Suggested Answer for SH2 H2 Chemistry 2019 Prelim Paper 2

1 (a) Brass is a mixture of copper and zinc. When a piece of brass is placed in dilute hydrochloric acid, only one of the metals present dissolves.

Explain the observation and write an equation for the reaction that occurs.

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^\ominus = -0.76V$

$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^\ominus = +0.34V$

$2H^+ + 2e^- \rightleftharpoons H_2 \quad E^\ominus = 0.00\ V$

For reaction between Zn and H^+,

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$

$= 0.00 - (-0.76)$

$= +0.76V$ (reaction is feasible)

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$ OR $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

For reaction between Cu and H^+,

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$

$= 0.00 - (0.34)$

$= -0.34V$ (reaction is not feasible)

Note: It is essential to calculate $E^\ominus_{cell}$ between metal and H^+ to conclude whether the reaction is feasible. Some answers suggest Zn is more likely to be oxidized than Cu but that does not explain why Cu do not react with H^+.

(b) Copper and zinc are the two electrodes in a *Daniell* cell. The cell is set up as shown in Fig 1.1.

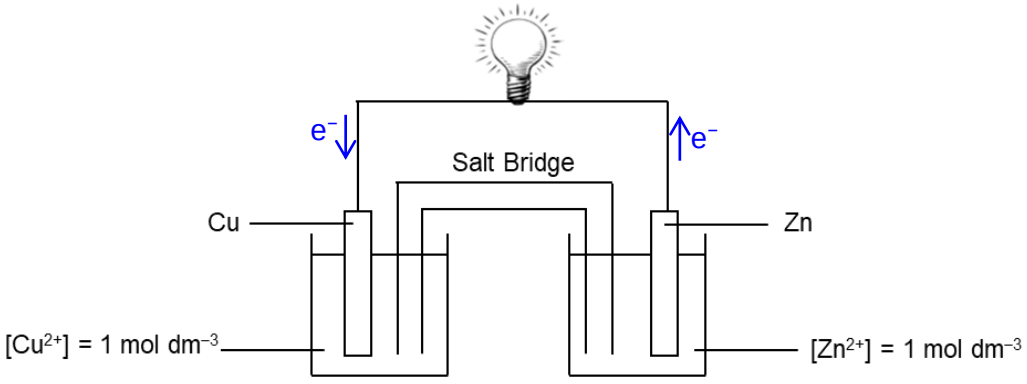

Fig 1.1

(i) Indicate the direction of electron flow **on Fig 1.1**. [1]

Note:

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^\ominus = -0.76V$

$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^\ominus = +0.34V$

Cu^{2+}/Cu half cell undergoes [R] and gain e^-

Zn^{2+}/Zn half cell undergoes [O] and lose e^-

Electrons flow from the anode (oxidation) to the cathode (reduction).

(ii) Write the equation for the reaction taking place and calculate $\Delta G^{\ominus}$ for the reaction.

$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$

$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$
$= +0.34 - (-0.76)$
$= +1.10V$

$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$
$= -2 \times 96500 \times 1.10$
$= -2.12 \times 10^5 \text{ J mol}^{-1}$

[3]

(iii) Discuss the effect of the following changes on the cell potential of the above cell.

(I) adding excess amount of aqueous ammonia into the Zn^{2+}/Zn half-cell

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^{\ominus} = -0.76V$

When excess amount of aqueous ammonia is added to Zn^{2+}/Zn half-cell, $[Zn(NH_3)_4]^{2+}$ complex ion will be formed.In order to partially offset the decrease in $[Zn^{2+}]$, oxidation of Zn is favoured to form more Zn^{2+}. Hence $E(Zn^{2+}/Zn)$ becomes more negative.

$E_{cell} = E^{\ominus}(Cu^{2+}/Cu) - E(Zn^{2+}/Zn)$

E_{cell} will become more positive.

(II) using a smaller copper electrode

Size of electrode will not affect the $E^{\ominus}$ of the reduction half-equation and E_{cell} since there is no shift in the position of the equilibrium.

Note: Solid does not affect position of equilibrium.

(iv) How many hours will it take for this galvanic cell to plate 15.0 g of metallic copper from 1 mol dm^{-3} solutions of $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ using a current of 5.0 A?

[R] $Cu^{2+} + 2e^- \rightarrow Cu$

Amount of Cu = $\frac{15.0}{63.5}$ = 0.2362 mol

Amount of electrons = 0.4724 mol

$Q = It = n_e F$

$t = \frac{0.4724 \times 96500}{5.0}$

$= 9117s$
$= 2.53h$

[2]

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(v) The Nernst equation is an equation that relates the cell potential, E_{cell}, of an electrochemical reaction to the standard cell potential, $E^{\ominus}_{cell}$. It can be simplified and written as

Nernst equation : $E_{cell} = E^{\ominus}_{cell} - \frac{RT}{zF} \ln Q$

where R is the ideal gas constant
T is temperature in Kelvin
z is the number of electron transferred
F is Faraday's constant
Q is $\frac{[Zn^{2+}]}{[Cu^{2+}]}$ for the *Daniell* cell

Using the above equation, calculate Q for the overall redox reaction of the *Daniell* cell when it reaches equilibrium at 25 ^{o}C.

