2017 JC1 H2 Chemistry Promotional Examination Paper 1

Section A: Structured Questions [35 marks]

Answer all the questions in the spaces provided.

S1 A pure sample of $NO_2(g)$ is introduced into an evacuated vessel and the following equilibrium is established at a constant volume.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g) \qquad \Delta H > 0$$

(a) At 80 °C, 30% of NO_2 has dissociated at equilibrium and the total pressure is 3 atm. Calculate the mole fraction of NO_2, NO and O_2 in the equilibrium mixture.

Mol	$2NO_2(g)$ ⇌	$2NO(g)$	$O_2(g)$
Initial / mol	y	0	0
Change / mol	-0.3y	+0.3y	+0.15y
Equilibrium / mol	0.7y	0.3y	0.15y

Total amount of gases at equilibrium = 0.7y + 0.3y + 0.15y = 1.15y
Mole fraction of NO_2 = 0.7y / 1.15 y = <u>0.609</u>
Mole fraction of NO = 0.3y / 1.15 y = <u>0.261</u>
Mole fraction of O_2 = 0.15y /1.15 y = <u>0.130</u>

[2]

(b) Calculate the value of K_p at 80 °C, giving its units.

P_{NO_2} = 0.609 x 3 = 1.83 atm
P_{NO} = 0.261 x 3 = 0.783 atm
P_{O_2} = 0.130 x 3 = 0.390 atm

$$K_p = \frac{P_{O_2}P_{NO}^2}{P_{NO_2}^2} = \frac{(0.390)(0.783)^2}{1.83^2} = \underline{0.0714}\ \underline{\text{atm}}$$

[2]

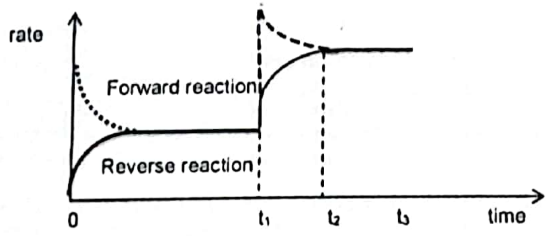
(c) **(i)** Explain how an increase in temperature would affect the value of K_p.

Increase in temperature favours the <u>endothermic reaction</u> or the reaction to remove excess heat. Hence, position of <u>equilibrium shift to the right</u>, and K_p value would <u>increase.</u>

[2]

(ii) Temperature of the reaction is raised at time t_1 and a new equilibrium is established at time t_2 and maintained till time t_3.

Complete the graph below showing how the rates of the forward and reverse reactions change from time t_1 to t_3. Use dotted line for the forward reaction and solid line for the reverse reaction.



Rate of forward, R_f, and rate of backward reaction, R_r, increases
$R_f > R_r$ (since temperature increases , there is a net endothermic reaction.)
R_f and R_r approaching each other and meet at t_2
$R_f = R_r$ from t_2 to t_3

[2]
[Total:8]

S2 **(a)** On heating gaseous phosphorus pentachloride, the following equilibrium is set up:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

When 12.0 g of phosphorus pentachloride were put into a sealed evacuated vessel of capacity 1.00 dm^3, and heated to 300 °C, the pressure increased to 3.50 x 10^5 Pa.

(i) Use the above data to calculate the average M_r of the gaseous mixture.

pV = nRT and n = m/M_r
M_r = mRT / (pV)
= (12.0)(8.31)(<u>300+273</u>) / [(3.50 x 10^5)(<u>1.00 x 10^{-3}</u>)]
= 163.3

[2]

(ii) Hence, determine the percentage dissociation of PCl_5 in the mixture.

The initial number of moles of $PCl_5(g)$ = 12.0 / 208.5 = 0.0576 mol

	$PCl_5(g)$ ⇌	$PCl_3(g)$ +	$Cl_2(g)$
Initial /mol	0.0576	0	0
Change /mol	-x	+x	+x
Equilibrium /mol	0.0576-x	x	x

Total number of moles of gaseous particles = 0.0576 – x + x +x
= (0.0576 + x) mol

