Name:	**Index No.:**	**CT Group: 12**

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CHEMISTRY **9647/03**

Paper 3 Free-Response **23 September 2013**

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any four questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

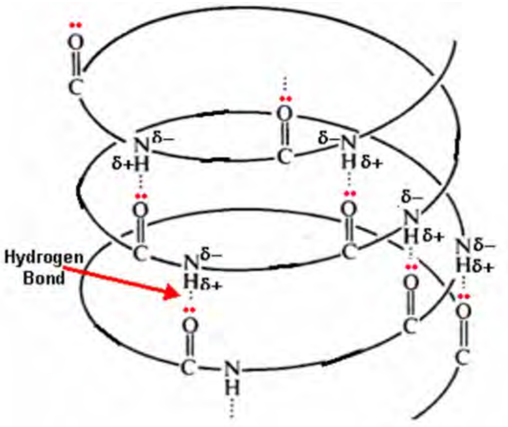
The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together.

This document consists of **13** printed pages.

Answer any four questions.

1 **(a)** With the aid of a diagram, describe how a polypeptide chain is held in the shape of an alpha helix. [3]

The α–helix has a regular coiled spiral polypeptide chain held in place by hydrogen bonds between peptide C=O group of one amino acid residue and peptide N–H group of another amino acid residue in the covalently bonded sequence. There are 3.6 amino acids per helical turn. The –R groups (side chains) point outside of the helix or label R group in diagram.



(b) Haemoglobin is the oxygen-carrying protein in red blood cells.

(i) With reference to the haemoglobin molecule, describe and explain what is meant by the term *quaternary structure* of proteins. In your answer, you should state the type of bonding or interaction involved.

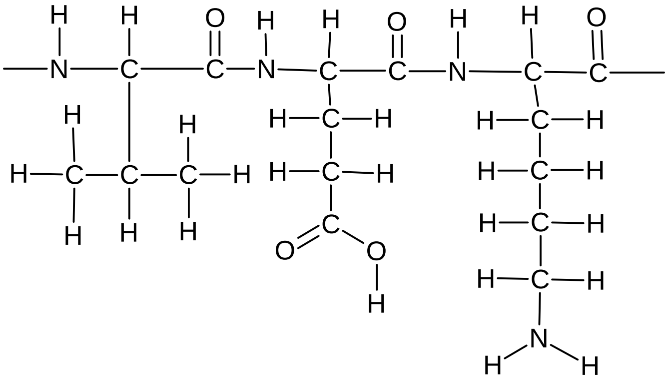
Quaternary structure refers to the specific orientation or spatial arrangement of polypeptide chains with respect to one another and the nature of interactions that stabilises this orientation. Haemoglobin consists of four separate polypeptide chains of two types: two α chains and two β chains. The haemoglobin molecule is nearly spherical with the four polypeptide chains packed closely together. Each polypeptide carries a haem group to form one of the four subunits in a molecule of haemoglobin. Each subunit folds and coils into a compact globular shape and joined together by van der Waals' forces, hydrogen bonds and ionic linkages.

(ii) A typical polypeptide chain of haemoglobin consists of 141 amino acids.

The R groups of 3 of the amino acids are given below.

amino acid	**formula of side chain (R in $RCH(NH_2)CO_2H$)**
glutamic acid	$-CH_2CH_2CO_2H$
valine	$-CH(CH_3)_2$
lysine	$-CH_2CH_2CH_2\,CH_2NH_2$

Use **all three** amino acids above to construct the displayed formula of a possible section of the polypeptide.



Displayed formula should be an open ended structure with N terminus of the left and C terminus on the right.

(iii) Uncoiling of the protein structure is favoured when temperature is higher than physiological conditions. With the aid of the equation,

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

suggest why this process is favoured at higher temperatures.

ΔH should be positive due to the overcome/disruption of various interactions (e.g. hydrogen bonding, disulfide bridges, van der Waals' forces, ionic linkages) between the R-groups of the constituent amino acids, which is an endothermic process.

ΔS should be positive when protein structure uncoils and increases in disorderliness.

In order for reaction to be spontaneous, ΔG has to be negative and it is favoured by high temperature.

[8]

(c) One molecule of haemoglobin can bind up to four molecules of oxygen, according to the following equation.

$$Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq) \qquad K_c = 3 \times 10^{20}\ mol^{-4}\ dm^{12}$$

(i) Write an expression for K_c for this reaction.

$$K_c = \frac{[Hb(O_2)_4]}{[Hb][O_2]^4}$$

(ii) Calculate the percentage of $Hb(O_2)_4$ in an Hb-$Hb(O_2)_4$ mixture when $[O_2] = 7.6 \times 10^{-6}$ mol dm^{-3}.

[3]

$$K_c = \frac{[Hb(O_2)_4]}{[Hb][O_2]^4}$$

$$3?\ 0^{20} = \frac{[Hb(O_2)_4]}{[Hb][7.6?\ 0^{-6}]^4}$$

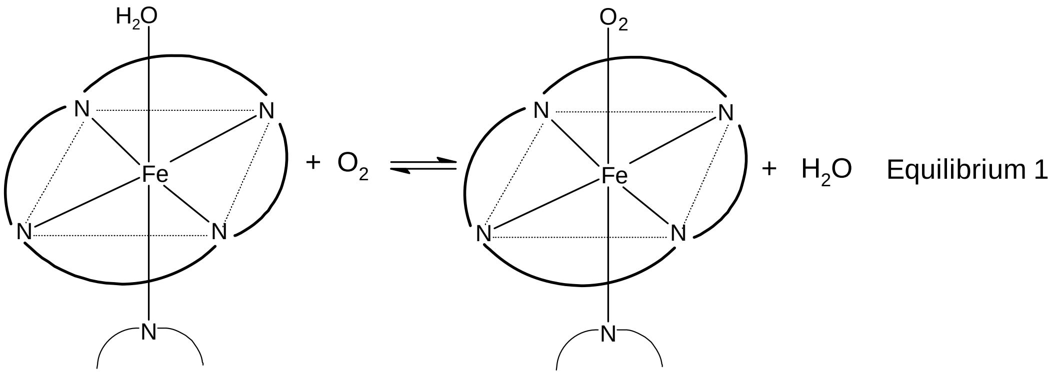
$$\frac{[Hb(O_2)_4]}{[Hb]} = 1.001 \quad [1/2]$$