At equilibrium, $E_{cell} = 0$

$$E^{\ominus}_{cell} = \frac{RT}{zF} \ln Q$$

$$1.10 = \frac{8.31 \times 298}{2 \times 96500} \ln Q$$

$$Q = 1.71 \times 10^{37}$$

[2]

(vi) In another set-up conducted at 25 ^{o}C, the concentration of Cu^{2+} ions and Zn^{2+} ions have been adjusted to 0.125 mol dm^{-3} and 0.002 mol dm^{-3} respectively.

Using the Nernst equation, calculate the e.m.f. of this cell.

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{zF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.10 - \frac{8.31 \times 298}{2 \times 96500} \ln \frac{[0.002]}{[0.125]}$$

$$= 1.15V$$

[2]

[Total: 17]

2 Saccharin is an artificial sweeting agent used in some soft drinks and produced in various ways. Fig 2.1 shows the original route by *Remsen and Fahlberg*, starting with methylbenzene undergoing electrophilic substitution reaction using chlorosulfonic acid, C*l*SO$_3$H. This is also known as aromatic sulfonation process.

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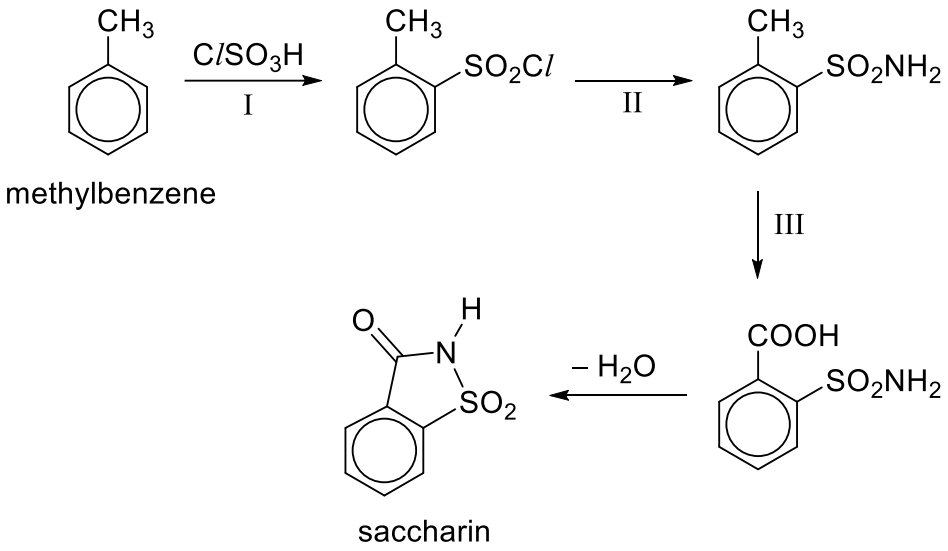
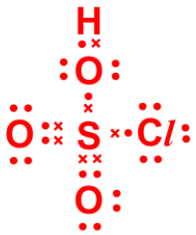


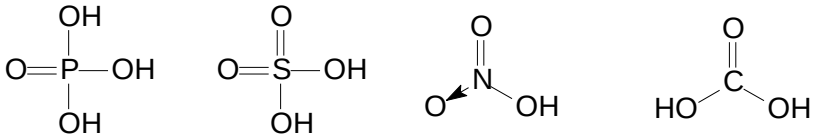
Fig 2.1

(a) Draw a dot-and-cross diagram of chlorosulfonic acid, C*l*SO$_3$H and hence state the bond angle for C*l*−S−O.



C*l*−S−O bond angle : 109.5°

Note: All acid compounds are covalent molecule. They only dissociate into ions in aqueous state. Acids containing H&O atoms lose H^+ from the O−H bonds when ionize in water. Examples of acid molecule structures:

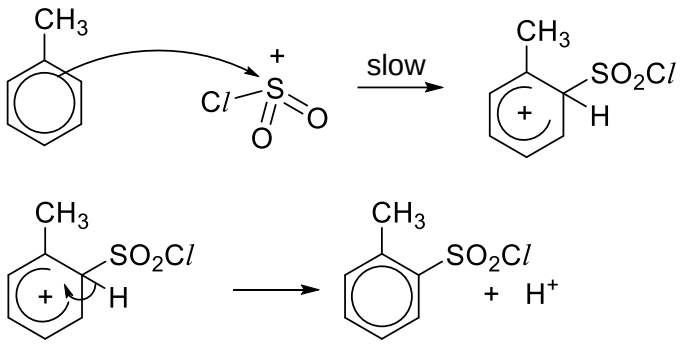


[2]

(b) **(i)** Reaction I of the aromatic sulfonation process involves the formation of an electrophile. Identify the electrophile.

