ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	**1 9 S**

CHEMISTRY

9729/03

Paper 3 Free Response

16 September 2020

2 hours

Candidate answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

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

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

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** the questions.

Section B

Answer **one** question.

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

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

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

For Examiner's Use		
Q1		**19**
Q2		**19**
Q3		**22**
Q4/5		**20**
Total		**80**

Section A

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

1 Elements in Group 17 are known as halogens. The term "halogen" means "salt-former" in Greek because these elements will readily react with alkali metal and alkaline earth metals to form important halide salts such as sodium chloride.

(a) Describe and explain how the volatilities of the halogens vary down Group 17. [2]

The volatility of the halogens decreases down the group. The halogens are non-polar simple covalent molecules held by instantaneous dipole-induced dipole interactions between the molecules. Due to the increasing size of the electron cloud of the halogens down the group, the id-id is stronger, which requires more energy to overcome.

……

(b) The table below shows the results of experiments in which the halogens, $\mathbf{X}_2$, $\mathbf{Y}_2$ and $\mathbf{Z}_2$ were added to separate aqueous solutions containing $\mathbf{X}^-$, $\mathbf{Y}^-$ and $\mathbf{Z}^-$ ions. The possible identities of the halogens are chlorine, bromine and iodine.

	$\mathbf{X}^-$ (aq)	$\mathbf{Y}^-$ (aq)	$\mathbf{Z}^-$ (aq)
$\mathbf{X}_2$	-	no reaction	$\mathbf{Z}_2$ formed
$\mathbf{Y}_2$	$\mathbf{X}_2$ formed	-	$\mathbf{Z}_2$ formed
$\mathbf{Z}_2$	no reaction	no reaction	-

(i) Based on the results in the given table, identify $\mathbf{X}_2$, $\mathbf{Y}_2$ and $\mathbf{Z}_2$. Explain your answer. [1]

X_2 is bromine, Y_2 is chlorine, Z_2 is iodine,

Y_2 is the strongest oxidising agent since it can oxidised both X^- and Z^-.

X_2 is a stronger oxidising agent that Z_2, since it can oxidised Z^-.

(ii) Describe and explain how the solubility of the solid silver halides, AgC*l*, AgBr and AgI, is affected by adding concentrated NH_3. [3]

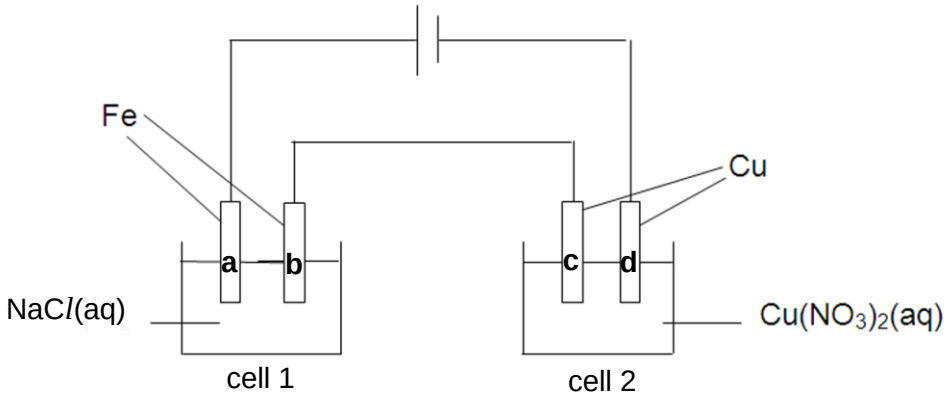
Upon addition of conc NH_3, the solubility increases due to the formation of soluble complex $[Ag(NH_3)_2]^{2+}$, which decreases the $[Ag^+]$ and ionic product.

White solid AgC*l* is soluble and cream solid AgBr is (partially) soluble, as $IP<K_{sp}$.

Yellow solid AgI is insoluble because it has the lowest K_{sp}, such that $IP>K_{sp}$.

……

(c) A student was presented the following set-up, which involved sodium chloride solution in one half-cell.



The student predicted the following:

- Hydrogen is produced at the cathode of cell 1 when concentrated or dilute sodium chloride solution is used.
- The anode of cell 2 would increase in mass.

(i) State which electrode, **a** to **d**, is the cathode of cell 1 and which is the anode of cell 2. [1]

Cathode: **b**

Anode: **c**

(ii) Do you agree with **each** of his prediction? Explain your answer. [3]

You should use relevant $E^{\ominus}$ values from the *Data Booklet* for cell 1.

For cell 1,

at cathode: $Na^+ + e^- \rightarrow Na$ $E^{\ominus} = -2.71$

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^{\ominus} = -0.83$

Water is preferentially reduced to hydrogen even with high concentration of Na^+ due to its much less negative in $E^{\ominus}$/large difference in $E^{\ominus}$. Hence, I agree with this prediction.

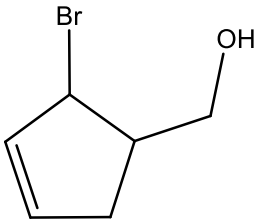
For cell 2,

At anode: $Cu \rightarrow Cu^{2+} + 2e^-$ $E^{\ominus} = +0.34$

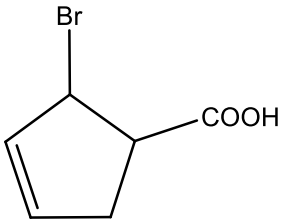
When an electric current is applied, copper at the anode is oxidised to Cu^{2+}. Hence the mass of the electrode/anode decreases, not larger. I do not agree with his prediction

……

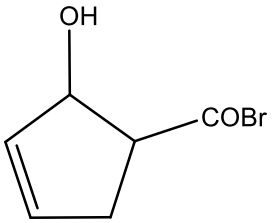
(d) Organohalogens are organic compounds that contain halogen atoms. The following compounds are examples of organohalogens.



