Catholic Junior College

JC2 Preliminary Examination

Higher 2

CANDIDATE NAME			
CLASS	**2T**	**INDEX**	

CHEMISTRY

9729/02

Paper 2 Structured Questions

26 August 2024

2 hours

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

WORKED SOLUTIONS

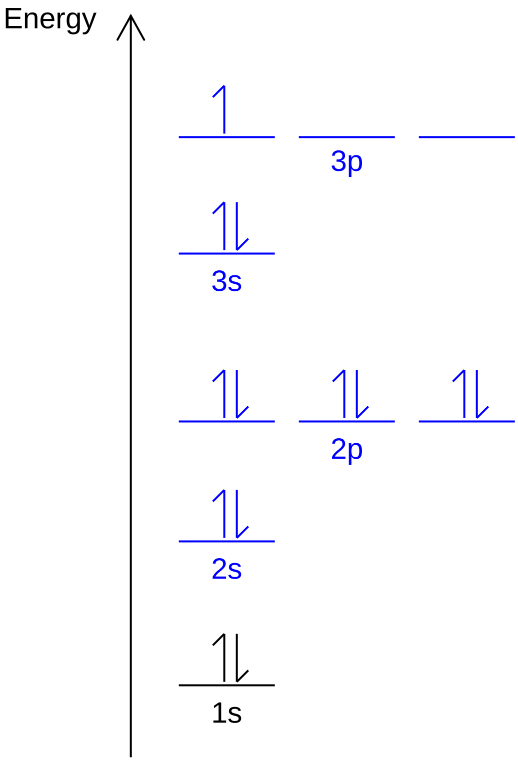
This document consists of **16** printed pages.

[Turn over

Answer **all** the questions in the space provided.

1 Tetrahalosilanes have the general formula Si**X**$_4$, where **X** represents one of the halogens. A sample of Si**X**$_4$ is atomised and ionised. The ions produced are then analysed.

(a) Complete the following energy level diagram to show the arrangement of electrons in the orbitals of Si^+ ion.



[2]

(b) In the first analysis, the second ionisation energy of silicon is recorded.
Write an equation for the second ionisation energy of silicon.

$Si^+(g) \rightarrow Si^{2+}(g) + e^-$ [1]

(c) Explain why the second ionisation energy of silicon is higher than that of the first.

The increase in the second ionisation energy is due to more energy required to remove the second electron from **an ion with** the **<u>same nuclear charge as the atom</u>** but **<u>attracting fewer electrons</u>** due to stronger electrostatic force of attraction between the nucleus and valence electrons. [1]

(d) In the second analysis, ions of **X**$^+$ are analysed.

A sample each of ${}^{28}_{14}Si^+$ and **X**$^+$ is passed through an electric field. The angles of deflection of ${}^{28}_{14}Si^+$ and **X**$^+$ are 5.6° and 2.0° respectively.

(i) Deduce, by calculation, the identity of **X**. [2]

Let the mass number or nucleon number of **X** be m.

$$\frac{1/28}{1/m} = \frac{5.6}{2.0}$$

m = 78.4

X is <u>Br</u>.

(ii) Suggest why there is another beam detected with an angle of deflection of 1.9°.

<u>Isotopes</u> of bromine with <u>lower charge/mass ratio</u>

………………………………………………………………………………………… [1]

[Total: 7]

2 This question is about phosphorus and its compounds.

(a) With reference to relevant electronic configurations where necessary, explain why the first ionisation energy of phosphorus is higher than the elements that come immediately before and after it in Period 3.

As compared to Si, P has a smaller (atomic) radius and greater nuclear charge while shielding effect by same number of inner electrons is similar. Therefore, nuclear attraction in P is larger and hence, 1st ionisation energy of P is higher than that of Si.

P $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$

S $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$

In S, the two electrons occupying the same 3p orbital (i.e. $3p_x$) give rise to inter-electronic repulsion. Thus, less energy is required to remove a paired 3p electron from S, as compared to the energy required to remove an unpaired 3p electron from P.

[3]

(b) With reference to structure and bonding, explain why the melting point of phosphorus is lower than the elements that come immediately before and after it in Period 3.

Si has a giant molecular structure with the Si atoms held together by an extensive network of strong covalent bonds. However, P_4 and S_8 have simple covalent structures with weak intermolecular instantaneous dipole-induced dipole forces of attraction that require less energy to overcome, thus P_4 (and S_8) have lower melting points than Si.