Electrophile : $^+SO_2Cl$ [1]

(ii) Hence, describe the mechanism for reaction I of the reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



Note:
arrow from benzene π electron to S atom of the electrophile to form arenium cation
arrow from C−H bond to center of arenium cation to regenerate aromaticity and lose H^+ [2]

(iii) State the types of reaction that occur during reactions II and III.

reaction II : nucleophilic substitution / condensation

reaction III : oxidation [2]

(iv) Suggest reagents and conditions for reactions II and III.

reaction II : excess ethanolic NH_3, heat in sealed tube (behave like C−C*l*)
(also accept NH_3(g) r.t.p. as it could react similar to acyl chloride)

reaction III : $KMnO_4$, dilute H_2SO_4, heat [2]

[Total : 9]

3 Perchlorate (ClO_4^-) compounds are used as oxidisers in some fireworks to aid the combustion reaction. These perchlorates can contaminate bodies of water near fireworks displays. Elevated concentrations of perchlorate in water can affect wildlife and it may also affect human health if it contaminates drinking water.

(a) One common perchlorate present in fireworks is ammonium perchlorate, NH_4ClO_4.
Given that the solubility of ammonium perchlorate is 30.6 g per 100 cm^3, express its solubility in mol dm^{-3} and hence, calculate the solubility product, K_{sp}, for NH_4ClO_4.

Solubility, $s = \frac{30.6}{117.5} \times 10 = 2.60$ mol dm^{-3}

K_{sp} of $NH_4ClO_4 = [NH_4^+][ClO_4^-] = (s)(s) = (2.60)^2$

$= 6.78$ mol^2 dm^{-6}

[2]

[Turn over

(b) A group of NJC students conducted a study to determine the perchlorate content of the water in the Singapore River before and after the fireworks display in the National Day Parade Rehearsal.

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They followed the methodology described below one week before the rehearsal:

- Collect a 100.0 cm^3 sample of the river water and acidify it with 10 cm^3 of 1 mol dm^{-3} sulfuric acid.
- The resulting solution is added to an excess of 50 cm^3 of 5×10^{-5} mol dm^{-3} iron(II) sulfate solution. The mixture is then made up to 250 cm^3. This is solution **X**.
- A 25.0 cm^3 sample of solution **X** is pipetted into a conical flask.

The 25.0 cm^3 solution is titrated against 1×10^{-6} mol dm^{-3} potassium manganate(VII) to determine the amount of remaining iron(II) ions in the sample.

(i) Write the half equation for the conversion of perchlorate ions to chlorine in the acidic medium and hence the overall equation for the reaction between perchlorate and iron(II) ions.

Half equation : [R] $2ClO_4^- + 16H^+ + 14e^- \rightarrow Cl_2 + 8H_2O$

Overall equation : $2ClO_4^- + 16H^+ + 14Fe^{2+} \rightarrow Cl_2 + 14Fe^{3+} + 8H_2O$

[2]

(ii) Describe how you would recognise the endpoint of the titration.

Mixture turns first permanent pink [1]

(iii) The 25.0 cm^3 sample of solution **X** required 30.00 cm^3 of potassium manganate(VII) for complete reaction.

Calculate the concentration of perchlorate ions in the river water.

Amt of $MnO_4^- = \frac{30}{1000} \times 1 \times 10^{-6} = 3.0 \times 10^{-8}$ mol

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Amt of Fe^{2+} in 25 $cm^3 = 5 \times 3.0 \times 10^{-8} = 1.50 \times 10^{-7}$ mol

Amt of Fe^{2+} in 250 $cm^3 = 1.50 \times 10^{-6}$ mol

Amt of Fe^{2+} that reacted with $ClO_4^- = (\frac{50}{1000} \times 5 \times 10^{-5}) - 1.50 \times 10^{-6}$
$= 1.0 \times 10^{-6}$ mol

$2ClO_4^- + 16H^+ + 14Fe^{2+} \rightarrow Cl_2 + 14Fe^{3+} + 8H_2O$

Amt of $ClO_4^- = \frac{1.0 \times 10^{-6}}{14} \times 2 = 1.429 \times 10^{-7}$ mol

$[ClO_4^-] = \frac{1.429 \times 10^{-7}}{(100/1000)} = 1.43 \times 10^{-6}$ mol dm^{-3}

[3]

(iv) Given that the perchlorate concentration in the Singapore River increased by 20% in the 24 hours after the fireworks display for the National Day Parade rehearsal, calculate the concentration of perchlorate ions in the river 24 hours after the fireworks display.

If you did not manage to work out an answer for **(b)(iii)**, you may assume the concentration of perchlorate ions in the river water is 2.5×10^{-6} mol dm^{-3}.

$[ClO_4^-] = 120\% \times 1.43 \times 10^{-6}$
$= 1.71 \times 10^{-6}$ mol dm^{-3}
OR
$[ClO_4^-] = 120\% \times 2.5 \times 10^{-6}$
$= 3.00 \times 10^{-6}$ mol dm^{-3}

[1]

(v) Table 3.1 shows the health effects on fishes due to varying concentration of perchlorate ion in the river.

types of fish	abnormalities in skeletal growth	increased angiogenesis	myocardial infarction
stickleback	5×10^{-6} mol dm^{-3}	1×10^{-4} mol dm^{-3}	1.5×10^{-4} mol dm^{-3}
Pike	5×10^{-7} mol dm^{-3}	2×10^{-6} mol dm^{-3}	1×10^{-5} mol dm^{-3}
catfish	1×10^{-7} mol dm^{-3}	1×10^{-6} mol dm^{-3}	5×10^{-5} mol dm^{-3}

Table 3.1

Using your answer in **b(iv)**, predict the type of health effect(s) experienced by each type of fish 24 hours after the fireworks display. Write "nil" if there is no effect.

types of fish	health effect(s)
stickleback	Nil
pike	abnormalities in skeletal growth
catfish	abnormalities in skeletal growth and increased angiogenesis

[2]

(c) Perchlorate ions can be metabolized in the tissue of stickleback fish.
The fish tissue concentration of perchlorate ions was investigated for one of the stickleback fish found in the Singapore River.