A



B



C

(i) Suggest and explain how the acidity of compound **A** might compare with that of compound **B**. [2]

A is less acidic than **B**.

The negative charge on the conjugate base of **C** is delocalised over two electronegative oxygen atoms of the O-C=O bond. Hence, the negative charge is dispersed and the carboxylate ion is more stable.

OR

The electron-donating alkyl group intensifies the negative charge on the conjugate base of **A** and the alkoxide ion is less stable.

(ii) Describe and explain the relative reactivity of compounds **A** and **C** with respect to hydrolysis. [2]

C undergoes hydrolysis faster than **A**.

The carbon of the acyl bromide in **C** is more electron deficient as it is bonded to 2 highly electronegative atoms O and Br, whereas the carbon of the C-Br in **A** is bonded to only 1 electronegative Br. Thus in C, the carbon attracts nucleophiles most strongly.

(iii) Suggest a simple chemical test to distinguish compounds **B** and **C**. State the observation and write equation(s) to explain the reactions that happened. [3]

Test: $AgNO_3(aq)$

For **B**: no cream ppt formed

For **C**: cream/pale yellow ppt formed

$RCOBr + H_2O \rightarrow RCOOH + HBr$

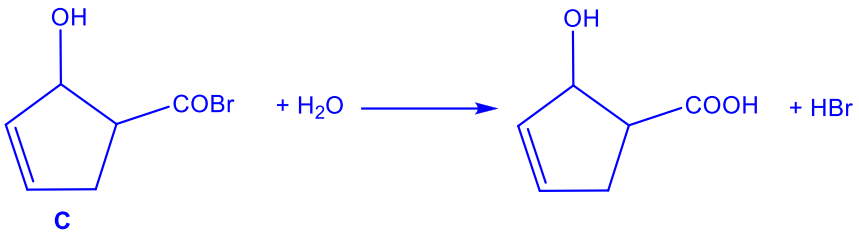
$Ag^+ (aq) + Br^- (aq) \rightarrow AgBr (s)$

OR

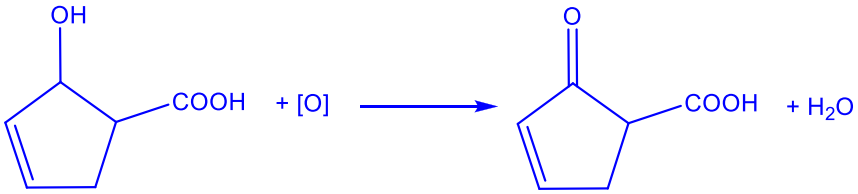
Test: $K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat

For **B**: orange solution remained

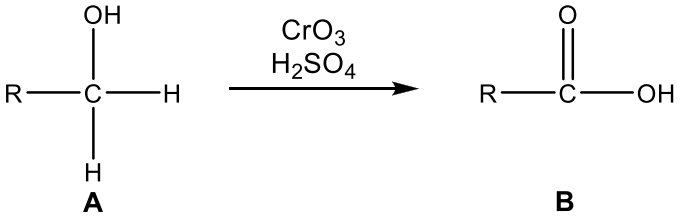
For **C**: orange solution turned green



C

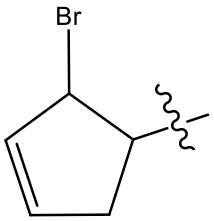


Jones oxidation can be used to oxidise compound **A** to compound **B**. Jones reagent uses chromium trioxide dissolved in sulfuric acid, to form chromic (VI) acid, $HCrO_4^-$. During the reaction, $HCrO_4^-$ is reduced to Cr^{3+}.



A **B**

where R is



(iv) Determine the change in oxidation number for the carbon atom that is directly bonded to oxygen atom in compounds **A** and **B**. [1]

For **A**: -1

For **B**: +3

Change in OS: +4

(v) Hence, using oxidation numbers, construct a balanced equation for this reaction. You should use RCH_2OH and RCO_2H to represent compounds **A** and **B** respectively. [1]

Since C OS +4, while Cr OS -3,

$4HCrO_4^- + 3RCH_2OH \rightarrow 4Cr^{3+} + 3RCO_2H$

$4HCrO_4^- + 3RCH_2OH + 16H^+ \rightarrow 4Cr^{3+} + 3RCO_2H + 13H_2O$

……

[Total: 19]

2 Ozone, O_3, is a powerful oxidising agent that can destroy viruses and bacteria. Ozone is used to disinfect water and sterilise food.

(a) To generate ozone for industrial use, electricity is passed briefly through oxygen gas. Some oxygen molecules decompose to form oxygen atoms, which collide with more oxygen gas to form ozone, until an equilibrium is reached.

$$3O_2\ (g) \rightleftharpoons 2O_3\ (g)$$

(i) Draw a dot-and-cross diagram to show the bonding present within an ozone molecule and suggest a value for its bond angle. [2]

Accept a bond angle between 110 to 119° (inclusive)

(ii) Write an expression for K_p for this equilibrium. [1]

$$K_p = \frac{(P_{O_3})^2}{(P_{O_2})^3}$$

(iii) The value of K_p under a particular set of industrial conditions is 5×10^{-8}. [2]

Deduce the sign and magnitude for ΔG at these conditions.

Since $K_p << 1$, position of equilibrium lies largely to the left and there is much more reactants than products, ΔG is positive and has a high magnitude.

(iv) Predict and explain the effect of compressing the volume of the reaction mixture on the yield of ozone. [2]

When V is decreased, P is increased. Position of equilibrium shifts right to decrease the amount of gaseous particles so as to decrease the pressure. Hence, this is done to increase the yield of ozone.