Fraction of $Hb(O_2)_4$ in mixture = $\frac{[Hb(O_2)_4]}{[Hb(O_2)_4]+[Hb]}$

% of $Hb(O_2)_4$ = $\frac{1.001[Hb]}{1.001[Hb]+[Hb]} \times 100\%$ = 50%

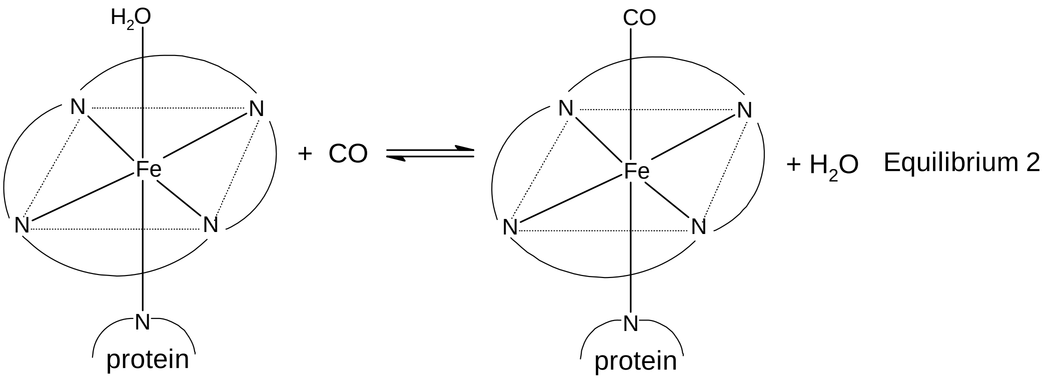
(d) **(i)** Carbon monoxide, CO, mainly causes adverse effects in humans by combining with haemoglobin to form carboxyhaemoglobin in the blood. This prevents haemoglobin from releasing oxygen in tissues, effectively reducing the oxygen-carrying capacity of the blood.

The equations below show the reactions of haemoglobin with oxygen and carbon monoxide respectively.



haemogloblobin

oxyhaemoglobin



haemoglobin carboxyhaemoglobin

CO is found to have 245 times more affinity for haemoglobin than O_2. Explain how excessive inhalation of CO will give rise to poisoning in the blood.

CO is a stronger ligand than H_2O (or O_2).

.

In the presence of CO, haemoglobin undergoes ligand exchange. CO displaces H_2O (or O_2) from haem to form carboxyhaemoglobin. Unlike H_2O and O_2, CO binds strongly and irreversibly to Fe as carboxyhaemoglobin is a more stable complex than oxyhaemoglobin.

(ii) Suggest a method for the treatment of carbon monoxide poisoning.

Treatment of carbon monoxide poisoning largely consists of administering pure / high concentration of oxygen so as to shift the position of equilibrium 1 to the right.

[3]

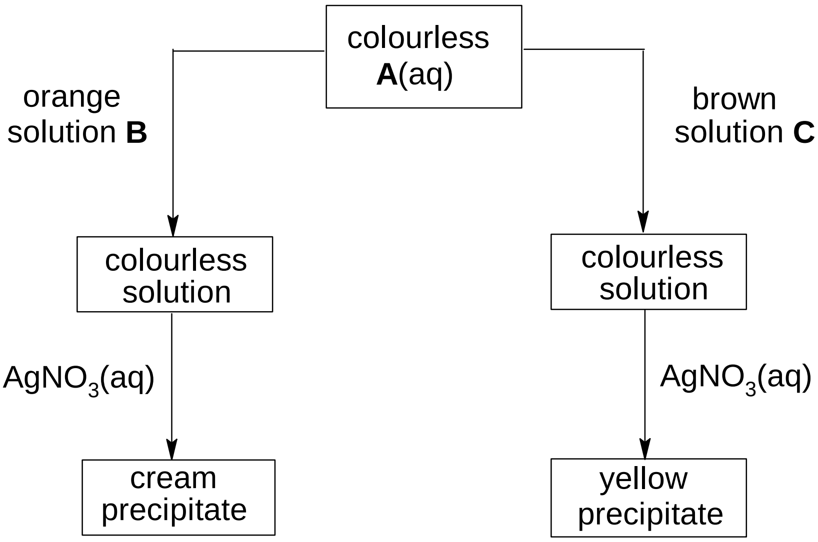
(e) Oxygen can be liquefied by pressure alone if its temperature is below the 'critical temperature' of -118°C. Above this critical temperature no amount of pressure will liquefy oxygen. Suggest a suitable value for the critical temperature of ammonia. Give your reasoning.

The critical temperature of a substance is determined by the strength of its intermolecular forces. Oxygen molecules are held together by weak intermolecular van der Waals' forces and so, it has a very low critical temperature. Below the critical temperature, this force is sufficiently strong to hold the molecules together (under some appropriate pressure) in a liquid. Above the critical temperature, the higher kinetic energy of the oxygen is sufficient to overcome the intermolecular forces of attraction. Ammonia molecules have hydrogen bonding between molecules that need to be overcome, which are stronger than the van der Waals' forces attraction. Therefore, critical temperature of ammonia > -118°C.

[3]

[Total: 20]

2 **(a)** The diagram below shows the reactions of a salt, **A**, in aqueous medium.



A has the following composition by mass:

K, 41.1%; S, 33.7%; O, 25.2%.

The relative formula mass, M_r, of **A** is 190.4. One formula unit of **A** contains only one type of anion.

(i) Determine the formula of the salt **A**.

Let the mass be 100g.

	K	S	O
Mass / g	41.1	33.7	25.2
Amount / mol	1.0512	1.0498	1.575
Ratio	1.0013	1.000	1.500
Simplest Ratio	2	2	3

Formula of salt is $K_2S_2O_3$.

(ii) Suggest the identities of **B** and **C**.

B: $Br_2(aq)$
C: $I_2(aq)$

(iii) By means of two ionic equations, show how the yellow precipitate is formed from **C**.

$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$
$I^-(aq) + Ag^+(aq) \rightarrow AgI(s)$

(iv) For the reaction of **A** and **B**, a titration was carried out to determine if the sulfur-containing product is $S_4O_6^{2-}$ or SO_4^{2-}.

It was found that 25.0 cm^3 of 0.200 mol dm^{-3} of **B** required 10.0 cm^3 of 0.125 mol dm^{-3} of **A** for complete reaction.

Use the data to determine the final oxidation state of sulfur in the product. Hence, write a balanced equation for the reaction of **A** and **B**.

25.0 x 0.200 mol of Br_2 ≡ 10.0 x 0.125 mol of **A**, $S_2O_3^{2-}$
4 mol of Br_2 ≡ 1 mol of $S_2O_3^{2-}$
4 mol of Br_2 ≡ 8 mol of e^- ≡ 1 mol of $S_2O_3^{2-}$

Each S atom will have a gain in O.S. by +4.

Final oxidation state of S = +2 + 4 = +6

$4Br_2 + S_2O_3^{2-} + 5H_2O \rightarrow 8Br^- + 2SO_4^{2-} + 10H^+$

(v) Construct a balanced equation for the reaction of **B** with hot aqueous potassium hydroxide.

$3Br_2(aq) + 6KOH(aq) \rightarrow 5KBr(aq) + KBrO_3(aq) + 3H_2O(l)$

[8]

(b) Pseudohalogens are a family of inorganic compounds which possess chemical properties similar to the halogens. Two examples of pseudohalogens are cyanogen $(CN)_2$ and thiocyanogen $(SCN)_2$.

