) Eugenoxyacetic acid is a colourless and odourless compound. It has shown anti-viral and anti-bacterial properties and is therefore used as antioxidant food preservative in food industry.

Eugenoxyacetic acid can be synthesised from eugenol found in clove essential oil as shown in the procedure below via S_N2 mechanism.



eugenol

eugenoxyacetic acid

Preparation of solution A

1. Dissolve 1.0 g of 2-chloroethanoic acid in 5.0 cm^3 of distilled water in a beaker. Add Na_2CO_3(s) slowly until the solution just becomes alkaline.

Preparation of eugenoxyacetic acid

2. Dissolve 0.6 g of NaOH(s) in 3.0 cm^3 of distilled water in a conical flask. Add 2.0 cm^3 eugenol to the flask.
3. Add solution **A** to the flask in step 2 and keep stirring the mixture for 60 min.
4. Cool the reaction mixture to room temperature and add HCl(aq). Collect the solid formed by suction filtration. Wash the solid with water to obtain a pale yellow solid which is the crude product.

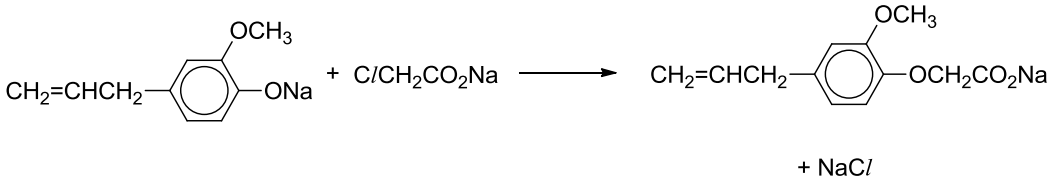
(i) How can you tell that the solution has just turned alkaline in step 1?

No more effervescence is observed on addition of Na_2CO_3(s).

(ii) Explain the role of NaOH(s) in step 2.

NaOH(s) acts as a base
to react with phenol.
The phenoxide formed is a stronger nucleophile to react with $ClCH_2CO_2Na$.

(iii) Write a balanced equation for the reaction in step 3.



(iv) Comment if an excess amount of NaOH(s) can be used in step 2.

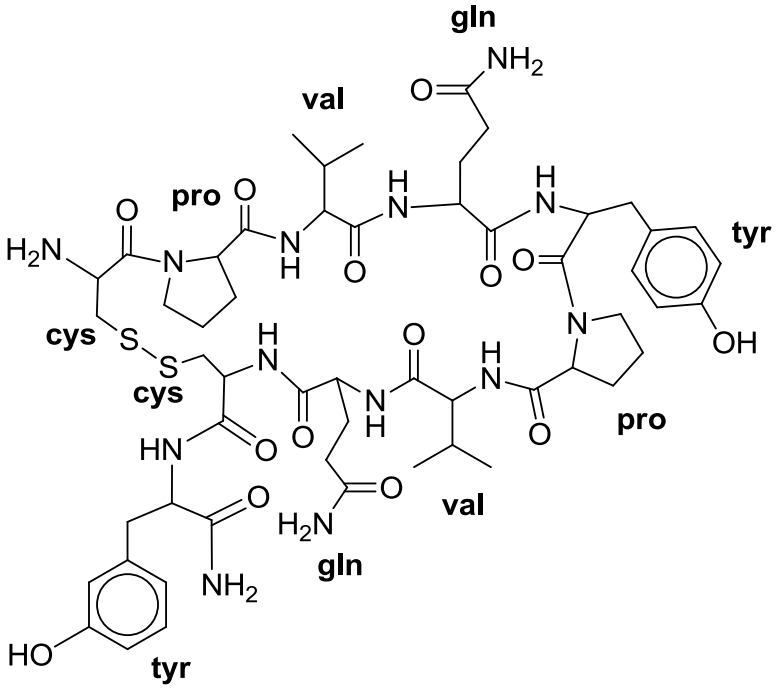
An excess amount of NaOH(s) should not be used
as the hydroxide ions can compete with the phenoxide to react with $ClCH_2CO_2Na$.

(v) Give a simple chemical test to confirm that eugenol is absent in the final product.

Dissolve the solid in ethanol and add neutral $FeCl_3$
at room temperature.
Absence of violet colouration would indicate that eugenol is absent.

[6]

(b) The structure of a small protein is given below, along with the abbreviated names of its constituent amino acids: **val**, **gln** etc.



(i) Use the abbreviated names of the amino acids to state the primary structure of the above protein.

cys-pro-val-gln-tyr-pro-val-gln-cys-tyr

(ii) This protein is ionised at pH 7. Identify **one** functional group that could be ionised at pH 7 by circling it on the structure above.

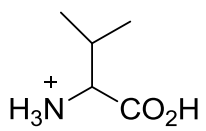
circle the phenol group

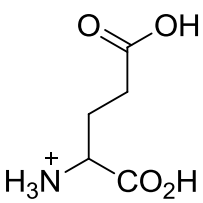
(iii) The biological function of the protein depends on its three dimensional shape. Describe how the particular amino acids in the above protein are likely to be involved in maintaining its three-dimensional shape.

Disulfide linkages between the **cys** amino acid residues.
Van der waals' forces of attraction between the $CH(CH_3)_2$ group of **val** residues (other plausible answers acceptable including between **val** and **pro**).
Hydrogen bonding between the $CH_2CH_2CONH_2$ group of **gln** residues (or **gln** with $CH_2C_6H_4OH$ group of **tyr**).

(iv) The activity of the above protein is destroyed by heating it under reflux with 6 mol dm^{-3} sulfuric acid for several hours.

Draw the structures of the organic products formed under these conditions from the part of the above protein containing the amino acids: **val**-**gln**





[7]

[Total: 13]