……

(b) The concentration of ozone in a sample of disinfectant can be determined by its reaction with alkaline potassium iodide. [3]

$$O_3 + 2I^- + H_2O \rightarrow I_2 + 2OH^- + O_2$$

The iodine formed can be estimated by its reaction with sodium thiosulfate.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

- 5 cm^3 of disinfectant concentrate was diluted with water to make 1 dm^3 of diluted disinfectant solution.
- 25.0 cm^3 of the diluted disinfectant solution was reacted with excess potassium iodide.
- The resultant mixture was titrated with 0.0100 mol dm^{-3} sodium thiosulfate. 22.40 cm^3 of sodium thiosulfate was required to reach end-point.

Calculate the concentration of ozone in the 5 cm^3 disinfectant concentrate.

Amt of I_2 = ½ x 0.0100 x (22.40/1000) = 1.12 x 10^{-4} mol

Amt of O_3 in 25 cm^3 = 1.12 x 10^{-4} mol

Amt of O_3 in 1 dm^3 = 1.12 x 10^{-4} / 25 x 1000 = 4.48 x 10^{-3} mol

$[O_3]$ = 4.48 x 10^{-3} / (5/1000) = 0.896 mol dm^{-3}

……

(c) Besides ozone, another active ingredient of ozone-based disinfectants is phosphorous pentachloride, PCl_5. PCl_5 is added to prolong the shelf life of the disinfectant. [2]

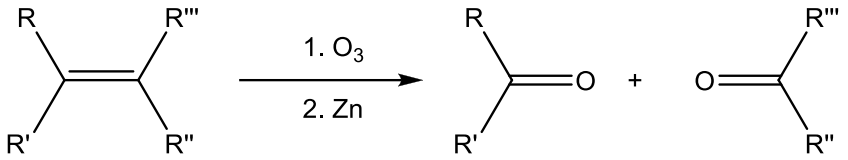
Write an equation for the reaction of PCl_5 with water. Hence, explain why PCl_5 undergoes hydrolysis readily with water.

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

P has empty and energetically accessible 3d orbitals to accept lone pair of electrons from water.

……

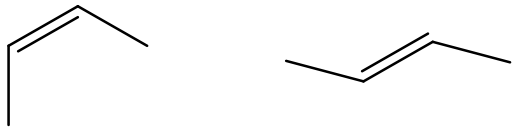
(d) Carbonyl compounds can be formed from alkenes through a reaction with ozone and zinc. This is known as ozonolysis.



R, R', R'' and R''' = H or alkyl or aryl

(i) Ozonolysis of alkene **D** produces ethanal as the only organic product. [1]

Draw and label the stereoisomers of alkene **D**.



cis trans

(ii) Compound **E**, $C_{10}H_{10}$, has a benzene ring and undergoes ozonolysis with ozone and zinc to form compound **F**, $C_{10}H_{10}O_2$. [6]

F gives a yellow precipitate when reacted with alkaline aqueous iodine. **F** forms a silver mirror with Tollens' reagent, but does not react with Fehling's solution.

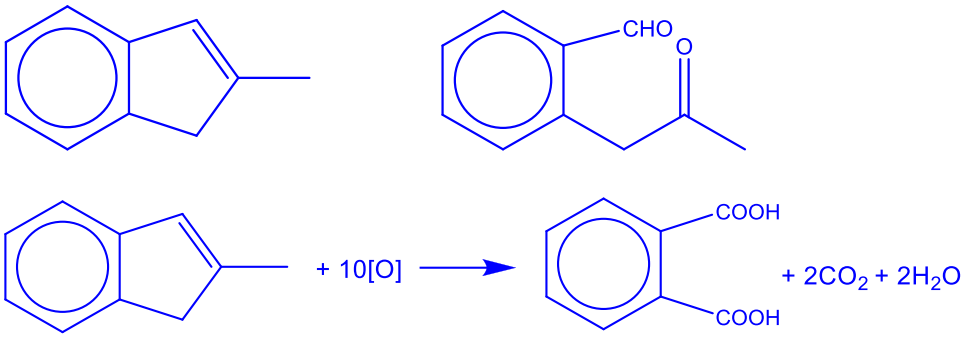
When **E** and **F** is heated with acidified potassium (VII) manganate, the same compound **G** is produced.

Deduce the structures of compounds **E** and **F**.

Write a balanced equation for the reaction of **E** to form **G**.

E ozonolysis → **F** $C_{10}H_{11}$ $C_{10}H_{10}O_2$	**E** is a cyclic alkene (only gives ONE product **F**). **F** has 2 carbonyl groups
F gives yellow ppt with idoform test	Oxidation **F** is a methyl ketone
F gives silver mirror with Tollen's reagent, but does not form ppt with Fehling's.	Oxidation **F** is a benzaldehyde
E or **F** + $KMnO_4$ → **G**	Oxidation

E **F**



G

.....

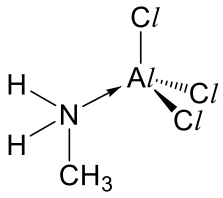
[Total: 19]

3 **(a)** Amines are Lewis bases. [2]

Explain what is meant by this statement. Illustrate your answer with an equation for a suitable reaction of an amine of your choice.

Amines are electron pair donors.

$CH_3NH_2 + AlCl_3 \rightarrow$



.....

(b) In an experiment, 50.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid is added to 50.0 cm^3 of 2.00 mol dm^{-3} ethylamine. The temperature increased from 26.0°C to 31.5°C.

The heat transfer for this reaction is 85% efficient.

(i) Calculate ΔH_r for the reaction. [2]

Assume that the specific heat capacity of the solution is 4.2 J g^{-1} K^{-1} and that the density of the solution is 1.0 g cm^{-3}.