The equations below represent the standard reduction potentials of cyanogen and thiocyanogen.

$(CN)_2 + 2H^+ + 2e^- \rightleftharpoons 2HCN$ $E^\ominus = +0.37$ V
$(SCN)_2 + 2e^- \rightleftharpoons 2SCN^-$ $E^\ominus = +0.77$ V

(i) Use the *Data Booklet* to predict what you would expect to observe when the following solutions are mixed. Write balanced equations for any reaction that occurs.

I $(CN)_2(aq)$ and $Br_2(aq)$

$(CN)_2 + 2H^+ + 2e \rightleftharpoons 2HCN$ $E^\ominus = +0.37$ V
$Br_2 + 2e \rightleftharpoons 2Br^-$ $E^\ominus = +1.07$V
Orange solution remains orange.
No reaction as both are oxidising agents.

II KSCN(aq) and acidified $KMnO_4$(aq)

$(SCN)_2 + 2e^- \rightleftharpoons 2SCN^-$ $E^\ominus = +0.77$ V
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ $E^\ominus = +1.52$ V

$E^\ominus_{cell} = -0.77 + (+1.52) = +0.75 \text{ V} > 0$,

Hence reaction is energetically feasible.

$10SCN^- + 2MnO_4^- + 16H^+ \rightarrow 5(SCN)_2 + 2Mn^{2+} + 8H_2O$

Purple solution of manganate(VII) decolourises.

(ii) A reaction occurs when an unknown metal, **D**, is added to $(SCN)_2$. The standard cell potential of the reaction is determined to be +0.43 V.

Use the *Data Booklet* to deduce the identity of metal **D**, showing your working clearly.

Reduction:
$(SCN)_2 + 2e^- \rightarrow 2SCN^-$ $E^\ominus_{red} = +0.77$ V

$E^\ominus_{cell} = E^\ominus_{ox}(Z/Z^{2+}) + E^\ominus_{red}((SCN)_2/SCN^-)$
$+0.43 = E^\ominus_{ox(}Z/Z^{2+}) + (+0.77)$
$E^\ominus_{ox}(Z/Z^{2+}) = -0.34$ V
$E^\ominus_{red}(Z^{2+}/Z) = +0.34$ V

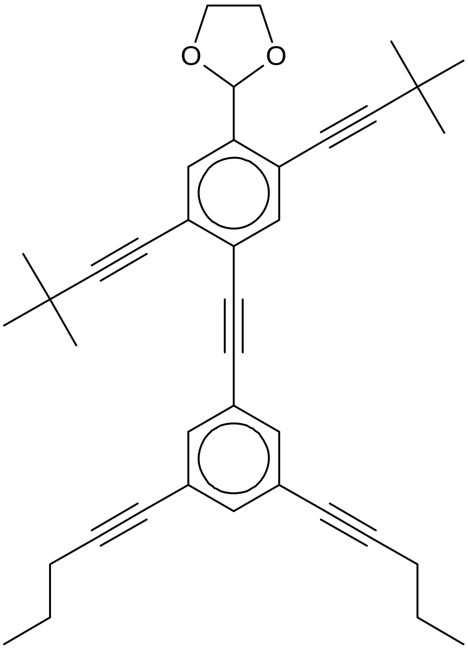
$Cu^{2+} + 2e^- \rightarrow 2Cu$ $E^\ominus_{red} = +0.34$ V

Hence, **D** is <u>copper</u>.

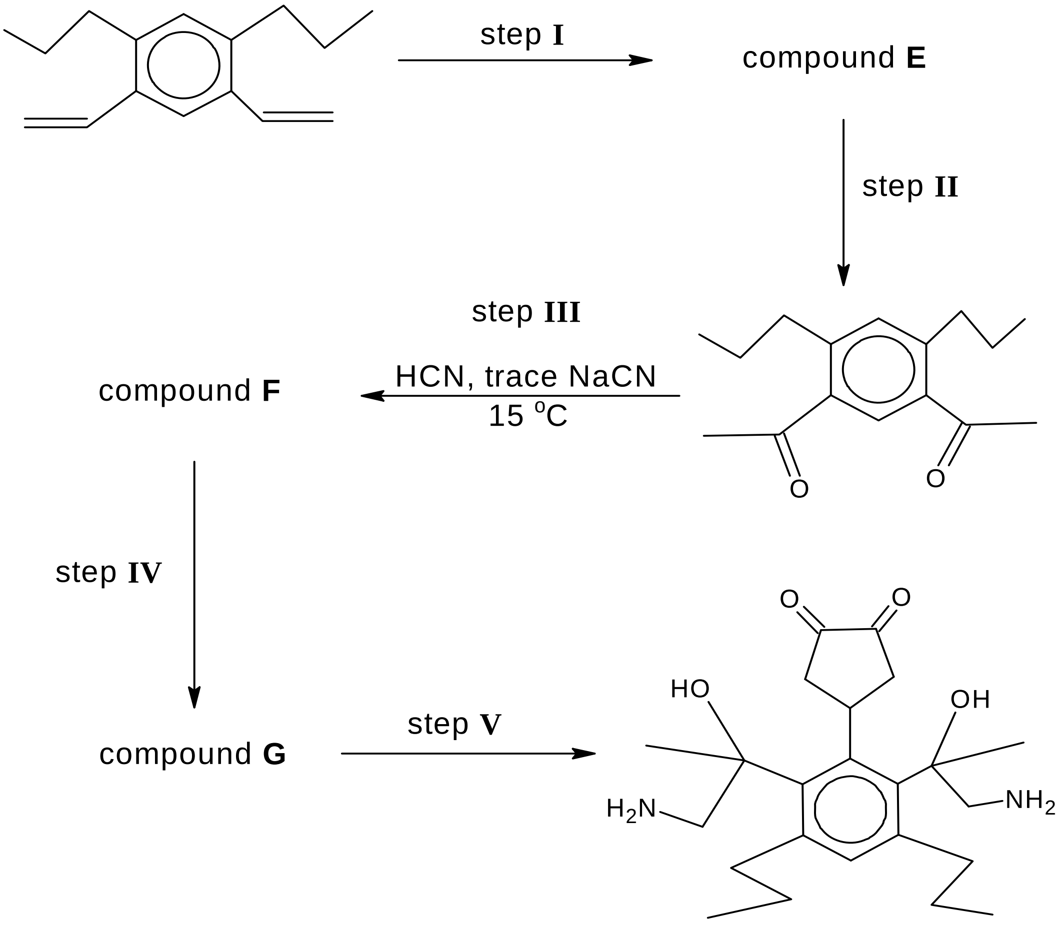
[5]

(c) NanoPutians are a family of organic molecules whose structural formulae resemble human forms. These compounds were designed and created by Dr James Tour from Rice University in 2003 as a part of a sequence of chemical education for young students.

One such molecule, named the NanoKid, is shown below.