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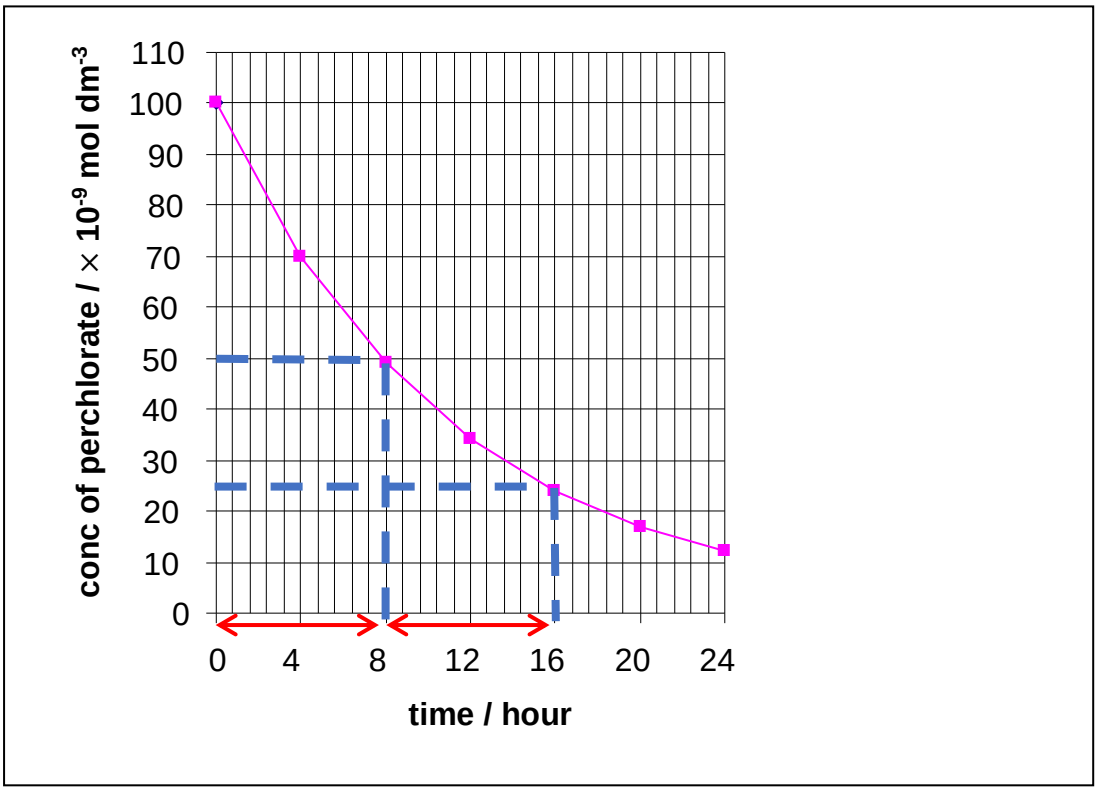
The following results was obtained.

Time/ hour	$[ClO_4^-]$ / $\times 10^{-9}$ mol dm^{-3}
0	100
4	70
8	49
12	34
16	24
20	17
24	12

Table 3.2

(i) Plot the data from Table 3.2 on the grid provided and use your graph to prove that the order of reaction with respect to perchlorate is one.



Clearly labelled axis
Construction line for $t_{½}$
All points plotted correctly
Constant half-life of 8 hours, hence first order wrt perchlorate ions. [3]

(ii) Using your graph in **c(i)**, determine the rate constant, *k*. Include units in your answer.

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For first order reaction, $t_{1/2} = \frac{\ln 2}{k}$

$k = 0.0866\ h^{-1}$

[2]

(iii) Hence, estimate the time taken for the perchlorate ions to reach 1% of its initial concentration.

$(\frac{1}{2})^n = (\frac{1}{100})$

$n = 6.64$

Time taken = $6.64 \times 8 = 53.15$ hours.
OR
need 7 half-lifes to reach 0.78%, time taken = $7 \times 8 = 56$ hours

[1]

[Total : 17]

4 Alkalinity refers to the capability of water to neutralize acid. Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0.

In the ocean, dissolved carbon dioxide from the atmosphere is in equilibrium with seawater concentrations of carbonic acid, H_2CO_3 and hydrogen carbonate, HCO_3^-. The ocean has a very large buffering capacity made possible with the presence calcium carbonate rocks in lakes and streams.

Relevant chemical equations and equilibrium constants at 293K that affects the ocean's pH and buffering capacity are shown below.

$CO_2(g) \rightleftharpoons CO_2(aq)$	$K_{CO2} = 3.44 \times 10^{-2}$
$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$	$K_{H2CO3} = 2.00 \times 10^{-3}$
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$	K_{a1}
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	K_{a2}

Fig 4.1 shows the molar fraction of H_2CO_3, HCO_3^- and CO_3^{2-} in a sample of river water at 293K.