HCl (aq) + $CH_3CH_2NH_2$ (aq) → $CH_3CH_2NH_3Cl$ (aq)

heat released (85%) = $mc\Delta T$ = (50 + 50)(4.2)(5.5) = 2310 J

heat released (100%) = $\frac{2310}{0.85}$ = 2717 J

Amt of HCl = 0.05 mol

Amt of amine = 0.10 mol

HCl is the limiting agent

ΔH_r = -2717/0.05 = - 54.3 x10^3 J mol^{-1} = -54.3 kJ mol^{-1}

(ii) Suggest and explain how the enthalpy change of reaction in **(i)** would differ when hexylamine is used in place of ethylamine. [1]

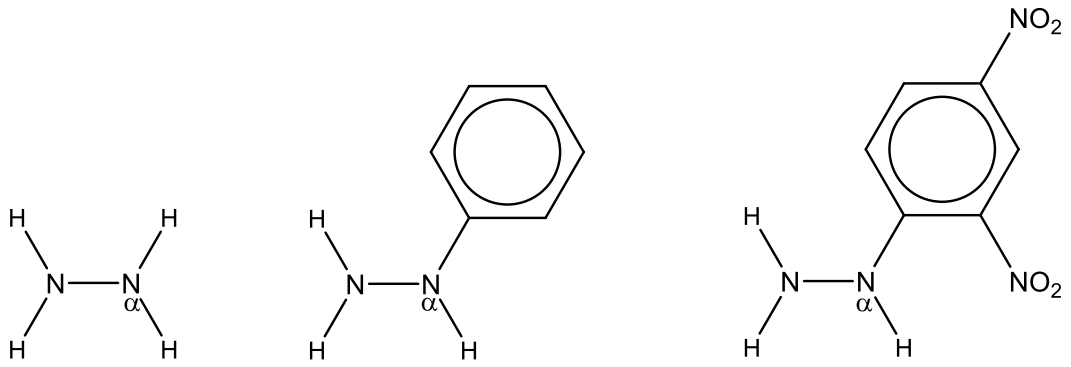
The enthalpy change of neutralisation/reaction is more exothermic with hexylamine since hexylamine is a stronger base than ethylamine. M

OR

The enthalpy change of neutralisation/reaction is about the same with hexylamine since hexylamine and ethylamine are primary amines, and should have the same basicity.

.....

(c) Hydrazine is a key building block for the preparation of many heterocyclic compounds via condensation. It is also a precursor to several pharmaceuticals including phenylhydrazine and 2,4-dinitrophenylhydrazine.



hydrazine phenylhydrazine 2,4-dinitrophenylhydrazine

(i) Describe and explain the relative basicities of the α-labelled nitrogen atom for hydrazine, phenylhydrazine and 2,4-dinitrophenylhydrazine in the gas phase. [3]

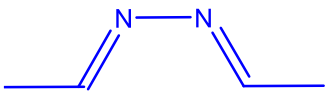
Decreasing basicity: hydrazine > phenylhydrazine > 2,4-DNPH

For phenylhydrazine and 2,4-DNPH, the lone pair of electrons on the nitrogen atom can delocalised into the benzene ring. Hence, it is less available for donation to H^+ and they are weaker bases than hydrazine.

For 2,4-DNPH, the 2 electron-withdrawing NO_2 further decreases the availability of the lone pair of electrons on N for donation to H^+. Hence, 2,4-DNPH is a weaker base than phenyl hydrazine.

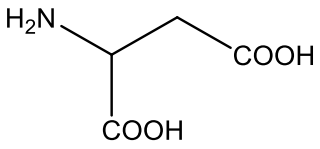
(ii) Two moles of ethanal react with 1 mole of hydrazine to form compound **H**. [1]

Draw the **skeletal** formula for **H**.



.....

(d) Amino acids is another class of compounds that possess the amine functional group. Research has suggested that supplements containing essential amino acids can help reduce inflammation in patients suffering from liver disease. An example of an essential amino acid is aspartic acid.



(i) Crystals of aspartic acid has a melting point of 270°C. [2]

Explain why the melting point of aspartic acid is much higher than that of 4-hydroxybutanoic acid (48°C).

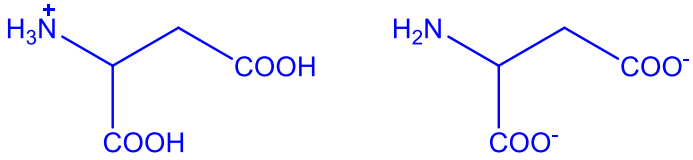
Aspartic acid exists as zwitterions. It has a giant ionic structure with strong ionic bonds between the zwitterions. Hydroxyethanoic acid is a simple covalent molecule with weak intermolecular hydrogen bonds. More energy is required to overcome the stronger ionic bonds between zwitterions than the intermolecular hydrogen bonds between hydroxyethanoic acid molecules. Hence glycine has a higher melting point. M

There are three pK_a values associated with aspartic acid:

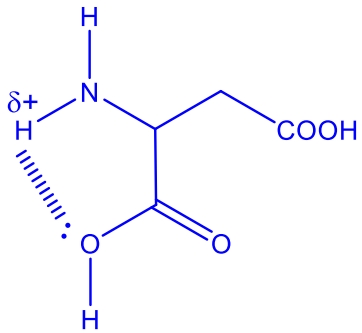
pK_{a1}	pK_{a2}	pK_{a3}
1.88	3.65	9.60

(ii) Make use of these pK_a values to suggest the major species present in solutions of aspartic acid with the following pH values. [2]

- pH 1
- pH 13



(iii) Draw a diagram of the monoanion of aspartic acid, showing the intramolecular hydrogen bond formed. [1]