Inspired by their discovery of the NanoPutians and a motivation to create a digital mascot for the school, a team of year two chemistry students from Pioneer Junior College devised the following reaction scheme to form “**Pion-mon**”.



"**Pion-mon**"

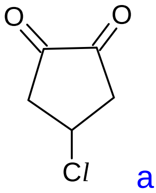
(i) Suggest reagents and conditions for steps **I**, **II**, **IV** and **V**.

Step **I**: $H_2O(g)$, H_3PO_4, 300°C, 60 atm
OR
concentrated H_2SO_4, followed by H_2O,heat

Step **II**: $K_2Cr_2O_7$, $H_2SO_4(aq)$, heat (note: $KMnO_4$ cannot be used!)

Step **IV**: $LiAlH_4$ in dry ether
OR
H_2, Ni, 200°C
OR
$NaBH_4$ in methanol

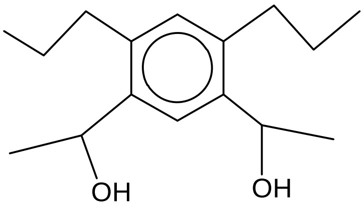
Step **V**:



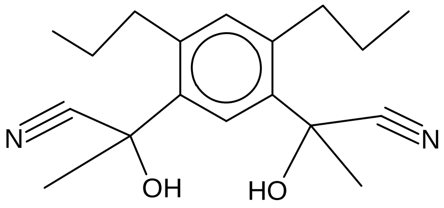
anhydrous $FeCl_3$, heat

(ii) Draw the structural formulae of compounds **E**, **F** and **G**.

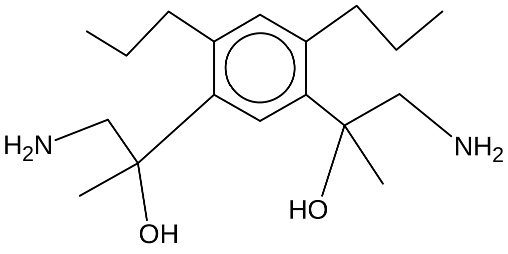
E:



F:



G:



[7]

[Total: 20]

3 **(a)** **(i)** Describe what you would see when separate samples of sodium and sulfur are burnt in air.

Na burns with orange flame, leaving behind a white residue of Na_2O.
S burns with blue flame, forming SO_2.

(ii) The oxides of sodium and sulfur resulting from the reactions in **(i)** both react with water. Write equations for these two reactions and describe the effect of the resulting solutions on Universal Indicator solution.

$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$
Solution of NaOH turns Universal Indicator solution purple.

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$
Solution of H_2SO_3 turns Universal Indicator solution red.

[4]

(b) Sulfurous acid is an aqueous solution of sulfur dioxide. Sulfurous acid, H_2SO_3, is a weak dibasic acid with $pK_1 = 2.15$ and $pK_2 = 7.21$.

(i) Calculate the pH of a 0.80 mol dm^{-3} solution of sulfurous acid (ignore the effect of pK_2 on the pH).

$[H^+] = \sqrt{K_1 \times \text{concentration}}$
$= \sqrt{10^{-2.15} \times 0.80}$
$= 0.0753$

pH = -lg (0.0753)
= 1.12

(ii) An amphiprotic species is one that reacts with an acid and a base. The pH of a solution containing an amphiprotic species is given by the following expression.

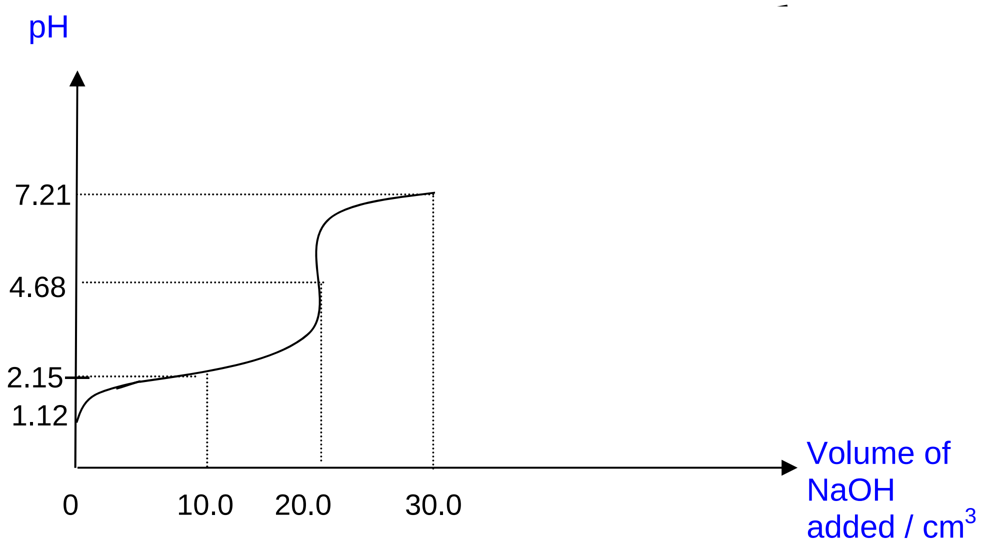
$$pH = ½(pK_1 + pK_2)$$

In the titration of H_2SO_3 with NaOH, an amphiprotic species is formed. Identify the amphiprotic species formed and calculate the pH of the solution.

Amphiprotic species formed = HSO_3^-

pH of the solution = (2.15 + 7.21)/2 = 4.68

(iii) Sketch the pH-volume added curve you would expect to obtain when 30 cm^3 0.40 mol dm^{-3} NaOH is added to 10.0 cm^3 of 0.80 mol dm^{-3} H_2SO_3. On your sketch, clearly mark the points you have calculated in **(i)** and **(ii)**.



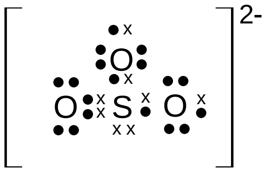
(iv) Suggest a suitable indicator from the following table to be used to detect the first equivalence point and state the colour change of the solution at this equivalence point.

indicator	pH range	acid solution	basic solution
bromocresol green	4 – 6	yellow	blue
bromothymol blue	6 – 8	yellow	blue
phenolphthalein	8 - 10	colourless	red

Bromocresol green
Colour change: yellow to green

(v) Draw the dot-and-cross diagram showing the electrons (outer shells only) in SO_3^{2-}, and use the VSEPR (valence shell electron pair repulsion) theory to predict its shape.

[9]



3 bond pairs and 1 lone pair
trigonal pyramidal

(c) The following two experiments **(I)** and **(II)** were carried out separately to determine enthalpy changes of neutralisation, ΔH_{neut}.

(I) 50 cm^3 of 0.80 mol dm^{-3} NaOH is mixed with 25 cm^3 of 0.80 mol dm^{-3} H_2SO_3 and the temperature rise was recorded as 6.7 ^oC.