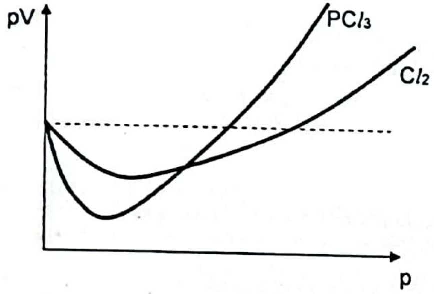
Mole fraction of each gas is $\frac{0.0576-x}{0.0576+x}$, $\frac{x}{0.0576+x}$ **and** $\frac{x}{0.0576+x}$.

$$208.5\times\frac{0.0576-x}{0.0576+x}+137.5\times\frac{x}{0.0576+x}+71.0\times\frac{x}{0.0576+x}=163.3$$

x = 0.0159 mol
Percentage dissociation = 0.0159 / 0.0576 × 100% = 27.6%

[2]

(iii) Sketch a graph to show how the value of the product pV changes with pressure for PCl_3 in the diagram below.



[1]

(b) (i) State the electronic configurations of phosphorus and sulfur.

P: $1s^2 2s^2 2p^6 3s^2 3p^3$
S: $1s^2 2s^2 2p^6 3s^2 3p^4$

[2]

(ii) With reference to the *Data Booklet*, explain how the first ionisation energy of phosphorus is compared to that of silicon and sulfur.

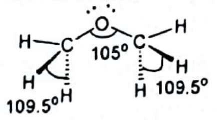
The first ionisation energies of phosphorus, silicon and sulfur are 1060, 786 and 1000 kJ mol⁻¹ respectively.
The first ionisation energy of phosphorus is higher than that of silicon because it has one more proton thus greater nuclear charge
but similar shielding effect due to same number of inner shell electrons,
thus greater effective nuclear charge.
The first ionisation energy of phosphorus is higher than sulfur as the electrons removed from sulphur is from a doubly occupied orbital while that of phosphorus is from a singly occupied orbital.
Thus, the inter-electronic repulsion between electrons in the same orbital leads to a lower first ionisation energy.

[3]

[Total: 10]

S3 **(a)** Dimethyl ether (DME), CH_3OCH_3, is a gas which can be synthesised from methanol, CH_3OH. Methanol can be obtained from biomass, such as plant waste from agriculture.

(i) Draw the shape of a molecule of dimethyl ether, CH_3OCH_3, showing the values of the bond angles about oxygen and carbon atoms.

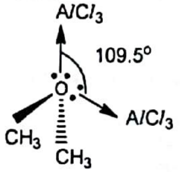


Two correct bond angles
Correct 3D shape drawn around O and C (with wedge and dash bond)

[2]

(ii) Explain why dimethyl ether form a product with gaseous $AlCl_3$ when they react in a molar ratio of 1:2. Draw a diagram to illustrate the shape of the product formed about the oxygen atom.

In $AlCl_3$, Al has one vacant orbital.
Hence, Al can accept the 1 lone pair of electrons from O in CH_3OCH_3 via dative covalent bonding to attain a stable octet configuration. As there are 2 lone pairs of electrons on the O atom, it will form 2 dative covalent bonds with 2 Al atom.



[2]

(iii) Explain why dimethyl ether is soluble in methanol.

Hydrogen bonding between dimethyl ether and methanol releases sufficient energy to overcome
hydrogen bonding between methanol molecules and
permanent dipole-permanent dipole interaction between dimethyl ether molecules.
Hence, dimethyl ether is soluble in methanol.

[2]

(iv) Explain why methanol has a lower boiling point than water.

Water molecule can form more hydrogen bonds per molecule than methanol.
Both methanol and water have an oxygen atom with two lone pairs of electrons but methanol has only one hydrogen atom bonded to oxygen whereas water has two hydrogen atoms bonded to oxygen.

[1]

(v) Some bond energies are given in the table below.

Bond	Bond energy, kJ mol⁻¹
C=O	740
C–O	360
C–F	485

Given that the sizes of fluorine and oxygen atoms are comparable, explain the relative strength of these bonds with reference to the bond energies given.

The larger the bond energy, the stronger the bond.
C=O bond is stronger than C-O bond due to the presence of greater number of shared electron pairs, resulting in greater attraction between the two nuclei.
F is a more electronegative atom than O, hence C–F bond is more polar
With stronger attraction between the partial charges.

