

Name:		Centre/Index Number:		Class:	
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DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

Paper 2 Structured Questions

9729/02

15 September 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.

Write in dark blue or black pen.

You may use an 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.

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

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

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

For Examiner's Use	
1	12
2	12
3	13
4	14
5	24
Total	75

This document consists of **19** printed pages and **1** blank page.

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

- 1 (a) Water chemistry plays an important role in aquariums. For disinfection purposes, chlorine, Cl_2 , and chloroamine, NH_2Cl , are introduced into our tap water to destroy bacteria and viruses. However, these two chlorine-containing compounds are extremely harmful to fishes as they cause gill burns and blood poisoning.

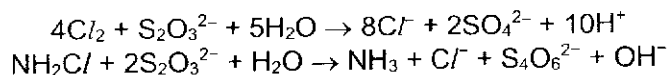
The typical concentration of some chemical species found in our tap water are listed in Table 1.1.

Table 1.1

chemical species	concentration / mol dm^{-3} .
Cl_2	3.24×10^{-5}
NH_2Cl	3.88×10^{-5}
PO_4^{3-}	1.26×10^{-7}
Fe (as Fe^{2+} & Fe^{3+})	1.08×10^{-7}

To prepare an aquarium tank, a water conditioner containing sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is added to the tank to remove both the aqueous chlorine and chloroamine present in tap water.

Sodium thiosulfate reacts with chlorine and chloroamine respectively as shown in the reactions below.



- (i) Calculate the volume of $0.010 \text{ mol dm}^{-3}$ sodium thiosulfate solution that would be required to prepare a tank containing 360 dm^3 of water.

[3]

- (ii) State the full electronic configuration of iron in $\text{Fe}_3(\text{PO}_4)_2$.

.....[1]

(b) The direct reaction of hydrogen with chlorine gives hydrogen chloride. However, hydrogen chloride is produced industrially by treatment of halide salts with sulfuric acid. On the other hand, hydrogen iodide, HI, is produced by the reaction of iodine with hydrogen sulfide or with hydrazine.

(i) Explain briefly why it is not industrially viable to produce HCl through the direct reaction of hydrogen with chlorine.

.....
[1]

(ii) Write a balanced equation showing the formation of HI from iodine and hydrogen sulfide. Hence, with reference to the *Data Booklet*, show that the reaction is spontaneous.



.....

[2]

(iii) Explain why the pK_a values decrease from HCl to HI.

.....

[2]

(c) In an experiment, a sample of chloride ions was vapourised and passed through an electric field. Analysis revealed that a beam of $^{37}\text{Cl}^-$ gives an angle of deflection of -1.0° .

(i) State the angle of deflection for a beam of deuterium nuclei in the same experimental set-up.

(D is deuterium, ^2_1H)

.....[1]

- (ii) Under identical conditions, a beam of particles, **Z**, each having 32 times the mass of a proton, was deflected by an angle of -2.3° . Given that the proton number of **Z** is 16, deduce the identity of **Z**.

[2]

[Total: 12]

- 2 The electrochemical oxidation of benzylic alcohols to the corresponding aldehydes via a two-phase electrolysis system was reported in 2007. An example is shown in Fig. 2.1.

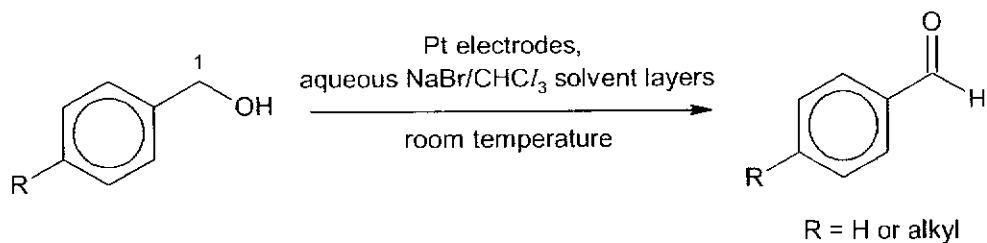
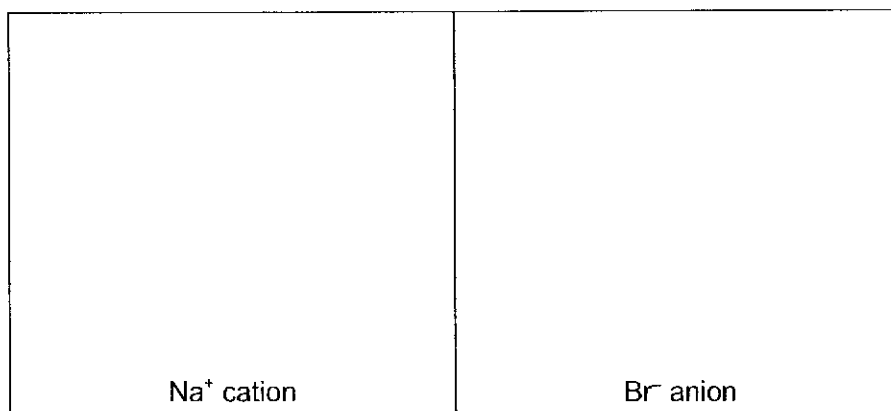