(II) 50 cm^3 of 0.80 mol dm^{-3} NaOH is mixed with 50 cm^3 of 0.80 mol dm^{-3} HCl and the temperature rise was recorded as 5.5 ^oC.

Given that the specific heat capacity of solution is 4.18 J cm^{-3} K^{-1}, calculate the ΔH_{neut} for each of the two reactions and account for the difference between the two values.

For reaction of NaOH with H_2SO_3
Heat evolved = 75 x 4.18 x 6.7 = 2100 J
n(H_2SO_3) = 25/1000 x 0.80 mol =0.0200 mol
n(NaOH) = 50/1000 x 0.80 = 0.0400 mol

$2NaOH + H_2SO_3 \rightarrow Na_2SO_3 + 2H_2O$

n(H_2O) formed = 0.0400 mol

$\Delta H_{neut} = -2100/(0.04 \times 1000) = -52.5$ kJ mol^{-1}

For reaction of NaOH with HCl
Heat evolved = 100 x 4.18 x 5.5 = 2299 J
n(HCl) = 50/1000 x 0.80 mol =0.0400 mol
n(NaOH) = 50/1000 x 0.80 = 0.0400 mol

$NaOH + HCl \rightarrow NaCl + H_2O$

n(H_2O) formed = 0.0400 mol

$\Delta H_{neut} = -2299/(0.04 \times 1000) = -57.5$ kJ mol^{-1}

H_2SO_3 is a weak acid, some of the heat liberated from neutralisation is used to further dissociate H_2SO_3. Therefore the enthalpy change of neutralisation for **(I)** is less exothermic.

[4]

(d) State and explain how the acidities of propan-1-ol, propanoic acid and phenol compare with each other.

Acid strength: $CH_3CH_2CO_2H > C_6H_5OH > CH_3CH_2CH_2OH$
Stability of anion: $CH_3CH_2CO_2^- > C_6H_5O^- > CH_3CH_2CH_2O^-$

$CH_3CH_2CO_2^-$ is the most stable because of the greatest extent of delocalisation of the negative charge between the two electronegative oxygen atoms. Phenol is more acidic than propan-1-ol due to overlap of p orbital of single negatively charged O and the p-orbitals of benzene carbon, resulting in negative charge of

O delocalising into benzene ring, thus $C_6H_5O^-$ is more stable than $CH_3CH_2CH_2O^-$. Electron-donating propyl group intensifies the negative charge on the O, resulting in a less stable $CH_3CH_2CH_2O^-$.

[3]

[Total: 20]

4 Data concerning some elements of Group II of the Periodic Table, at 298 K, are given in the table. Further data may be found in the *Data Booklet*.

	Mg	Ca	Sr
$\Delta H_{\text{hydration}}$ of M^{2+} / kJ mol^{-1}	–1980	–1650	–1480
$\Delta S_{\text{hydration}}$ of M^{2+} / J mol^{-1} K^{-1}	–293	–238	–222
solubility of sulfate / mol dm^{-3}	1.8	4.7×10^{-2}	7.5×10^{-4}

(a) **(i)** Using the data provided, account for the trend of solubility of the Group II sulfates down the group.

$\Delta H_{\text{solution}}$ MSO_4 = - L.E + $\Delta H_{\text{hydration}}(M^{2+})$ + $\Delta H_{\text{hydration}}(SO_4^{2-})$

|lattice energy| $\propto \left|\dfrac{q_+ \times q_-}{r_+ + r_-}\right|$ and $r_- >> r_+$.

Magnitude of lattice energy of Group II sulfates decreases slightly down the group because of the large anionic radius of SO_4^{2-}. Thus, increase in cationic radius down the group has little effect on lattice energy.

Since the anion is common, $\Delta H^{\theta}_{\text{hyd}}(SO_4^{2-})$ is the same for $MgSO_4$ and $BaSO_4$.

With a smaller ionic radius, Mg^{2+} has a higher charge density than Ba^{2+}. Hence, $\Delta H^{\theta}_{\text{hyd}}(Mg^{2+})$ is more exothermic than $\Delta H^{\theta}_{\text{hyd}}(Ba^{2+})$, and $\Delta H^{\theta}_{\text{sol}}(MgSO_4)$ is more exothermic than $\Delta H^{\theta}_{\text{sol}}(BaSO_4)$. Down the group, solubility of sulfates decreases.

(ii) Calculate $\Delta G_{\text{hydration}}$ of Mg^{2+}, leaving your answer in kJ mol^{-1}.

$$\begin{aligned}\Delta G^{\theta}_{\text{hyd}} &= \Delta H^{\theta}_{\text{hyd}} - T\Delta S^{\theta}_{\text{hyd}} \\ &= -1980 - (298)(-293/1000) \\ &= \underline{-1890 \text{ kJ mol}^{-1}}\end{aligned}$$

[4]

(b) To separate the two Group II metal ions, Mg^{2+} and Sr^{2+}, a student added solid sodium carbonate, Na_2CO_3, slowly to a solution, which contains a mixture of 0.100 mol dm^{-3} $MgCl_2$ and 0.100 mol dm^{-3} $SrCl_2$.

[K_{sp} of $MgCO_3$ = 3.5×10^{-8} mol^2 dm^{-6}; K_{sp} of $SrCO_3$ = 1.1×10^{-10} mol^2 dm^{-6}]

(i) State which metal ion is precipitated first. Hence, calculate the concentration of carbonate ion in the solution, in mol dm^{-3}, needed for the first trace of precipitate to be seen.

As the 2 carbonates have the same formula type, the lower K_{sp} of $SrCO_3$ shows its lower solubility. Thus $\underline{Sr^{2+}}$ is precipitated first.

When $SrCO_3$ precipitates; ionic product ($SrCO_3$) = K_{sp} ($SrCO_3$)
$[Sr^{2+}][CO_3^{2-}] = 1.1\times10^{-10}$
$[CO_3^{2-}]_{min} = 1.1\times10^{-10} / 0.100 = \underline{1.10 \times 10^{-9} \text{ mol dm}^{-3}}$

(ii) Determine the concentration of this metal ion, in mol dm^{-3}, remaining in the solution when the other metal ion just starts to precipitate.

As $MgCO_3$ starts to precipitate, ionic product ($MgCO_3$) = K_{sp} ($MgCO_3$)
$[CO_3^{2-}] = 3.5 \times 10^{-8} / [Mg^{2+}]$
$= 3.5 \times 10^{-8} / 0.1 = \underline{3.5 \times 10^{-7} \text{ mol dm}^{-3}}$
$\therefore$ $[Sr^{2+}]$ remaining in solution = $1.1\times10^{-10} / 3.5 \times 10^{-7}$
= 3.14×10^{-4} mol dm^{-3}

(iii) For an effective separation, less than 1% of this metal ion should remain in solution.
By means of calculation, determine if the above separation is effective.