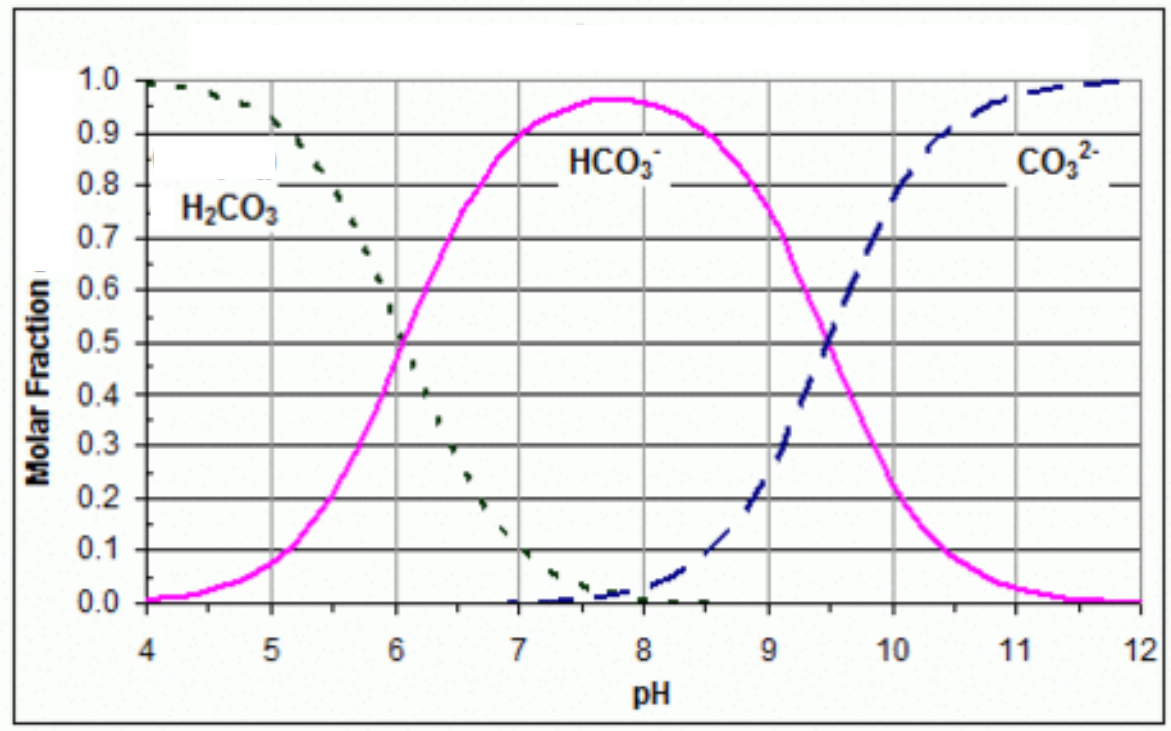

Fig 4.1

(a) (i) With reference to Fig 4.1, state the two pH values where the mixture are at its maximum buffering capacity.

pH of maximum buffering capacity : 6 and 9.5 [1]

(ii) Hence deduce the values for K_{a1} and K_{a2}.

pH = pK_{a1} = 6 (where [H_2CO_3] and [HCO_3^-] are equal])
$K_{a1} = 1 \times 10^{-6}$ mol dm^{-3}

pH = pK_{a2} = 9.5 (where [HCO_3^-] and [CO_3^{2-}] are equal])
$K_{a2} = 3.16 \times 10^{-10}$ mol dm^{-3}

[2]

(iii) Explain why the calculated value of K_{a1} is larger than K_{a2}?

It is **easier/less energy required** to dissociate/ give out a **positively charge H^+** ion from a **neutral molecule**, H_2CO_3, than from a negatively charged HCO_3^- ion. Thus position of equilibrium lie more to the right for K_{a1}.

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(iv) Aquatic organisms survive within specific pH range.
Suggest with equations, how the hydrogen carbonate and carbonate system in natural water ensures the survival of aquatic organisms.

Large reservoir of CO_3^{2-} neutralises **small amount** of H^+ added.

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \text{ with full arrow}$$

Large reservoir of HCO_3^- neutralises **small amount** of OH^- added

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \text{ with full arrow}$$

Hence **pH of the buffer** solution remains **approximately the same.**

(v) Table 4.1 gives the corresponding component of the gas in atmosphere. Determine the concentration of carbon dioxide in mol dm^{-3} in the atmosphere and hence determine the concentration of carbon dioxide dissolved in pure water at room temperature and pressure.

component in dry air	volume ratio of gas in dry air / ppm
oxygen	209 500
nitrogen	780 840
carbon dioxide	399
argon	9300

Table 4.1

[ppm refers to parts per million]