Fig. 2.1

- (a) State the reagents and conditions for the conversion of benzylic alcohols to the corresponding aldehydes in a school laboratory.
[1]
- (b) The two-phase electrolysis system comprises the aqueous NaBr and organic CHCl_3 layers.
- (i) Draw simple diagrams to illustrate how a water molecule can be attached to a sodium cation, and to a bromide anion in the aqueous layer. Label each diagram to show the type of interaction involved.

[2]



- (ii) Predict and explain which layer the benzylic alcohols would predominantly dissolve in.

.....

[2]

- (c) (i) Describe the change in oxidation state of the benzylic carbon, labelled 1 in Fig. 2.1, when the alcohol is oxidised to the corresponding aldehyde.

.....
.....[1]

- (ii) In experiment 1 where R = H in Fig. 2.1, one mole of benzylic alcohol is oxidised to give 96 % yield of aldehyde.

Using your answer in (c)(i), determine the charge, in Faraday, required to yield the aldehyde.

[1]

- (iii) Current efficiency describes the efficiency with which charge is transferred in an electrolysis system and is given by the equation below.

$$\text{current efficiency} = \frac{\text{charge required}}{\text{charge passed}} \times 100\%$$

In experiment 1, 5.5 F of charge is passed per mole of benzylic alcohol.

Using your answer in (c)(ii), calculate the current efficiency of experiment 1.

[1]

- (iv) Some data obtained from experiments 2 and 3 are shown in Table 2.1.

Table 2.1

Experiment No.	R group in Fig. 2.1	Current efficiency / %
2	-CH ₃	42.5
3	-C(CH ₃) ₃	64.0

Using the data provided in Table 2.1, deduce the relationship between the electronic effect of the R group on the benzene ring and the current efficiency of the electrochemical process.

.....

[1]

- (v) Hence, suggest how you would expect the current efficiency when R = -OCH₃ to compare with that when R = -CH₃. Explain your reasoning.

.....

[1]

- (d) In the two-phase electrolysis system, two platinum electrodes are placed in the upper aqueous NaBr layer and the bromide ions are oxidised at the anode.

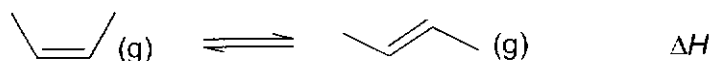
State the polarity of the anode and quote relevant values from the *Data Booklet* to explain the preferential production of bromine at the electrode.

.....

[2]

[Total: 12]

- 3 (a) The cis-trans isomerisation of but-2-ene in the gas phase is promoted by transition metal catalysts.