% of Sr^{2+} remained in solution = $3.143 \times 10^{-4} / 0.100 \times 100$ %
= 0.314 % < 1%
Separation is effective.

[4]

(c) When magnesium chloride is added to water, a solution is formed which has a pH of 6.5. When aluminium chloride is added to water, the resulting solution has a pH of 3. With the aid of equations, explain the difference in observations.

[3]

Dissolution
$MgCl_2(s) + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$

Hydrolysis
$[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H^+(aq)$

Dissolution
$AlCl_3(s) + 6H_2O \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

Hydrolysis

$[Al(H_2O)_6]^{3+}$ (aq) $\rightleftharpoons$ $[Al(H_2O)_5(OH)]^{2+}$ (aq) + H^+(aq)

Al^{3+} has higher charge density than Mg^{2+}, thus undergoes greater extent of hydrolysis to release more H^+, thus pH is lower.

(d) Compound **L**, $C_5H_7O_2N$, is a cyclic compound which is optically active and neutral.

On heating **L** with aqueous NaOH, a pungent gas that turned moist red litmus blue was liberated. Upon acidification of the reaction mixture with aqueous HC*l*, **M**, $C_5H_8O_4$, was formed.

M reacts with LiA*l*H$_4$ to form **N**, $C_5H_{12}O_2$. On passing over hot Al_2O_3, **N** forms **P**, C_5H_8. **P** decolourises aqueous Br_2. When **P** is heated with acidified $KMnO_4$ solution, **Q,** $C_3H_4O_3$ is formed, together with effervescence that forms a white precipitate with limewater.

Q reacts with aqueous Na_2CO_3 with effervescence and forms a yellow precipitate when warmed with alkaline aqueous I_2.

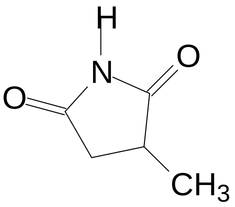
Given that compounds **M, N, P** are **Q** are all non-cyclic compounds, deduce the structures of compounds **L, M, N, P,** and **Q**, and explain the chemistry of the reactions described.

[9]

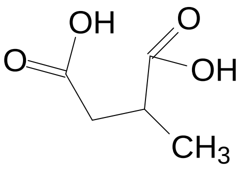
Information / Type of reaction	**Deductions**
Compound **L**, $C_5H_7O_2N$, is a cyclic neutral compound which is optically active.	As **L** contains N and is neutral, **L** is likely to be amide. **L** contains at least 1 chiral carbon.
L undergoes alkaline hydrolysis with aqueous sodium hydroxide to form compound **M.** Upon acidification with aqueous hydrochloric acid, $C_5H_8O_4$.	Gas that turns moist red litmus blue is NH_3(g). **L** is cyclic amide. (cyclic – thus only 1 product) **M** is carboxylic acid (formed from hydrolysis of amide).
M is reduced by LiA*l*H$_4$ to form **N**, $C_5H_{12}O_2$.	**N** is primary alcohol.
N undergoes elimination of H_2O with hot Al_2O_3, to form **P**, C_5H_8. **P** undergoes electrophilic addition with bromine**.**	**P** contains alkene.

When **P** undergoes oxidative cleavage with acidified potassium manganate to form **Q,** $C_3H_4O_3$, together with effervescence that forms a white precipitate with limewater.	Gas evolved is CO_2**.** As there is a loss of two carbon atoms, **P** contains two terminal alkenes $=CH_2$.
Q undergoes acid-base reaction with $Na_2CO_3(aq)$.	**Q** contains a carboxylic acid**.**
Q undergoes oxidation with alkaline aqueous iodine to form a yellow precipitate.	**Q** contains CH_3CO- group.

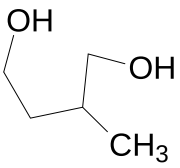
[Total: 20]



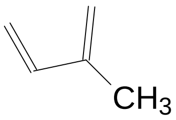
L



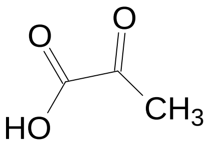
M



N



P



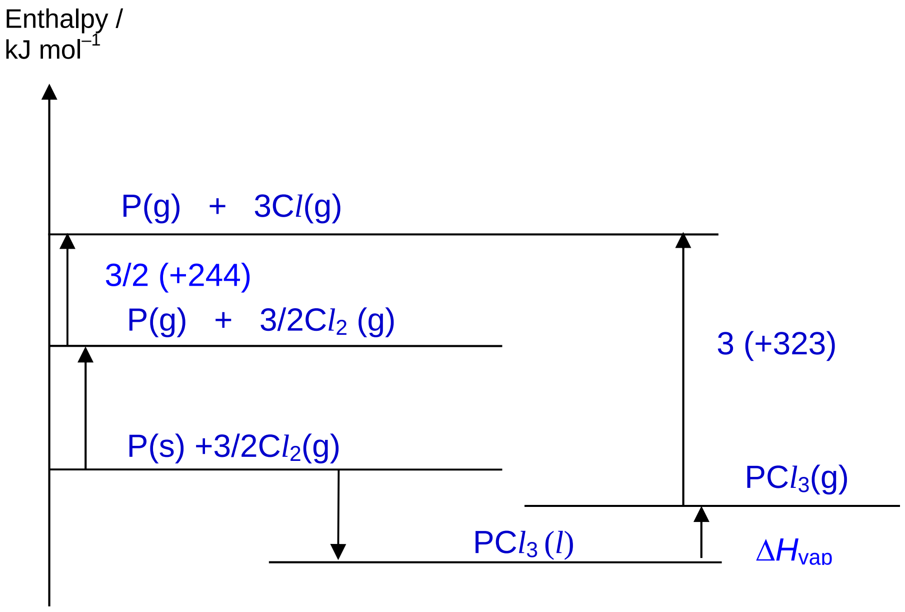
Q

5 **(a)** Phosphorus trichloride can be prepared by the reaction of white phosphorus with chlorine. Some related thermochemical data are shown below.

enthalpy change of formation of $PCl_3(l)$	–320 kJ mol^{-1}
bond energy of P−C*l* bond in PCl_3	+323 kJ mol^{-1}
enthalpy change of atomisation of phosphorus	+314 kJ mol^{-1}

Using the above data, together with relevant data from the *Data Booklet*, construct an energy level diagram to determine the enthalpy change of vaporisation of $PCl_3(l)$.

[4]



-320 = 314 + 3/2(244) –3 (+323)-ΔH_{vap} PCl_3 (l)

$\therefore$ ΔH_{vap} PCl_3 (l)= +31.0 kJ mol^{-1}

(b) **(i)** Carbon and silicon are both elements of Group IV. Each forms a tetrachloride. CCl_4 has no reaction with water while SiCl_4 reacts violently with water. Briefly account for the difference in behaviour with water.

Either CCl_4 has no reaction with water because C atom has no available low-lying d orbitals to form dative/ co-ordinate bonds with water molecules.