In 1 dm^3 of air,

$$\text{vol. of } CO_2(g) = \frac{399}{1000000} \times 1 = 3.99 \times 10^{-4} \text{ dm}^3$$

$$\text{amount of } CO_2(g) = \frac{3.99 \times 10^{-4}}{24} = 1.663 \times 10^{-5} \text{ mol}$$

$$\text{concentration of } CO_2(g) = 1.663 \times 10^{-5} \text{ mol dm}^{-3}$$

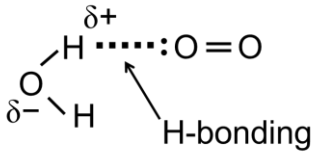
$$3.44 \times 10^{-2} = \frac{[CO_2(aq)]}{[CO_2(g)]}$$

$$3.44 \times 10^{-2} = \frac{[CO_2(aq)]}{1.663 \times 10^{-5}}$$

$$[CO_2(aq)] = 5.71 \times 10^{-7} \text{ mol dm}^{-3}$$

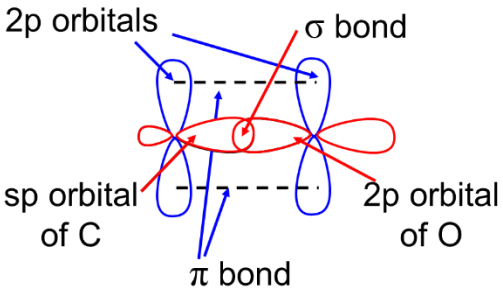
[3]

(vi) The concentration of dissolved O_2 is found to be 2.5×10^{-4} mol dm^{-3}. With the aid of a diagram, show how oxygen can dissolve in water.



- Lone pair electron on oxygen of O_2
- $\delta+$ on H and $\delta-$ on O of H_2O
- Label hydrogen bonding between lone pair of O (from O_2) and the $\delta+$ on H [1]

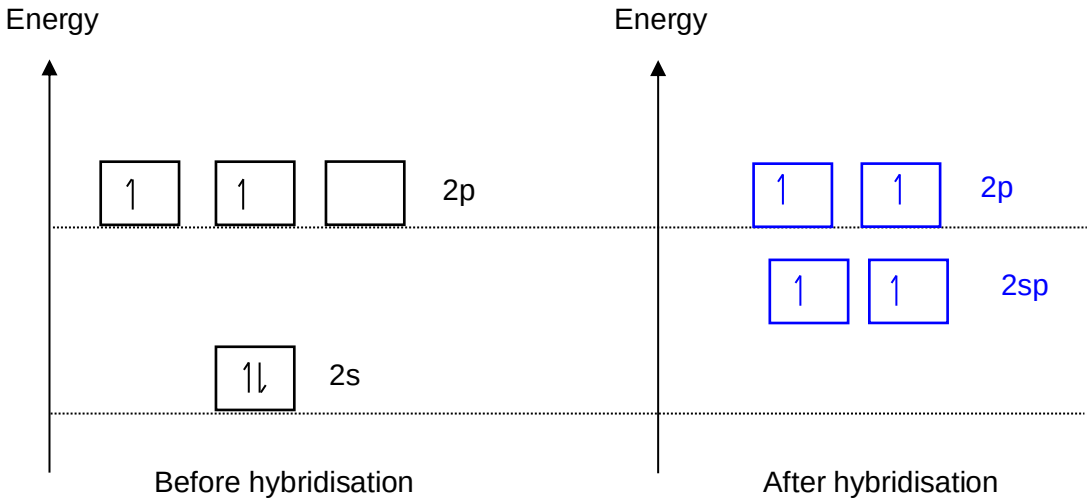
(b) **(i)** Draw the labelled diagram to show the orbitals that form the C=O bond in CO_2, and state the type of hybridisation involved.



sp hybridisation

For your information: O atom in CO_2 is actually sp^2 hybridised. For O atom, sp^2 hybrid orbital is used for sigma bonding and the unhybridised p orbital for pi bonding. However, for A level H2 Chemistry, we only study hybridisation for central atom and we can assume that terminal O atoms do not undergo hybridisation. [2]

(ii) Indicate the energy level of the orbitals involved in the σ(sigma) and π(pi) bonding of CO_2 on the energy level diagram provided. You should use boxes to represent the orbitals and half arrows to represent electrons.



- Correct label of the orbitals
- Energy level of the 2 2sp hybrid orbital in between energy level of p and s orbitals
- Energy of the 2 unhybridised p orbital at the same energy level
- Correct number of electrons in each orbitals. [2]

(c) Calcium carbonate is an important compound that ensures the alkalinity of river water. When calcium carbonate is heated, it decomposes according to the equation below.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of solid $CaCO_3$ to a rigid 1 dm^3 container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100K. As the container was heated, the total pressure of the $CO_2(g)$ in the container was measured over time. The data are plotted in Fig 4.2.