P_4 has fewer electrons than S_8, hence its intermolecular instantaneous dipole-induced dipole forces of attraction are weaker and require less energy to overcome, thus P_4 has a lower melting point than S_8.

[2]

The most important oxide of phosphorus is phosphorus(V) oxide, P_4O_{10}. It is a powerful dessicant and dehydrating agent.

(c) Write a balanced equation for the reaction of P_4O_{10} with water and state the pH of the resulting solution.

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ pH = 2 ……………………………………………………………

……………………………………………………………………………………… [1]

The structure of phosphorus(V) sulfide, P_4S_{10}, is closely related to that of P_4O_{10}.

(d) Reaction of P_4S_{10} with water gives two products. One of the products is the same as the product of the reaction in **(c)**, the other product is a gaseous compound. Suggest a balanced equation for this reaction.

$P_4S_{10} + 16H_2O \rightarrow 4H_3PO_4 + 10H_2S$ ……………………………………………… [1]

EXAMINER'S COMMENTS

(c) Equation was well written for most. However, quite a number of students gave a pH of 1 or above 4.

(d) This proved to be challenging for many students. Most wrong answers tried to give SO_2 as the other product which would result in an equation that is not balanced. Students should note at review that **no redox occurred for P_4S_{10} to its product, same as P_4O_{10} did not undergo redox with water**, hence SO_2 is not possible as an answer.

(e) In vapour form, phosphorus(V) sulfide exists as P_2S_5 molecules. When P_2S_5 is heated under a vacuum together with caesium sulfide, Cs_2S, and sulfur, it produces an ionic compound **R** which has the following composition by mass:
Cs, 58.1%; P, 6.78%; S, 35.1%.

(i) Calculate the empirical formula of compound **R** and hence deduce its chemical formula, given that the relative formula mass, M_r, is 914.6.

Let mass of a sample of the salt be 100g.

	Cs	P	S
Mass/g	58.1	6.78	35.1
A_r	132.9	31.0	32.1
Moles (% mass/A_r)	58.1/132.9 = 0.437	6.78/31.0 = 0.219	35.1/32.1 = 1.09
Simplest ratio	2	1	5

Empirical formula is Cs_2PS_5

Let the chemical formula be $(Cs_2PS_5)_n$.

M_r of $(Cs_2PS_5)_n = 914.6$

$(2(132.9) + 31.0 + 5(32.1))\ n = 914.6$

$457.3n = 914.6$, therefore $n = 2$

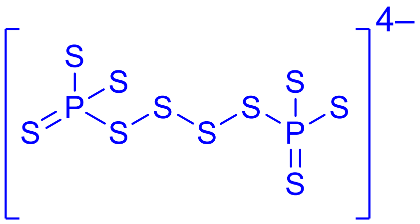
Chemical formula of compound is $Cs_4P_2S_{10}$

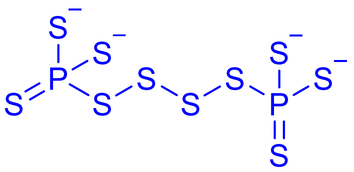
[2]

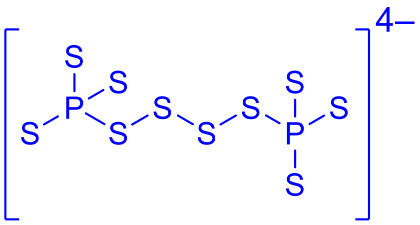
(ii) Compound **R** contains Cs^+ cation and an anion. Given that the cation and anion of compound **R** are present in a 4:1 ratio, write the formula of the anion.

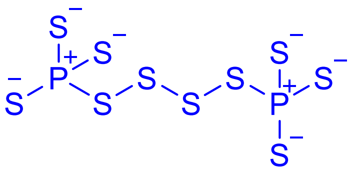
Anion: **$P_2S_{10}^{4-}$** ……………………………………………………………… [1]

(iii) Suggest the structure of the anion, given that there are three S–S single bonds, a plane of symmetry exists within the anion structure and the constituent atoms show their usual valencies.