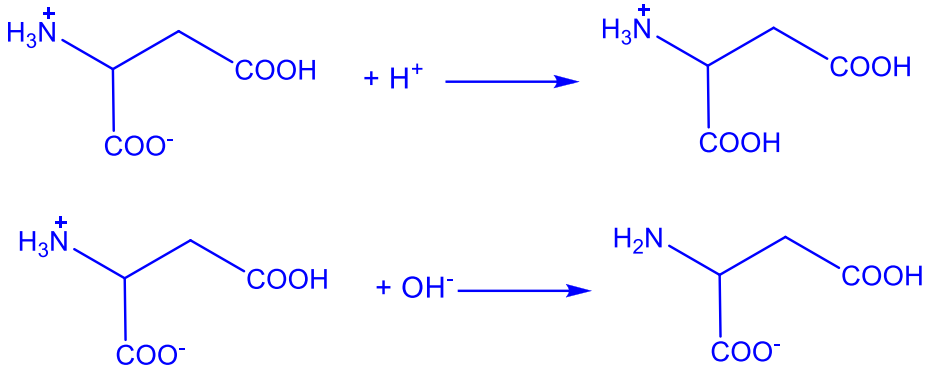
(iv) Use pK_{a1} to calculate the pH of a 0.200 mol dm^{-3} solution of aspartic acid. [1]

$10^{-1.88} = [H^+]^2 / 0.200$

$[H^+] = 0.0513$ mol dm^{-3}

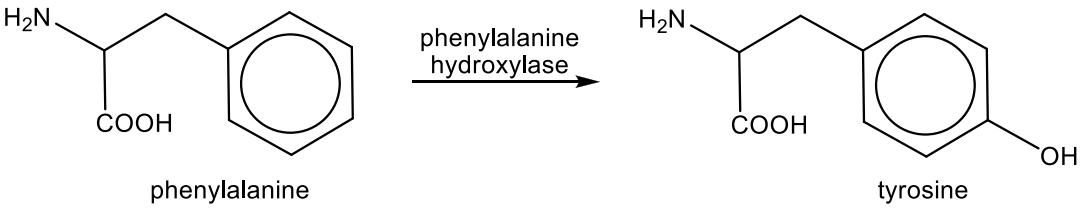
pH = 1.28

(v) Write equations to show how the zwitterion of aspartic acid maintains the pH of a solution. [2]



.....

(e) Phenylalanine is another essential amino acid. It is broken down into tyrosine by an enzyme, phenylalanine hydroxylase, in the liver. Tyrosine aids in reduction of body fat.



phenylalanine tyrosine

(i) Suggest a simple chemical test to detect the presence of tyrosine. State the observation you would expect. [1]

Test: neutral $FeCl_3$ (aq)

Observation: violet colouration

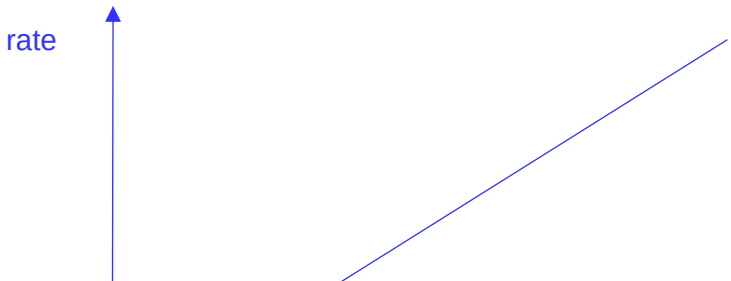
OR

Test: Br_2 (aq)

Observation: orange solution decolourised

The breakdown of phenylalanine by liver cells is a first-order reaction.

(ii) Sketch the graph of rate against concentration of phenylalanine. [1]



(iii) Using your answer in **(e)(i)**, outline a suitable experiment for obtaining the graph in **(e)(ii)**. [3]

You may find it useful to use $\frac{1}{\text{time}}$ to represent the reaction rate.

Prepare 4/5 reaction mixtures of different known [phenylalanine] and fixed amount of liver/phenylalanine hydroxylase.

To each reaction mixture, add a fixed/constant known amount of neutral $FeCl_3$ or Br_2 (aq).

Measure the time taken for violet to show or orange solution to decolourise. From there, determine the rate by rate = 1/time.

.....

[Total: 22]

Section B

Answer **one** question from this section.

4 Coronavirus disease 2019 (COVID-19) is an infectious disease that has spread globally. One of the most common symptoms developed by people affected with COVID-19 is difficulty in breathing.

(a) During breathing, the lungs take in oxygen gas and remove carbon dioxide gas. During inhalation, the volume of the lungs increases, causing air to flow into the lungs. During exhalation, the volume of the lungs decreases, causing air to flow out of the lungs.

Fig. 4.1 shows the volume of the lungs during inhalation (V_{in}) and exhalation (V_{ex}) at 30°C. The volume of gas taken in for each breath can be determined from the difference in volume of the lungs during inhalation and exhalation.