[2]

(b) Potassium hydrogen tartrate, $KHC_4H_4O_6$ (KHT) is a sparingly soluble salt. In a saturated solution with undissolved solid KHT, the following equilibrium is established.

$$KHC_4H_4O_6(s) \rightleftharpoons K^+(aq) + HC_4H_4O_6^-(aq)$$

At 25 °C, the solubility of KHT in water is 0.032 mol dm^{-3}.

(i) Write an expression for the solubility product, K_{sp}, of KHT. Hence calculate the value of K_{sp}.

K_{sp} = $[K^+][HT^-]$
K_{sp} = (0.032)(0.032)
= <u>1.02×10^{-3}</u> $mol^2\ dm^{-6}$

[2]

(ii) State the effect, if any, on the solubility and K_{sp} of KHT when solid potassium chloride is added to a saturated solution of KHT.

Solubility of KHT <u>decreases</u>.
K_{sp} remains <u>unchanged</u>.

[2]

(iii) The hydrogen tartrate ion, $HC_4H_4O_6^-$ (HT^-), is a weak monobasic acid and its concentration in the saturated solution of KHT can be determined by titration with a strong base like sodium hydroxide of known concentration.

In a titration experiment, 20.00 cm^3 of 0.0400 mol dm^{-3} aqueous sodium hydroxide was needed to neutralise a saturated solution of KHT at 25 °C.

Calculate the volume of saturated solution of KHT used in the titration.

no. of moles of (HT^-)
= no. of moles of (NaOH)
= 20.00 / 1000 x 0.0400
= 0.000800 mol

Volume of saturated solution of KHT used
= 0.000800 / 0.032 x 1000
= 25.0 cm^3

[1]

500 cm^3 of 0.50 mol dm^{-3} potassium chloride is added to 500 cm^3 of saturated KHT solution to form a solution A at 25 °C.

(iv) Calculate the concentration of hydrogen tartrate ion, HT^-, in solution A.

	KHT(s)	$\rightleftharpoons$	K^+(aq)	HT^-(aq)
initial/mol	**0**		**0.266**	**0.016**
change/mol	**+ x**		**− x**	**− x**
equilibrium/mol	**x**		**0.266 − x**	**0.016 − x**

Concentration of K^+ = $\frac{500 \times 0.5}{1000} + \frac{500 \times 0.032}{1000}$ = 0.266 mol dm^{-3}
$[K^+][HC_4H_4O_6^-] = 1.02 \times 10^{-3}$
$[HC_4H_4O_6^-] = \frac{1.02 \times 10^{-3}}{0.266}$
$= 3.83 \times 10^{-3}$ mol dm^{-3}

[1]

(v) Hence, calculate the mass of KHT precipitated.

Number of moles of KHT precipitated
= (0.032 × 500/1000) − (3.83×10^{-3})
= 1.22×10^{-2} mol
M_r of KHT = 39.1 + 5(1.0) + 4(12.0) + 6 (16.0) = 188.1
Mass of KHT precipitated
= $1.22 \times 10^{-2} \times 188.1$
= 2.29 g

[2]

[Total: 17]

Section B: Essay Questions [40 marks]

Answer both questions on the writing paper provided.
Begin each question on a fresh sheet of paper.

E1 (a) The sulfur-iodine cycle has been proposed as a means of producing hydrogen fuel more efficiently than by electrolysis.

At high temperatures, the sulfur-iodine cycle involves three gas-phase equilibria:

	Equation			ΔH_r°/ kJ mol^{-1}
1	$I_2(g) + SO_2(g) + 2H_2O(g)$	→	$H_2SO_4(g) + 2HI(g)$	ΔH_1°
2	$2H_2SO_4(g)$	→	$2SO_2(g) + 2H_2O(g) + O_2(g)$	+439
3	$2HI(g)$	→	$H_2(g) + I_2(g)$	+11

(i) Conditions are chosen so that the three equilibrium reactions above all proceed from left to right. Assuming that all the products of reaction **1** are consumed in reactions **2** and **3**, write an overall equation for the sulfur-iodine cycle. [1]

$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$ Or $H_2O(g) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$

(ii) Standard enthalpy change of formation for $H_2O(g)$, ΔH_f° is −242 kJ mol^{-1}.