[1]

[Total: 11]

3 Compound **G** is a colourless liquid with the formula $C_xH_y(OH)_z$.

When 3.00×10^{-4} mol of **G** was dissolved in an inert solvent and an excess of sodium metal added, 10.8 cm^3 of hydrogen gas, H_2, was produced.

In a vessel with 50.0 cm^3 of oxygen gas, the complete combustion of 3.00×10^{-4} mol of **G** is carried out. When the mixture is cooled, a total volume of 46.4 cm^3 of gas remains.

When this gaseous mixture is passed repeatedly over NaOH(s), the final volume of gas which remains is 24.8 cm^3.

All volumes are measured at room temperature and pressure.

(a) **(i)** Write the equation for the reaction of ethanol with an excess of sodium metal.

$CH_3CH_2OH + Na \rightarrow CH_3CH_2O^-Na^+ + \frac{1}{2}H_2$ .... [1]

(ii) Show that the value of **z** for **G** is 3.

Number of moles of $H_2 = \frac{10.8}{24000} = 0.00045$ mol

Each $C_xH_y(OH)_z$ gives $\frac{0.00045}{0.0003} = \frac{3}{2}\ H_2$

Since each OH gives $\frac{1}{2}\ H_2$, **z = 3**

[1]

(iii) Complete the following equation for the complete combustion of **G**, using **x** and **y**.

$$C_xH_y(OH)_3(l) + \boxed{\left(x + \frac{y+3}{4} - \frac{3}{2}\right)}\ O_2(g) \rightarrow \boxed{x}\ CO_2(g) + \boxed{\frac{y+3}{2}}\ H_2O(l)$$ [1]

(iv) Hence determine the value of **x** and **y** for **G**.

Vol. of CO_2 formed = 46.4 – 24.8 = 21.6 cm^3

Number of moles of $CO_2 = \frac{21.6}{24000} = 0.0009$ mol

Each $C_xH_y(OH)_3$ gives $\frac{0.0009}{0.0003} = 3\ CO_2$, hence, x = **3**

Vol. of O_2 reacted = 50 – 24.8 = 25.2 cm^3

Number of moles of $O_2 = \frac{25.2}{24000} =$ **0.00105 mol**

Each $C_xH_y(OH)_3$ requires $\frac{0.00105}{0.0003} = 3.5\ O_2$

From the combustion equation in (iii),

$3.5 = x + \frac{y+3}{4} - \frac{3}{2}$, sub x = 3

$3.5 = 3 + \frac{y+3}{4} - \frac{3}{2}$

$2 = \frac{y+3}{4}$

Thus, y = 8 – 3 = **5** – Similar to 2022/P2/Q3(f)

[3]

(b) Compound **H**, is an optically inactive five-membered unsaturated cyclic compound with molecular formula $C_6H_{10}O$. It decolourises aqueous bromine and gives off misty acid fumes when reacted with PCl_5.

Upon heating **H** with hot concentrated $KMnO_4$, a single product, **J**, $C_6H_{10}O_5$, is formed.
1 mol of **J** reacts with only 3 mol of PCl_5 giving misty acid fumes.
1 mol of **J** reacts with only 1 mol of Na_2CO_3 giving effervescence.

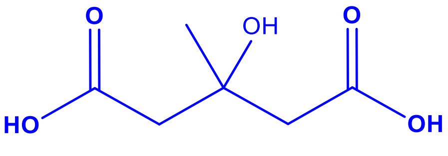
(i) Name the type of reaction occurring when **H** reacts with aqueous bromine.

Electrophilic Addition …………………………………………………………………… [1]

(ii) Compound **J** does not contain a chiral centre. Hence, deduce the structure of **J**, explaining the chemistry of the reactions of **J**.

1 mol of **J** undergoes **nucleophilic substitution** with 3 mol of **PCl_5**, hence that 3 **OH group (alcohol or carboxylic acid)** is present.

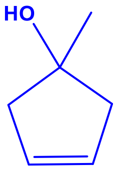
1 mol of **J** undergoes **acid-base reaction** with 1 mol of **Na_2CO_3**, hence there are 2 **–CO_2H groups.**



J

[3]

(iii) Draw the skeletal formula for **H**.



H

[1]

(c) $NaBH_4$ is a mild reducing agent that contains the anion $[BH_4]^-$ which can react with C=O bonds. But it cannot react with C=C bonds in alkenes. Explain why.