OR

Si atom in SiCl_4 has available low-lying empty d-orbitals, which can accept lone pair of electrons from water molecules, allowing dative bond formation between H_2O and Si before the Si-Cl bond needs to be broken.

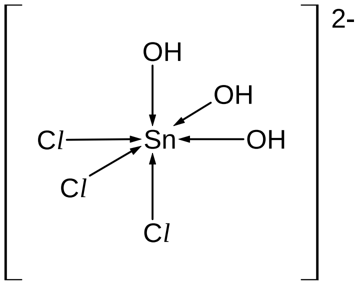
(ii) Tin is another element in Group IV.

When tin(IV) chloride reacts with potassium hydroxide in a small amount of water, potassium chloride is produced, together with an anhydrous salt **R** having the formula of $K_2SnCl_3O_3H_3$.

R is an ionic salt. One formula unit of **R** contains one type of anion and one type of cation.

Suggest the formula of the anion present in **R**. Hence, draw a possible structure of the anion.

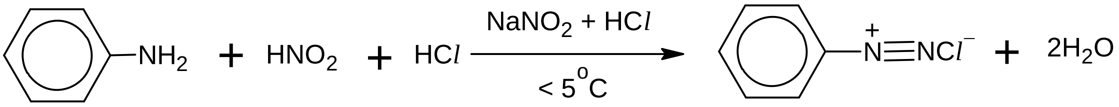
Formula of anion in R: $[SnCl_3O_3H_3]^{2-}$



[3]

(c) Diazonium salts are important intermediates in the synthesis of many other substituted aromatic compounds. The following equation shows the formation of phenyldiazonium chloride.

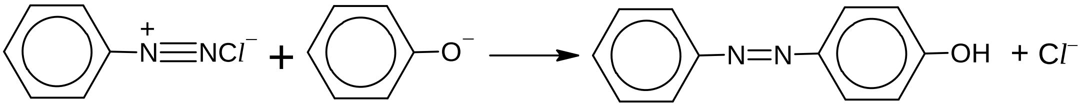
<u>reaction **1**</u>



phenyldiazonium chloride

Azo dyes are common organic compounds which can be synthesised from diazonium salts. They are often brightly coloured due to the presence of the chromophore functional group, -N=N-. The following reaction shows how one such azo dye can be manufactured.

<u>reaction **2**</u>

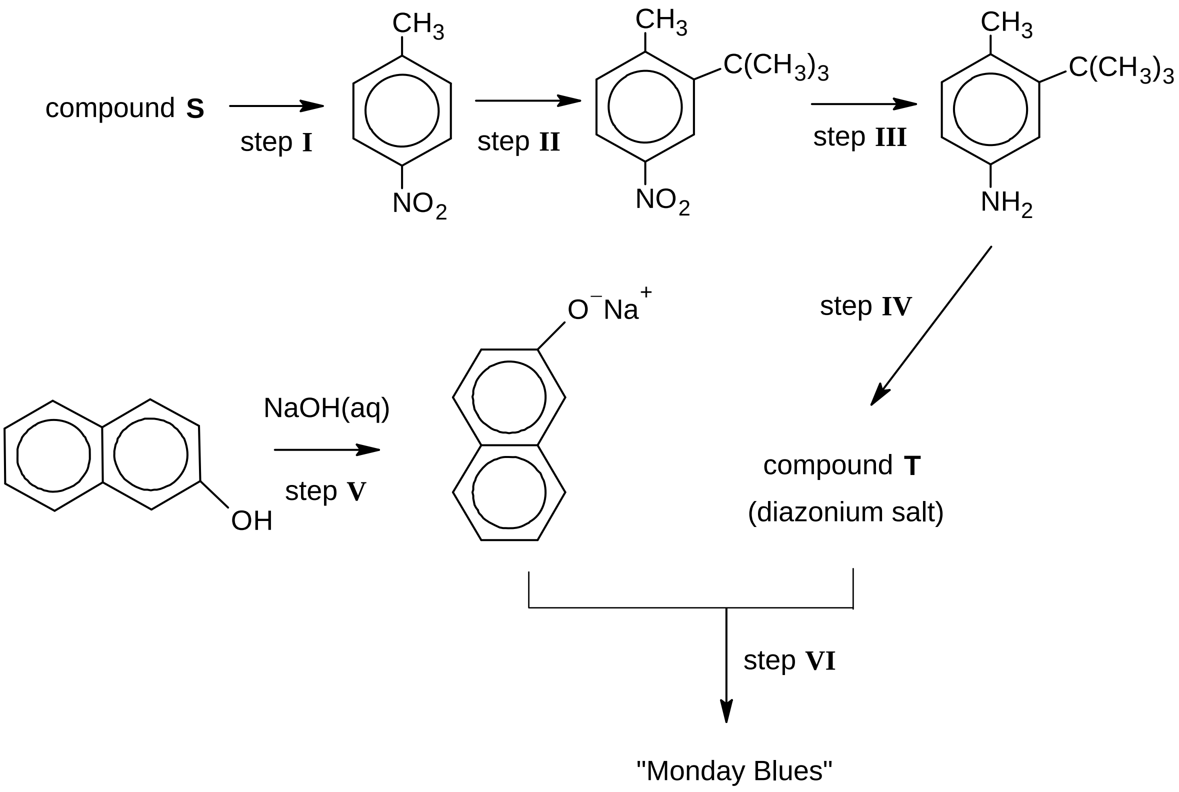


azo compound

(i) State the type of reaction that occurs in reaction **2**.

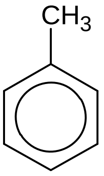
Electrophilic substitution

A research chemist is tasked to create new azo dyes. Using reaction **1** and **2**, he proposed the following reaction scheme to a new azo dye named “Monday Blues”.

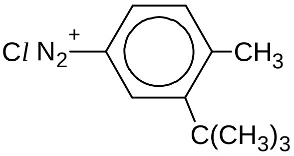


(ii) Suggest the structures of compounds **S**, **T**, and “Monday Blues”.

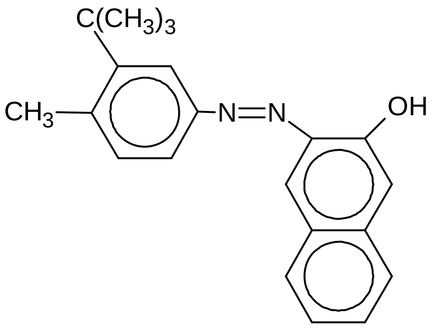
S:



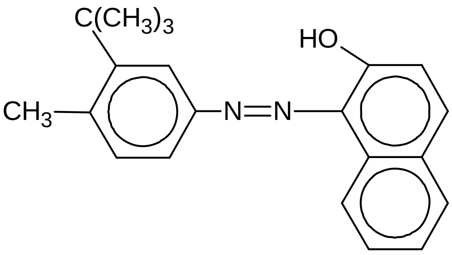
T:



“Monday Blues”:



OR



(iii) Give the reagents and conditions for steps **I**, **II** and **III**.