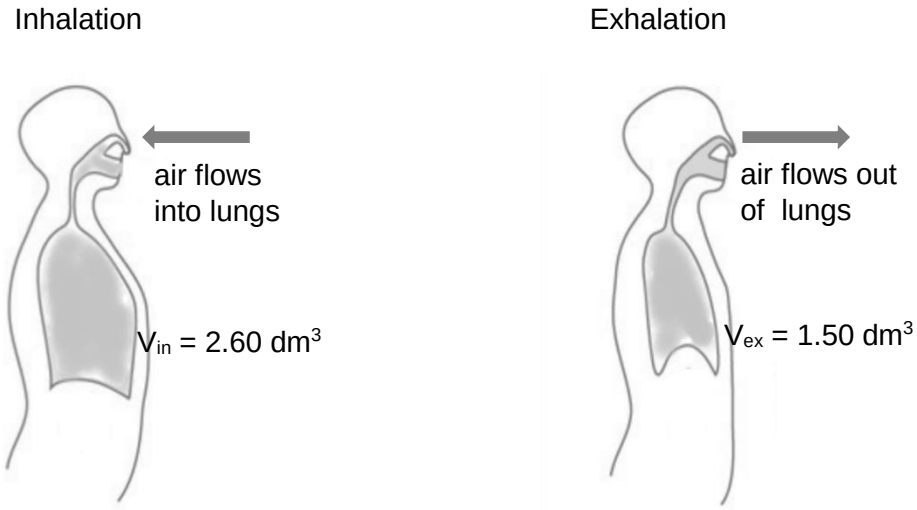


Fig. 4.1

Image taken from https://courses.lumenlearning.com/boundless-biology/chapter/breathing/

(i) Calculate the amount, in moles, of oxygen gas taken in for each breath at 1 atm and 30°C, given that the percentage by volume of atmospheric oxygen is 21%. [2]

Vol of gas = 2.60 – 1.50 = 1.10 dm^3

$101325 \times (1.1 \times 10^{-3} \times 0.21) = (n) \times 8.31 \times (30 + 273)$

Amt of O_2 = 0.00930 mol

(ii) The pressure in the lungs during inhalation was found to be 758 Torr at 30°C (1 Torr = 133 Pa). [1]

Assuming that the amount of gas inhaled and exhaled is the same, calculate the pressure in the lungs during exhalation at 30°C.

(758) x 2.60 = P x 1.5

P = 1310 Torr (3sf)

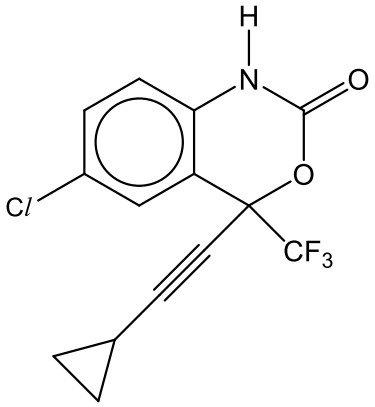
(iii) Explain the relative deviations from ideal gas behaviour of oxygen gas and carbon dioxide gas. [1]

CO_2 would deviate more from ideal gas compared to O_2.

This is because, CO_2 has more electrons and forms stronger instantaneous dipole-induced dipole interactions between molecules/intermolecular forces of attraction

……

(b) Anti-HIV drugs were used in the early treatment of COVID-19. One such anti-HIV drug is efavirenz.

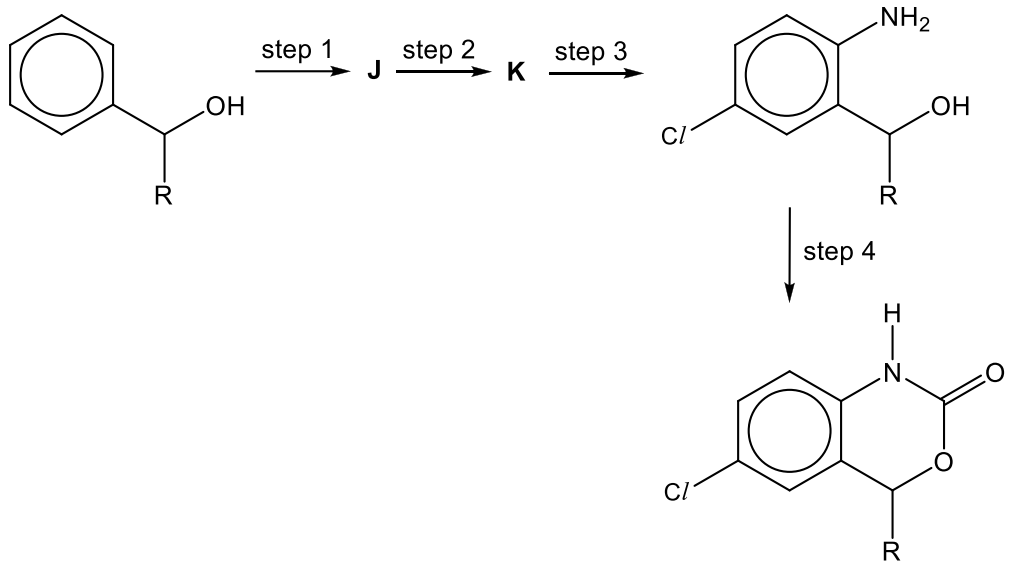


efavirenz

(i) Besides benzene ring, alkyne (C≡C) and fluoroalkane, name three other functional groups in efavirenz. [1]

amide, ester, chlorobenzene

(ii) Efavirenz can be made using appropriate reagents by the following 4-step synthesis. [5]



efavirenz

Suggest the structures of compounds **J** and **K** and the reagents and conditions for the four steps.

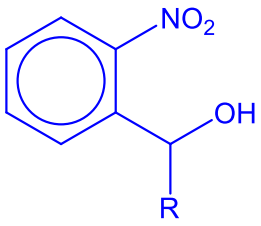
Step 1: conc HNO_3, conc H_2SO_4

Step 2: Sn, conc HC*l* heat, followed by NaOH

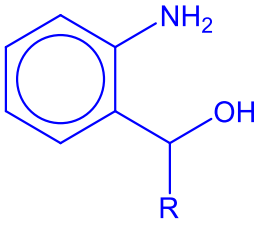
Step 3: Cl_2

Step 4: $COCl_2$ or ClCOOH

J:



K:



(iii) It was found that the nitrogen atom in efavirenz is sp^2 hybridised. [3]

Explain why this hybridisation results in partial double bond character in the C-N bond in efavirenz. Hence, use the *Data Booklet* to predict the bond energy of the C-N bond in efavirenz.