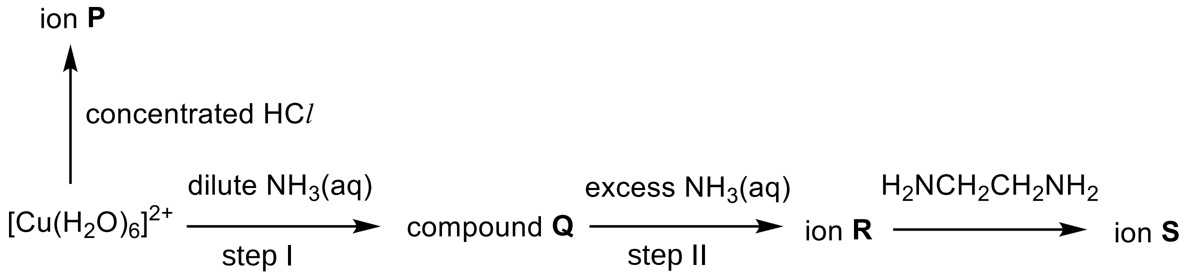
For C=O bond, the carbon is electron deficient since it is attached to an O atom, thus $[BH_4]^-$ is attracted to it.

However, the C=C of the alkene is electron-rich, which repels $[BH_4]^-$. [2]

Or C=C of alkene is non-polar, therefore do not attract nucleophile $[BH_4]^-$.

[Total: 13]

4 This question is about some reactions of copper compounds.



(a) Write the electronic configuration of Cu atom in *spdf* notation.

$1s^2 2s^2 2p^6 3s^2 3p^6\ 3d^{10} 4s^1$ [1]

(b) **(i)** Identify ion **P.**

$[CuCl_4]^{2-}$ [1]

(ii) Copper forms an octahedral complex with fluorine with the formula $[CuF_6]^{4-}$. Suggest why ion **P** is formed instead of $[CuCl_6]^{4-}$.

Since Cl^- has a larger ionic size/radius than F^-, there will be steric repulsion / hindrance around Cu^{2+}**.**

Hence, Cu^{2+} cannot accommodate more than four Cl^- ions. [1]

(c) Describe the observations in steps I and II and write balanced equations for the two reactions.

Observations in step I: **Pale blue ppt formed**

Equation: **$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$**

Observations in step II: **Pale blue ppt dissolves to form a deep blue solution**

Equation: **$Cu^{2+}(aq) + 4NH_3(aq) + 2H_2O(l) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$** [3]

or $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$

(d) Ethylenediamine, $H_2NCH_2CH_2NH_2$, (abbreviated as **en**) is a bidentate ligand. When a dilute aqueous solution containing ethylenediamine is added to ion **R**, a purple solution of ion **S** is formed.

The stability constant, K_{stab}, is the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions or molecules. The following shows the stability constant, K_{stab}, for the formation of three possible copper complexes with the **en** ligand from $[Cu(H_2O)_6]^{2+}$.

$[Cu(H_2O)_6]^{2+} + \textbf{en} \rightleftharpoons [Cu(H_2O)_4(\textbf{en})]^{2+} + 2H_2O$ $K_{stab1} = 3.55 \times 10^{10}$

$[Cu(H_2O)_6]^{2+} + 2\textbf{en} \rightleftharpoons [Cu(H_2O)_2(\textbf{en})_2]^{2+} + 4H_2O$ $K_{stab2} = 3.98 \times 10^{19}$

$[Cu(H_2O)_6]^{2+} + 3\textbf{en} \rightleftharpoons [Cu(\textbf{en})_3]^{2+} + 6H_2O$ $K_{stab3} = 3.98 \times 10^{18}$

(i) From the K_{stab} values shown above, suggest the likely formula of ion **S**.

$[Cu(H_2O)_2(en)_2]^{2+}$ [1]

(ii) Explain why hydrazine, H_2NNH_2, cannot act as a bidentate ligand.

If H_2NNH_2 is used, an unstable 3–membered ring complex will be formed due to ring strain, resulting in the bond angle in the complex to be too small [1]

(e) Ethanedioate, $C_2O_4^{2-}$, is another bidentate ligand. When excess potassium ethanedioate, $K_2C_2O_4$, is added to a solution containing $Cu^{2+}(aq)$ ions, a pale blue precipitate containing CuC_2O_4 is formed.
The K_{sp} of CuC_2O_4 is 4.30×10^{-10} mol^2 dm^{-6}.