Step **I**: concentrated H_2SO_4, concentrated HNO_3, 30°C

Step **II**: $(CH_3)_3CCl$, anhydrous $FeCl_3$, heat

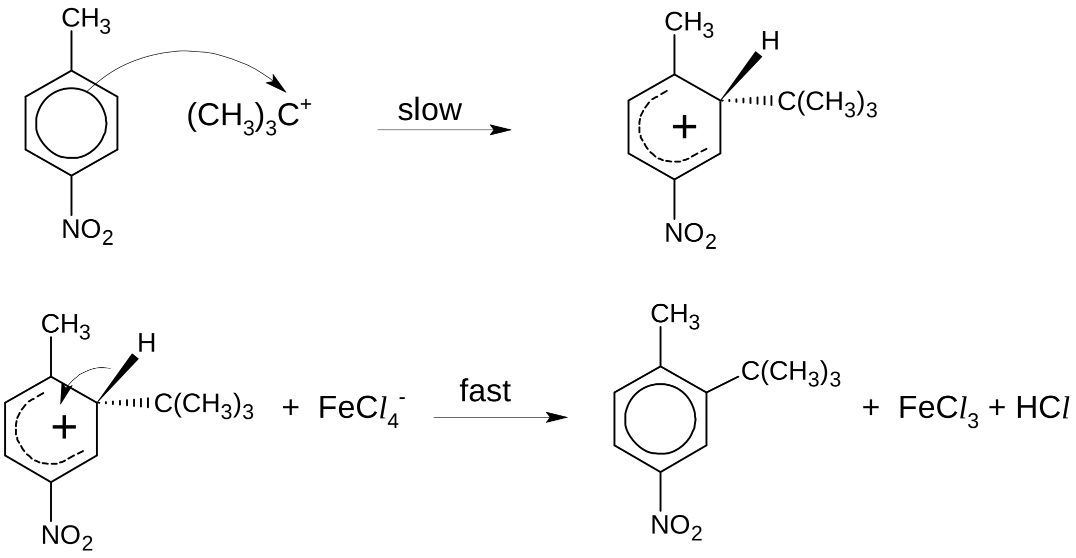
Step **III**: Sn, concentrated HC*l*, heat, followed by NaOH(aq)

(iv) Give a mechanistic account for the reaction in step **II**.

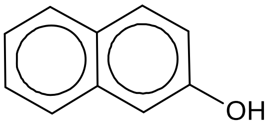
[9]

Electrophilic substitution

$$(CH_3)_3CCl + FeCl_3 \rightleftharpoons (CH_3)_3C^+ + FeCl_4^-$$

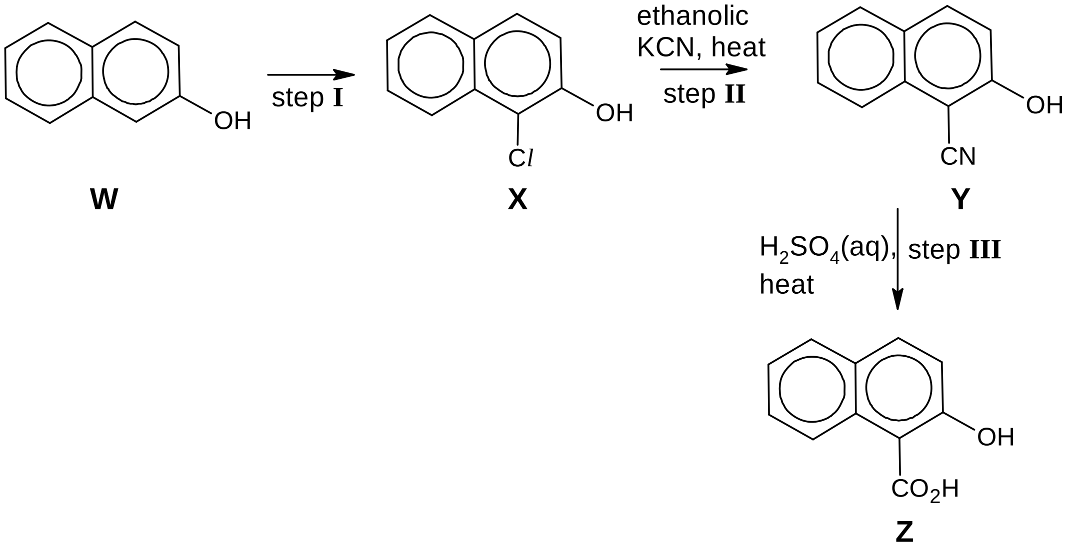


(d) 2-naphthol is a compound used in the synthesis of “Monday Blues” in **(c)**.



2-naphthol

A research assistant proposed to synthesise compound **Z**, a precursor to a drug, starting from 2-naphthol, compound **W**, by the following route.



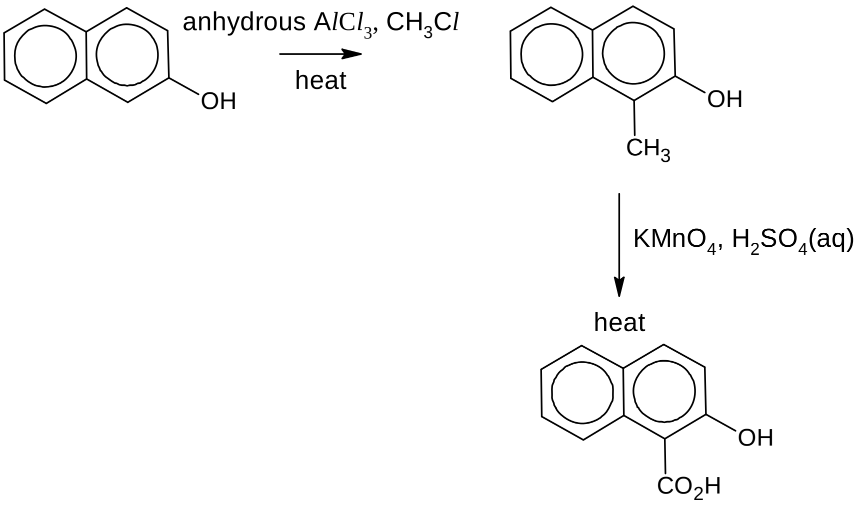
(i) Give the reagents and conditions for step **I**.

Cl_2 in CCl_4

(ii) The reaction scheme proposed by the research assistant above failed to give the desired product. Suggest an explanation for this.

Step **II** will fail because X is an aryl halide, which does not undergo nucleophilic substitution under normal conditions because the C-C*l* bond is strong (with partial double bond character) due to the overlapping of the p-orbital of C*l* with p orbitals of benzene ring.

(iii) Suggest a 2-step synthetic route to form compound **Z,** starting from compound **W**, 2-napthol.



[4]

[Total: 20]

End of paper