Using the data given, construct an energy cycle to determine ΔH_1°. [3]

$$\begin{tikzcd}
I_2(g) + SO_2(g) + 2H_2O(g) \arrow[r, "\Delta H_1^\circ"] & H_2SO_4(g) + 2HI(g) \arrow[d, "\frac{+439}{2}"] \\
 & SO_2(g) + H_2O(g) + \frac{1}{2} O_2(g) + 2HI(g) \arrow[dl, "+11"] \\
SO_2(g) + H_2O(g) + \frac{1}{2} O_2(g) + H_2(g) + I_2(g) \arrow[uu, "-242"] &
\end{tikzcd}$$

Using Hess' Law,

$\Delta H_1^\circ = -(-242) - 11 - (439/2)$
$= +11.5\ \text{kJ mol}^{-1}$

(b) Consider the reaction,

$$SF_6(g) + 4H_2O(g) \rightarrow H_2SO_4(g) + 6HF(g)$$

(i) State and explain the sign of ΔS for the reaction. [1]

Gas particles are the most randomly arranged. The <u>number of gas particles has increased.</u>
Hence, $\Delta S > 0$.

(ii) Use the data on standard enthalpy change of formation below to calculate the standard enthalpy change for this reaction.

	$SF_6(g)$	$H_2O(g)$	$H_2SO_4(g)$	$HF(g)$
ΔH_f°/ kJ mol^{-1}	–1210	–242	–735	–273

[2]

$\Delta H_r^\circ = (\sum \Delta H^\circ_{f\ \text{of products}}) - (\sum \Delta H^\circ_{f\ \text{of reactants}})$
$= -735 + 6(-273) - [-1210 + 4(-242)]$
$= -195\ \text{kJ mol}^{-1}$

(iii) By considering the entropy and enthalpy changes, predict the spontaneity of the reaction of sulphur hexafluoride with water. [2]

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
Since $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$,
$\Delta G^\circ < 0$ for all temperature.
Reaction of SF_6 with water is thermodynamically <u>spontaneous</u>.

(c) Hydrogen can be used to generate electricity in a fuel cell. The earliest hydrogen fuel cell used phosphoric acid, H_3PO_4, as an electrolyte. H_3PO_4 is a *weak Bronsted Acid* that is often used to form buffer solutions with near-physiological pH.

(i) Explain fully what is meant by the phrase *weak Bronsted Acid.* [1]

A weak Bronsted acid is defined as a <u>proton donor</u> that is <u>partially ionised</u> in solution.

A student purchased a bottle of concentrated phosphoric acid, H_3PO_4 from an online merchant. The following information regarding the H_3PO_4 purchased was provided by the merchant:

General description
In aqueous solutions, phosphoric acid, H_3PO_4 behaves as a triprotic acid. The triprotic acid has three ionisable hydrogen atoms, which can be lost sequentially.

Properties:
- Total volume: 1.00 dm^3
- Concentration: 14.7 mol dm^{-3}
- Relative Molecular Mass of H_3PO_4: 98.0
- $K_{a1} = 7.5 \times 10^{-3}$ mol dm^{-3}
- $K_{a2} = 6.2 \times 10^{-8}$ mol dm^{-3}
- $K_{a3} = 4.8 \times 10^{-13}$ mol dm^{-3}

(ii) Calculate the volume of water that needs to be added to dilute 10 cm^3 of the 14.7 mol dm^{-3} H_3PO_4 solution to a final concentration of 0.500 mol dm^{-3}. [1]

$C_1V_1 = C_2V_2$
$(14.7)(10) = (0.5)V_2$
$V_2 = 294$ cm^3
Hence, volume of water needed $= 294 - 10$
$= 284$ cm^3

(iii) Write down the expression for K_{a2} of H_3PO_4 [1]

$$K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

(d) The student plans to prepare a buffer solution that contains the species $H_2PO_4^-$ and HPO_4^{2-}.

(i) With the aid of equations, explain how this $H_2PO_4^-/HPO_4^{2-}$ buffer solution maintains a fairly constant pH when
- a small amount of acid is added

$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$
When a small amount of acid is added, the <u>large reservoir of HPO_4^{2-}</u> removes the excess H^+, keeping the pH fairly constant.

- a small amount of base is added [3]

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$
When a small amount of base is added, the <u>large reservoir of $H_2PO_4^-$</u> removes the excess OH^-, keeping the pH fairly constant.

(ii) To prepare the buffer solution, the student added 8.0 cm^3 of 1.00 mol dm^{-3} NaOH to 10.0 cm^3 of 0.500 mol dm^{-3} H_3PO_4.