(i) Write an expression for the solubility product, K_{sp}, of CuC_2O_4.

$K_{sp} = [Cu^{2+}][C_2O_4^{2-}]$ [1]

(ii) Calculate the solubility (in mol dm^{-3}) of CuC_2O_4 in water.

$$CuC_2O_4\,(s) \rightleftharpoons \underset{x}{Cu^{2+}\,(aq)} + \underset{x}{C_2O_4^{2-}\,(aq)}$$

$$K_{sp} \text{ of } CuCrO_4 = [Cu^{2+}][C_2O_4^{2-}]$$
$$= (x)(x)$$
$$= 4.30 \times 10^{-10}$$

$$\therefore \text{Solubility, } x = \sqrt{4.30 \times 10^{-10}}$$
$$= \underline{2.07 \times 10^{-5}} \text{ mol dm}^{-3}$$

[1]

(iii) The K_{sp} of FeC_2O_4 is 2.00×10^{-7} $mol^2\ dm^{-6}$.
Deduce which precipitate, FeC_2O_4 or CuC_2O_4 will be formed first if $K_2C_2O_4$ is added slowly into a solution containing 0.015 mol dm^{-3} of Fe^{2+} and 0.025 mol dm^{-3} of Cu^{2+}.

For CuC_2O_4 ppt to form,

Min $[C_2O_4^{2-}]$ needed $= \frac{4.30 \times 10^{-10}}{0.025}$

$= 1.72 \times 10^{-8}$ **mol** dm^{-3}

For FeC_2O_4 ppt to form,

Min $[C_2O_4^{2-}]$ needed $= \frac{2.00 \times 10^{-7}}{0.015}$

$= 1.33 \times 10^{-5}$ **mol** dm^{-3}

$\therefore$ Since less $[C_2O_4^{2-}]$ needed to form CuC_2O_4 ppt, it will precipitate first.

[2]

(iv) When dilute H_2SO_4 is slowly added to CuC_2O_4 the pale blue precipitate dissolves to form $H_2C_2O_4$ and a blue solution of Cu^{2+}. Explain why the precipitate dissolves.

Formation of $H_2C_2O_4$ causes decrease in $[C_2O_4^{2-}]$. Hence, the position of equilibrium to shift to the right thus the ionic product of CuC_2O_4 is less than K_{sp} resulting in the pale blue precipitate dissolving

$CuC_2O_4\ (s) \rightleftharpoons Cu^{2+}\ (aq) + C_2O_4^{2-}\ (aq)$ Hence, the presence of $[Cu(H_2O)_6]^{2+}$ gives rise to a blue solution.

[1]

(v) It has been suggested that the blue solution formed in **(iv)** turns colourless after some time with the liberation of CO_2 gas.

$$2CO_2 + 2H^+ + 2e^- \rightleftharpoons H_2C_2O_4 \qquad E^\ominus = -0.49\ V$$

With reference to relevant data from the *Data Booklet* and the equation given above, write an equation and calculate the standard cell potential, $E^\ominus_{cell}$ to account for the above observation.

[R]: $Cu^{2+} + e^- \rightarrow Cu^+$ $E^\ominus = +0.15\ V$

[O]: $H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$ $E^\ominus = -0.49\ V$

Overall: $2Cu^{2+} + H_2C_2O_4 \rightarrow 2Cu^+ + 2CO_2 + 2H^+$

$E^\ominus_{cell}$= 0.15 – (−0.49 V) = +0.64V> 0 (Feasible)

The Cu^{2+}(aq) formed oxidises $H_2C_2O_4$ to form CO_2 while itself is reduced to Cu^+(aq), giving rise to a colourless solution. [2]

[Total: 15]

5 Pyruvic acid is an important compound in biochemistry as it is involved in metabolic pathways in our body, including formation of lactic acid in anaerobic metabolism.

Some reactions in the laboratory involving these acids are shown in Fig. 5.1.