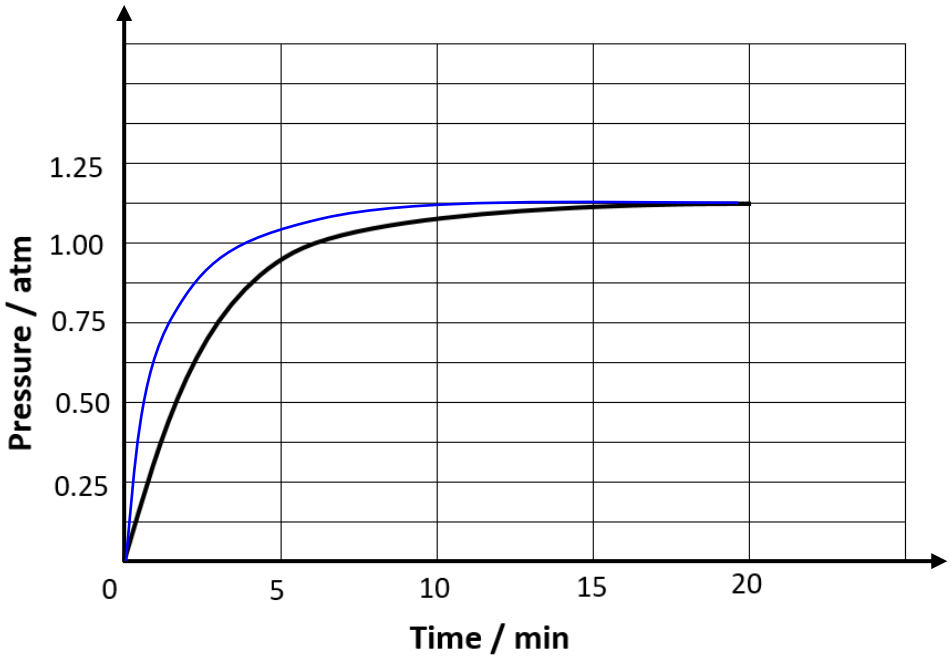


Fig 4.2

(i) The student repeated the experiment, but this time the student crushed another 50.0 g sample of $CaCO_3(s)$ into powdered form. Sketch the resultant graph **on the same axis provided in Fig 4.2**. [1]

steeper gradient but same final pressure

(ii) After 20 minutes, some $CO_2(g)$ was injected into the container, initially raising the pressure to 2.5 atm while keeping the temperature constant. Would the final pressure inside the container be less than, greater than, or equal to its initial pressure at 20 minutes? Explain your reasoning.

$K_p = P_{CO_2}$

K_p changes only when temperature changes. Since **K_p only dependent on P_{CO2} in the equation.** The final pressure after adding more CO_2 will still be **1.125atm / equal to its initial pressure at 20 minutes**.

[2]

[Total : 18]

5 **(a)** Alkene can undergo oxidation with ozone, O_3, to give carbonyl compounds. This reaction is known as *ozonolysis*.

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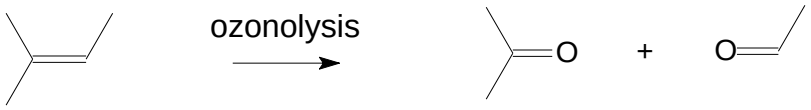


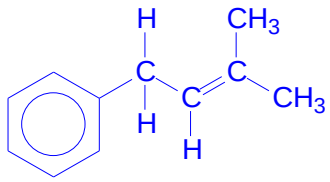
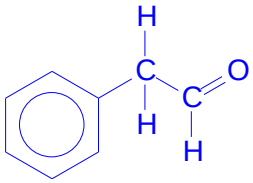
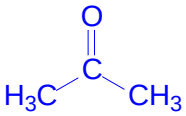
Alkene **J**, $C_{11}H_{14}$, undergoes *ozonolysis* to give compound **K**, C_8H_8O, and compound **L**, C_3H_6O.

Compound **K** gives a brick red precipitate when warmed with alkaline Cu^{2+} tartrate complex.

Compound **L** gives a yellow precipitate when warmed with alkaline I_2.

Alkene **J** gives compound **L** and benzoic acid, $C_6H_5CO_2H$, as the only organic products when heated with acidified $KMnO_4$.

(i) Suggest the structures of compounds **J**, **K** and **L**. [3]

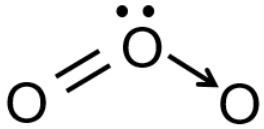
		
Compound **J**	Compound **K**	Compound **L**

(ii) Write an equation for the reaction of alkene **J** with $KMnO_4$, using [O] to represent the oxidising agent.

$C_{11}H_{14} + 6[O] \longrightarrow C_3H_6O + C_6H_5COOH + CO_2 + H_2O$

[1]

(iii) Draw the structure of O_3 to illustrate its shape and show any dative covalent bond it may contain.



bent and dative bond

[1]

(b) Cycloalkenes can undergoes *syn* and *anti* addition as shown in Fig 5.1.

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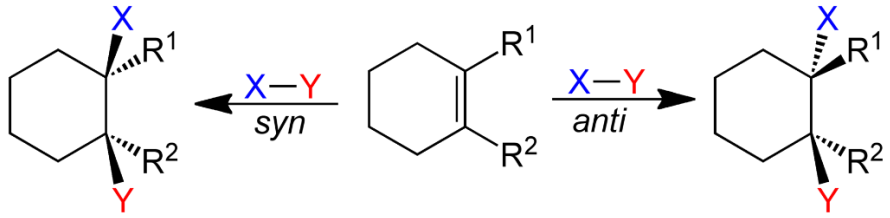
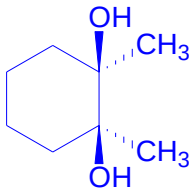
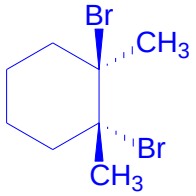