Calculate the pH of the resultant buffer solution formed. [3]

No. of moles of H_3PO_4 = (10/1000) x 0.500 = 0.00500 mol
No. of moles of OH^- added = (8/1000) x 1 = 0.00800 mol

$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$
No. of moles of OH^- reacted with H_3PO_4 = 0.00500 mol
No. of moles of $H_2PO_4^-$ formed = 0.00500 mol

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$
No. of moles of OH^- reacted with $H_2PO_4^-$ = 0.00300 mol
No. of moles of $H_2PO_4^-$ left = 0.00200 mol
No. of moles of HPO_4^{2-} formed = 0.00300 mol
$[H_2PO_4^-] = (0.00200 / 0.018)$ mol dm^{-3}
$[HPO_4^{2-}] = (0.00300 / 0.018)$ mol dm^{-3}

$K_{a2} = \frac{[H^+][HPO_4^{2}]}{[H_2PO_4]}$
$[H^+] = K_{a2} \times \frac{[H_2PO_4]}{[HPO_4^{2}]}$
$= 6.2 \times 10^{-8} \times (0.002/0.003)$
$= 4.13 \times 10^{-8}$ mol dm^{-3}
$pH = -\log_{10}(4.13 \times 10^{-8})$

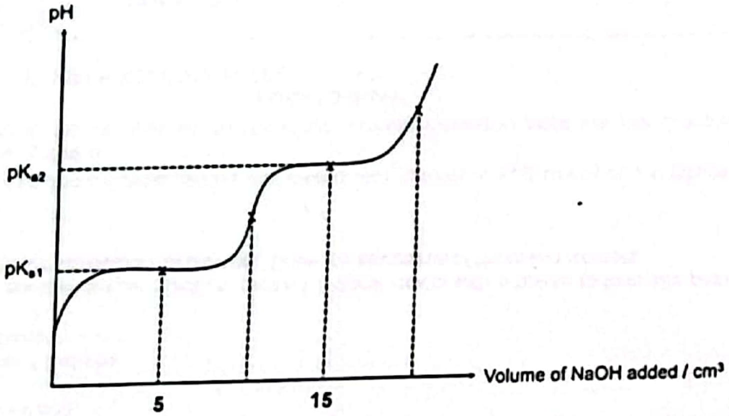
= 7.38

Alternatively,

$$\text{pH} = \text{pK}_{a2} + \lg \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$
$$= -\lg(6.2 \times 10^{-8}) + \lg(0.003 / 0.002)$$
$$= 7.38$$

(iii) Sketch the titration curve of pH against volume of NaOH when 10.0 cm^3 of 0.500 mol dm^{-3} H_3PO_4 is titrated against 20.00cm^3 of 0.500 mol dm^{-3} NaOH.

Label the co-ordinates corresponding to the points of maximum buffering capacity. [2]



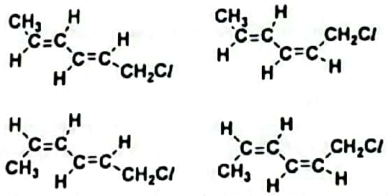
Shape
pK$_{a1}$ (or calculated value of 2.12)
5 cm^3
pK$_{a2}$ (or calculated value of 7.21)
15 cm^3

[Total: 20]

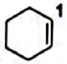
E2 Alkenes are hydrocarbons that contain at least one carbon-carbon double bond. Dienes are hydrocarbons that contain two carbon-carbon double bonds and they display reactivity similar to alkenes.

(a) Compound **A** has the formula $CH_3CH{=}CHCH{=}CHCH_2Cl$. It is a diene which exhibit isomerism.

Draw all the possible stereoisomers of compound **A**. [2]



(b) Cyclohexene and cyclohexa-1,4-diene are cyclic alkenes.



cyclohexene

cyclohexa-1,4-diene

(i) State the total numbers of sigma and pi bonds in a molecule of cyclohexa-1,4-diene. [1]

14 sigma bonds
2 pi bonds

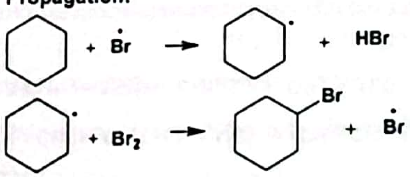
(ii) State the type of hybridisation that carbon 1 undergoes and the shape around it. [2]
sp^2
trigonal planar