When the N atom is sp^2 hybridised, it would have an unhybridised p orbital that is parallel to and can overlap sideways with the p orbitals of the benzene ring and C=O. The lone pair of electrons of N is able to delocalise into the π electron cloud of the benzene ring and C=O, resulting in a partial double bond character.

C-N bond = +450 kJ mol^{-1}

Accept any value between 305 to 610

……

(c) Lignans are a class of natural products widely produced by various plant species. They are widely researched in their anti-viral activities. One such lignan is styron, $C_9H_{10}O$.

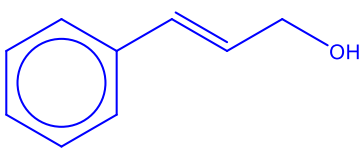
Styron decolourises bromine water to give a compound with molecular formula $C_9H_{11}O_2Br$. When treated with hot acidified $K_2Cr_2O_7$, styron forms compound **L**. **L** liberates CO_2 from Na_2CO_3(aq). When treated with hot acidified $KMnO_4$, styron forms compound **M**, $C_7H_6O_2$, which is a white precipitate.

N is a constitutional isomer of styron. It does not decolourise bromine water. When treated with hot $K_2Cr_2O_7$, **N** forms compound **P**. **P** gives an orange precipitate with 2,4-DNPH.

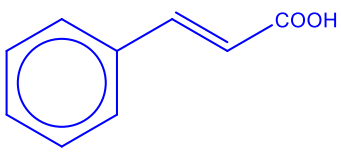
Deduce the structures of compounds **L**, **M**, **N**, **P** and styron, explaining the reactions described.

[7]

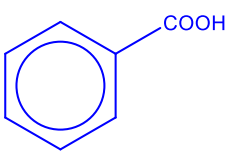
styron + Br_2 (aq) → $C_9H_{11}O_2Br$ $C_9H_{10}O$	C:H ≈ 1:1, styron has benzene ring. Electrophilic addition Styron has alkene/C=C
styron + $K_2Cr_2O_7$ → **L** $C_9H_{10}O$ **L** + Na_2CO_3 → CO_2	Oxidation Styron is a 1^o ~~or 2^o~~ alcohol ~~or aldehyde~~ Neutralisation/acid-carbonate reaction **L** has a –COOH / is a carboxylic acid
styron + $KMnO_4$ → **M** $C_9H_{10}O$ $C_7H_6O_2$	Oxidation



styron



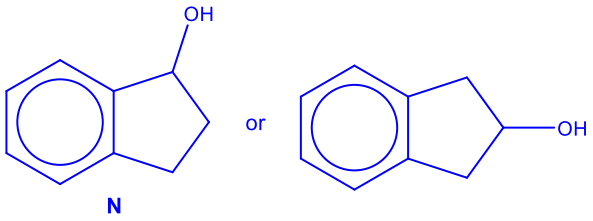
L



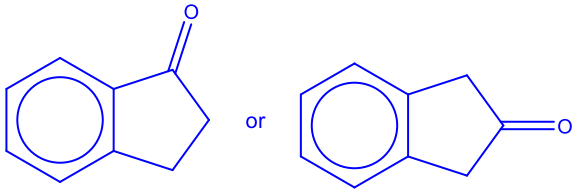
M

N does not decolourise Br_2 (aq)	C:H ≈ 1:1, **N** has benzene ring.

$C_9H_{10}O$	**N** does not have alkene/C=C or phenol
N + $K_2Cr_2O_7$ → **P** $C_9H_{10}O$ **P** + 2,4-DNPH → orange ppt	Oxidation (do not double award) **N** is a ~~1°~~ ~~or~~ 2° alcohol Condensation **P** is ~~an aldehyde or~~ a ketone



N



P

……

[Total: 20]

5 Iron and platinum are used in several inorganic and organic reactions.

(a) The reaction between $S_2O_8^{2-}$ and I^- ions is very slow. When a small amount of $Fe^{2+}(aq)$ is added to the mixture, the rate of reaction increases. [4]

With reference to relevant $E^{\ominus}$ values, describe the catalytic role of Fe^{2+} in the I^- / $S_2O_8^{2-}$ reaction.

Both I^- and $S_2O_8^{2-}$ are negatively charged and would repel each other. Hence, the activation energy of the uncatalysed reaction is very high. Fe^{2+} is a homogeneous catalyst that speeds up the rate of reaction by providing an alternative pathway of lower activation energy.

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

$E_{cell} = (+2.01) - (+0.77) = +1.24\ V$

$2Fe^{3+} + 2I^- \rightarrow I_2 + 2Fe^{2+}$

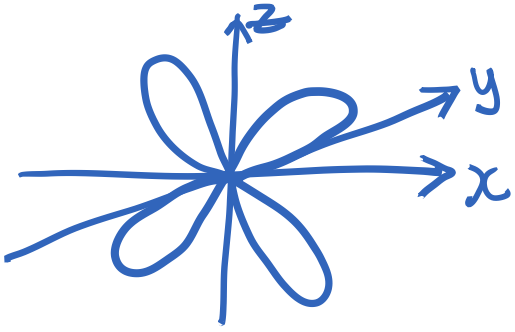
$E_{cell} = (+0.77) - (+0.54) = +0.23\ V$

Fe^{2+} is regenerated at the end of the reaction.

.....

(b) **(i)** $Fe^{3+}(aq)$ can be represented as its aqua complex, $[Fe(H_2O)_6]^{3+}$. In this aqua complex, the five 3d orbitals are no longer degenerate. They split into two energy levels. The $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are in the higher energy level. [1]

Draw a fully labelled diagram of a 3d orbital from the **lower** energy level.