Fig 5.1

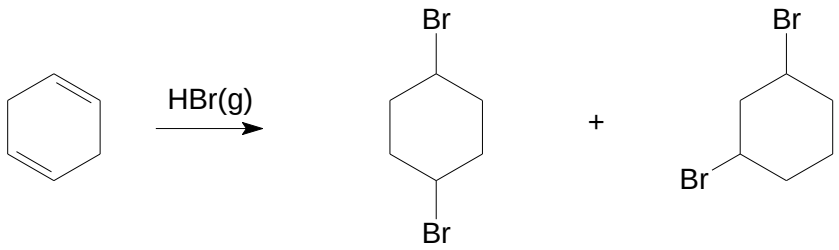
An example of *syn* addition is the oxidation of alkene to diol.
An example of *anti* addition is the bromination of alkene.

Using information from Fig 5.1, suggest the structure of the product for the reaction of 1,2−dimethylcyclohexene with the following reagents.

cold alkaline $KMnO_4$	
Br_2 in CCl_4	

[2]

(c) Fig 5.2 shows the reaction of cyclohexa−1,4−diene with HBr(g).

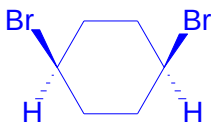
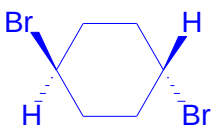


Cyclohexa−1,4,−diene 1,4−dibromocyclohexane 1,3−dibromocyclohexane

Fig 5.2

(i) 1,4−dibromocyclohexane exhibits cis-trans isomerism.

Draw the structures of the stereoisomers.

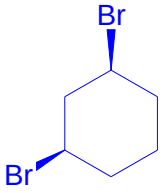
cis isomer	trans isomer
	

[2]

[Turn over

(ii) 1,3−dibromocyclohexane contains two chiral carbons. This gives rise to only three stereoisomers, of which two are optically active.

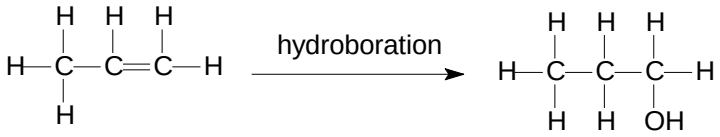
Suggest the structure of the *optically inactive* stereoisomer and explain why it has no optical activity.



This stereoisomer contains an internal plane of symmetry. **The rotation of plane polarised light by each chiral carbon is completely cancelled out by the other chiral carbon.**

[2]

(d) Hydroboration can be used to convert an alkene to an alcohol.



Hydroboration involves a two-step reaction as shown in Fig 5.3:

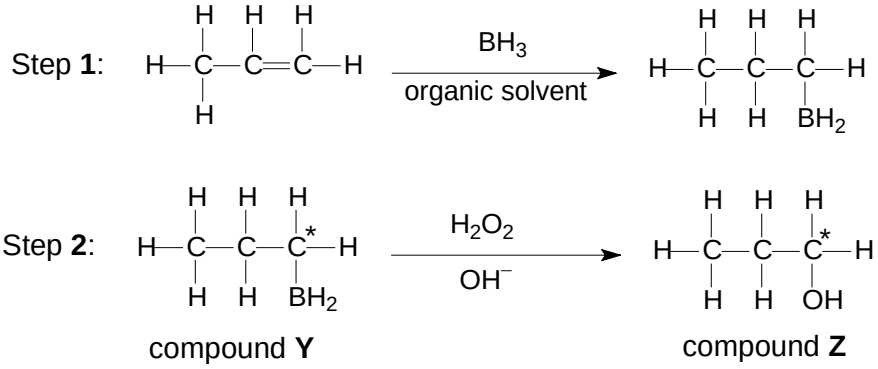


Fig 5.3

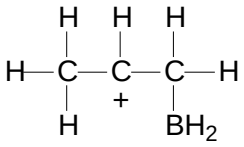
The electronegativity data for some elements are given in Table 5.1.

element	B	C	H	O
electronegativity	2.0	2.5	2.1	3.6

Table 5.1

For Examiner's Use

(i) Step **1** is an electrophilic addition reaction. Draw the structure of the carbocation intermediate involved in step **1**.



Note: Based on the data on electronegativity, B is δ+ and H is δ– (B is less electronegative than H). Thus BH_2^+/BH_3 is the electrophile.

[1]

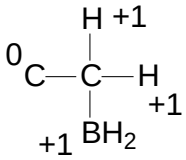
(ii) State the oxidation number of the carbon atoms labelled * in compound **Y** and **Z**, and hence deduce the role of H_2O_2 in step **2**.

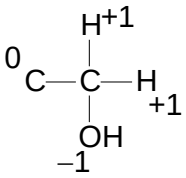
Oxidation number of C* in **Y** is −3

Oxidation number of C* in **Z** is −1

Role of H_2O_2: as oxidising agent

Note:
Oxidation number of C atom in organic compound is obtained by looking at the atoms surrounding the C atom.





H and B atoms are less electronegative than C atom, the single bonded H and B atoms would be assigned an oxidation number of +1 relative to the C atom.
O is more electronegative than C, the single bonded O is assigned O.N of −1 relative to the C.

[2]

[Total : 14]