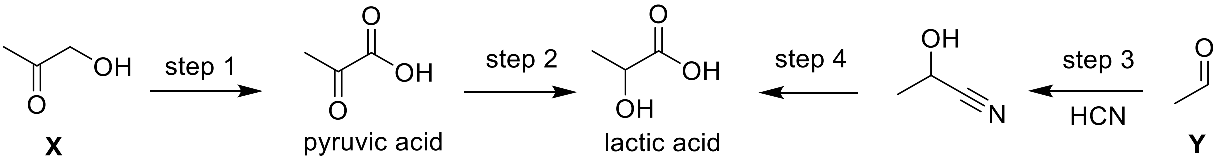


Fig. 5.1

(a) Give the systematic name for lactic acid.

2-hydroxypropanoic acid .... [1]

(b) Name the two functional groups present in **X.**

Ketone and primary alcohol .... [1]
– similar to 2022/P2/Q5(a)

(c) State the number of σ bonds and π bonds in pyruvic acid.

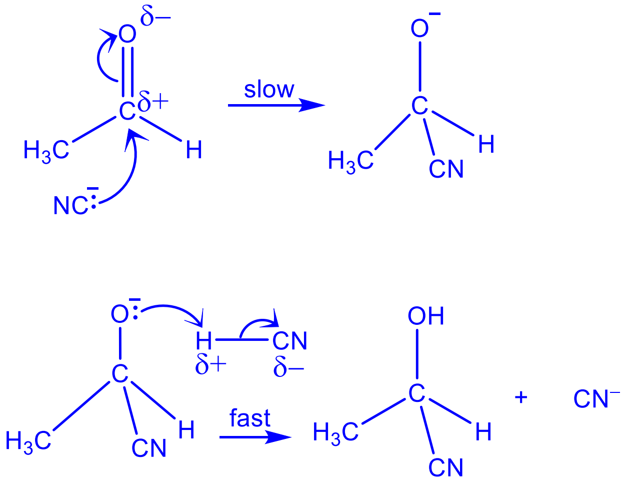
Number of σ bonds: 9 …………… Number of π bonds: 2 – similar to 2022/P2/Q5(b) [1]

(d) State the types of reaction and reagents and conditions for step 1 and for step 2.

Step 1: Oxidation, $KMnO_4$ / $K_2Cr_2O_7$ with dilute H_2SO_4, heat under reflux

Step 2: Reduction, H_2 with Ni, heat OR $NaBH_4$ in methanol (room temp) [2]

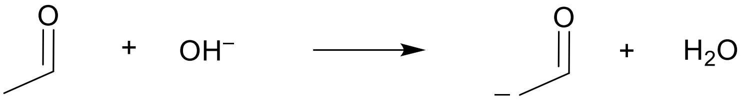
(e) Draw the nucleophilic addition mechanism for step 3. Show relevant lone pairs of electrons, dipoles, and curly arrows in your answer.



[2]

[Turn over

(f) Compound **Y** reacts with NaOH to form an anionic intermediate as shown below in Fig. 5.2.



Y

Fig. 5.2

This anion is represented by two different structures as shown below in Fig. 5.3. The actual structure of the anion is between these two structures, with the negative charge delocalised over both the oxygen and the carbon atoms.

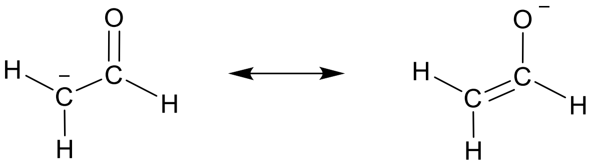
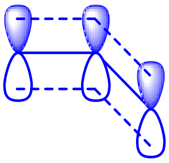


Fig. 5.3

(i) With the aid of a suitable diagram, suggest how the delocalisation of electrons occurs in this anion.



In this anion, **p orbitals of the two C atoms and O atom overlap sideways** to form a delocalised π electron cloud. Hence the π electrons can be delocalised over C-C-O group. [2]

(ii) Deduce the number of delocalised electrons in this anion.

4 delocalised π electrons. [1]

(iii) Compound **Y** behaves as an acid in reactions shown in Fig. 5.1 and 5.2.
Identify the type of acid behaviour shown by **Y** in each of these reactions. Explain your answers.

Fig. 5.1: **Lewis** Acid behaviour as shown by **Y** **accepting electron pair** from CN^- ion as it undergoes nucleophilic addition.

Fig. 5.2: **Brønsted**-Lowry Acid behaviour as shown by **Y** **donating H^+** to OH^-.