(iii) Cyclohexene undergoes hydrogenation to form cyclohexane.
Describe the mechanism for the bromination of cyclohexane to form bromocyclohexane. [3]

Mechanism: Free radical substitution

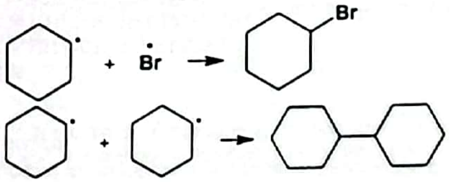
Initiation:

Propagation:



Termination:

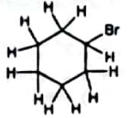
$2\,Br\cdot \rightarrow Br_2$



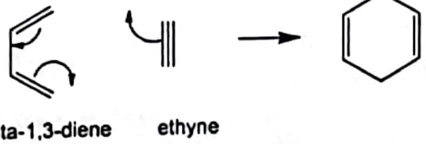
(iv) Bromocyclohexane undergoes further substitution to form 1,3-dibromocyclohexane.

State the probability of forming 1,3-dibromocyclohexane from bromocyclohexane. [1]

Probability to form 1,3–dibromocyclohexane from bromocyclohexane = 4/11



Cyclohexa-1,4-diene can be made by heating buta-1,3-diene with ethyne. The diagram below shows the movement of electron pairs, represented by curly arrows, needed to generate the cyclohexa-1,4-diene in a single step.



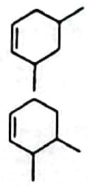
(v) In a similar type of reaction, cyclohexene can be formed from two alkenes.

Suggest the names of the two alkenes that would react to form cyclohexene in this type of reaction. [2]

buta-1,3-diene
ethene

(vi) In another similar reaction, penta-1,3-diene reacts with propene to form two products that are constitutional isomers. Draw the structures of these two isomers. [1]

penta-1,3-diene



(c) B, C and D are compounds with molecular formula C_6H_{12}.

B does not decolorise aqueous bromine but will decolourise bromine in sunlight.

C decolourises aqueous bromine and reacts with HBr to give $CH_3CHBrCH_2CH(CH_3)_2$. On oxidation with hot, acidified potassium manganate(VII), C gives E, $C_5H_{10}O_2$, as the only organic product.

D undergoes oxidation with hot, acidified potassium manganate (VII) to give $CH_3CH_2CO_2H$ as the only organic product.

(i) Suggest the identities of the organic compounds B, C, D and E by giving their structural formulae. [4]

B is 
C is $CH_2{=}CHCH_2CH(CH_3)_2$
D is $CH_3CH_2CH{=}CHCH_2CH_3$
E is $(CH_3)_2CHCH_2CO_2H$

(ii) Write the balanced equation for the oxidation of C to E. [1]
You may use [O] to represent the oxidation of C.

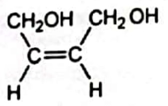
$CH_2{=}CHCH_2CH(CH_3)_2 + 5[O] \rightarrow (CH_3)_2CHCH_2CO_2H + CO_2 + H_2O$

OR $C_6H_{12} + 5[O] \rightarrow C_5H_{10}O_2 + CO_2 + H_2O$

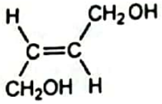
(iii) Give the structural formula of the major product obtained when $CH_3CHBrCH_2CH(CH_3)_2$ reacts with hot alcoholic potassium hydroxide. [1]

$CH_3CH{=}CHCH(CH_3)_2$

(d) It was observed that the boiling point of *cis*-but-2-ene-1,4-diol is lower than that of the trans isomer. Suggest a reason for this observation. [2]



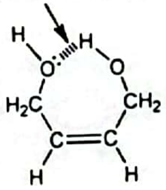
cis-but-2-ene-1,4-diol



trans-but-2-ene-1,4-diol

Both compounds are held together by intermolecular hydrogen bonding. However, due to the presence of intramolecular hydrogen bonding in cis-but-2-ene-1,4-diol, intermolecular hydrogen bonding between the cis isomers is less extensive. Thus, less energy is required to break the hydrogen bonding between cis-but-2-ene-1,4-diol than trans-but-2-ene-1,4-diol.

hydrogen bonding



[Total: 20]