$3d_{xz}$

all three axes must be shown, with correct corresponding orbital label

(ii) Both solutions of $Al^{3+}(aq)$ and $Fe^{3+}(aq)$ are acidic. [2]

With the aid of an equation, explain why $Fe^{3+}(aq)$ solution is acidic.

$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$

Fe^{3+} has a high charge density and high polarising power. Hence, it polarises the electron cloud of water, causing the O-H bond in water to weaken and break to give H^+.

(iii) Describe how the reaction of Al^{3+}(aq) with excess NaOH(aq) differs from that of Fe^{3+}(aq) with excess NaOH(aq). Write equations for any reactions that occur. [2]

Al^{3+}(aq) reacts with NaOH(aq) to form a white precipitate, which dissolves in excess NaOH(aq) to form a colourless solution.

$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$

$Al(OH)_3(s) + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$

OR

Al^{3+}(aq) reacts with excess NaOH (aq) to give a colourless solution.

$Al^{3+}(aq) + 4OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$

Fe^{3+}(aq) reacts with NaOH(aq) to form a red-brown ppt that is insoluble in excess NaOH(aq)

$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$

……

(c) **(i)** Alkenes can be reduced to alkanes by hydrogen with a platinum catalyst. [3]

Outline the mode of action of the catalyst in this reduction reaction.

Pt is a heterogenous catalyst.

During adsorption, the reactants (alkene and hydrogen) form weak interactions with the catalyst surface so that they are held in the correct orientation for reaction. During reaction, bonds are broken/weakened and bonds are formed. During desorption, the interactions between the product and catalyst breaks and the product leaves the catalyst surface.

(ii) Platinum complexes have been researched extensively due to its anti-cancer properties. One such platinum complex is *cis*-platin, which can be synthesised from $PtCl_4$. [3]

The central atom, platinum, in $PtCl_4$ is surrounded by six pairs of electrons arranged in an octahedral shape. An octahedral arrangement is shown in Fig. 5.1.

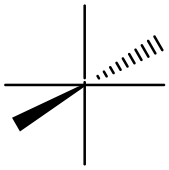
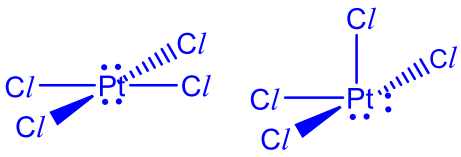


Fig. 5.1

Two different molecular arrangements of $PtCl_4$ are possible.

Draw clear diagrams of these two arrangements. Hence, apply the principles of the VSEPR theory to discuss the relative stabilities of these two possible arrangements.



The square planar arrangement/the one on the left is more stable.

For the one on the left, the two lone pair of electrons are on opposite side /180° away, which minimises lone pair-lone pair repulsion.

For the one on the right, the two lone pair electrons are next to each other/90° away, which experiences greater lone pair-lone pair repulsion.

(iii) Platinum compounds are also commonly used in cross-coupling reactions, where two different compounds come together through the formation of carbon-carbon bonds. [5]

One such cross-coupling reaction between an amine and a nitro compound is shown in Fig. 5.2.

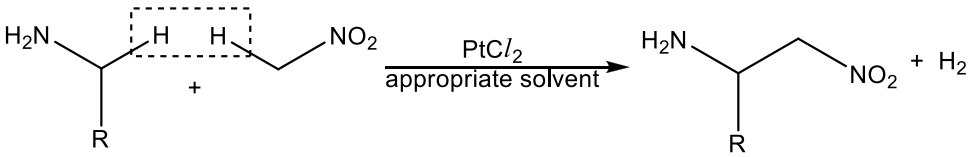
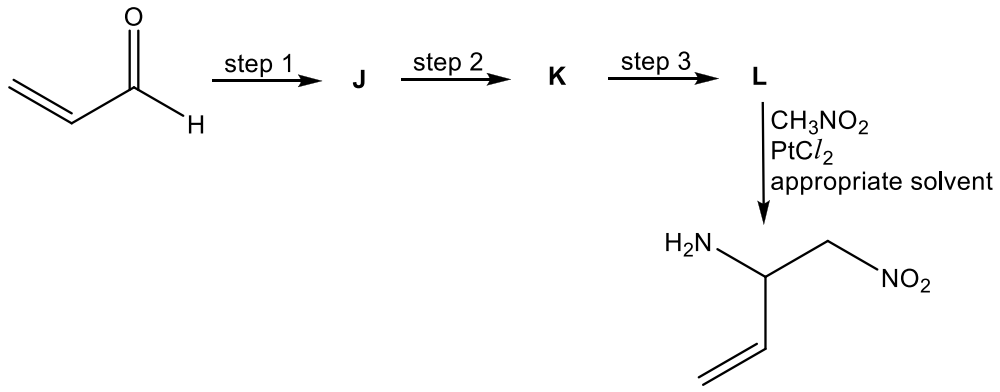


Fig. 5.2

The cross-coupling reaction in Fig. 5.2 is used in the following 4-step synthesis.

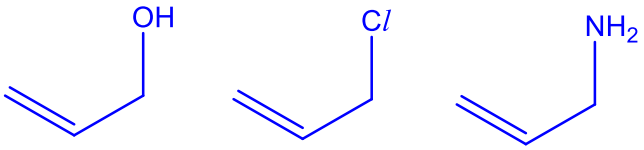


Suggest the structures of compounds **J** to **L** and the reagents and conditions for steps 1 to 3.

Step 1: $NaBH_4$ or $LiAlH_4$ in dry ether

Step 2: $SOCl_2$ or PCl_5 or PCl_3, heat

Step 3: excess conc NH_3, heat



.....

[Total: 20 marks]