[2]

(iv) Another molecule of **Y** can react with the anion formed in Fig. 5.2 to give a final product of $CHOCH_2CH(OH)CH_3$ as shown in Fig. 5.4.

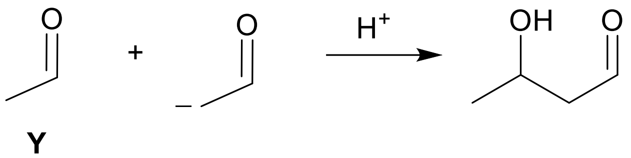
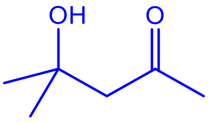


Fig. 5.4

Suggest the final product formed when two molecules of CH_3COCH_3 undergo the same reaction with NaOH followed by H^+.

$(CH_3)_2C(OH)CH_2COCH_3$



[1]

(g) Write a balanced equation for the reaction of compound **Y** (liquid) with alkaline aqueous iodine, including state symbols.

$CH_3CHO(l) + 3I_2(aq) + 4OH^-(aq) \rightarrow HCO_2^-(aq) + CHI_3(s) + 3I^-(aq) + 3H_2O(l)$ [2]

[Total: 15]

6 **(a)** The nickel–cadmium battery (Ni–Cd battery) is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes. The cathode consists of nickel oxy-hydroxide, NiO(OH), as the active material and is separated from the anode made of finely divided cadmium metal. The electrolyte used is a mixture of potassium hydroxide, KOH, in water. During discharge, $Ni(OH)_2(s)$ and $Cd(OH)_2(s)$ are formed at the cathode and anode respectively.

(i) Construct the half-equations at the electrodes of this Ni–Cd electrochemical cell. Hence, give the overall balanced equation for the reaction that occurs during discharge.

Anode: **$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$** [1]

Cathode: **$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$** [1]

Overall: **$Cd + 2\ NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$** [1]

(ii) Ni–Cd batteries can be recharged by applying a current across the two electrodes.
Calculate the time taken to recharge a Ni–Cd battery at a current of 2.0 A, if 5.62 g of cadmium was converted to $Cd(OH)_2$.
[A_r of Cd = 112.4]

Amount of Cd = $\frac{5.62}{112.4}$ = 0.0500 mol

Amount of electrons required, n = 0.0500 x 2 = 0.100 mol

Total charge = n x F = 0.100 x 96500 = 9650 C

Time required = $\frac{9650}{2.0}$ = 4825 s (or 80.4 min)

[2]

(iii) Overcharging the Ni–Cd battery may result in the formation of other products at the electrodes. With reference to the *Data Booklet* and species present in a Ni–Cd battery, predict the possible products at the electrodes of the Ni–Cd battery by writing the relevant half equations.

Anode: **$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$** [1]

Cathode: **$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$** [1]

(b) The propane-oxygen fuel cell is another efficient source of electrical energy. The overall reaction for this fuel cell is identical to the combustion of propane in oxygen.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

(i) Given that the standard enthalpy change of combustion of propane is –2220 kJ mol^{-1}, calculate the energy that is being produced by the propane-oxygen fuel cell if 100 g of propane is used, assuming that it is 70% efficient.

Amount of propane used = $\frac{100}{3(12.0)+8(1.0)}$ = 2.27 mol

Energy produced = 2.27 x 2220 = 5040 kJ

Energy produced by fuel cell = $\frac{70}{100}$ x 5040 = 3530 kJ

[2]

(ii) In this propane-oxygen fuel cell, O_2 is reduced. Explain, with reference to relevant standard electrode potential values from the *Data Booklet*, why the electrolyte used is more often acidic than alkaline.

Acidic: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ +1.23V

Alkaline: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ +0.40V

O_2 is more readily reduced in acidic condition as compared to alkaline condition as it has a more positive standard electrode potential.

.... [2]

(iii) Air may be used instead of pure oxygen as the oxidising agent. Suggest one advantage of using air as an oxidising agent.

Air is readily available / cheaper / lower cost.

.... [1]

(c) Give the name of the mechanism for the synthesis of 2-bromopropane from propane in the laboratory. State the reagent(s) and conditions used.

Name of mechanism: **Free radical substitution** [1]

Reagent(s) and conditions: **(limited) Br_2, *uv* light / high temperature** [1]

[Total: 14]