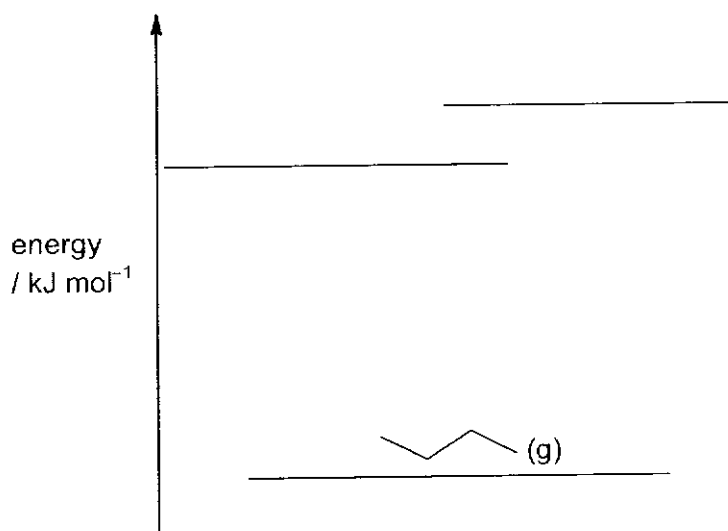


- (i) Complete the energy diagram below by drawing arrows to show how the enthalpy changes in Table 3.1 can be used to determine ΔH , the enthalpy change of conversion of cis-but-2-ene to trans-but-2-ene in the gas phase.

Label each level with the appropriate formulae.

Table 3.1

gaseous alkene	enthalpy change of hydrogenation / kJ mol^{-1}
cis-but-2-ene	-119
trans-but-2-ene	-115



[2]

- (ii) Use the energy diagram in (a)(i) to calculate a value for ΔH .

[1]

- (iii) Comment on the difference in stability of the cis-trans isomers of but-2-ene. Use the concept of steric effects in your answer.

.....

[1]

- (iv) Using your answer in (a)(ii), calculate ΔS for the conversion of cis-but-2-ene to trans but-2-ene at equilibrium at 355 K.

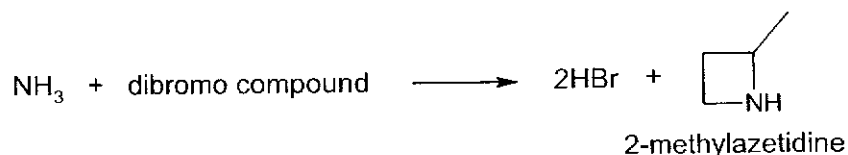
[1]

- (b) But-2-ene reacts with hydrogen bromide to form 2-bromobutane.

- (i) Draw the structures of the four dibromo compounds that could be formed when 2-bromobutane reacts with bromine in ultraviolet light. Ignore any stereoisomers formed.

[2]

2-methylazetidine can be synthesised by reacting ammonia with a dibromo compound.



- (ii) Using your answer in (b)(i) or otherwise, name the dibromo compound that reacted with ammonia to form 2-methylazetidine.

.....[1]

(iii) Describe and explain the relative basicity of ammonia and 2-methylazetidine.

.....
.....
.....
.....
.....[2]

(c) Magnesium, silicon and sulfur are Period 3 elements.

(i) On Fig. 3.1, sketch a graph of melting point against electronegativity for each of the three elements.

[1]

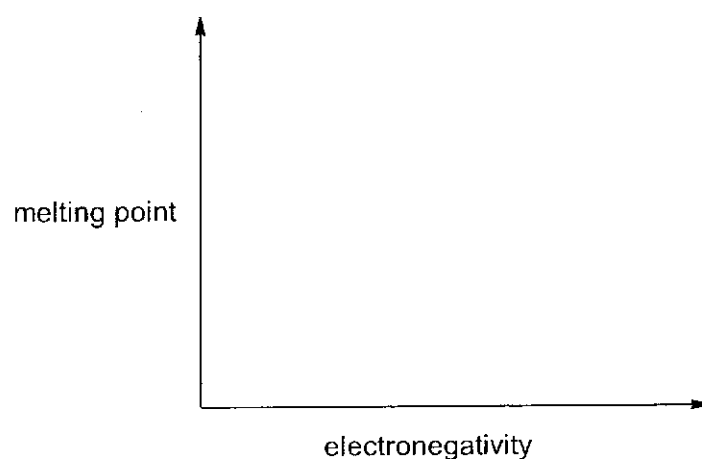


Fig. 3.1

(ii) Explain the variation in melting point for the three elements.

.....
.....
.....
.....
.....
.....[2]

[Total: 13]

- 4 (a) Sodium boron hydride, NaBH_4 , is commonly used in the pharmaceutical industries as a selective reducing agent. Aqueous NaBH_4 is used to reduce butanal to butan-1-ol.

The reaction kinetics between butanal using excess of NaBH_4 is studied. The concentration of butanal was determined at regular intervals as the reaction progressed.

Two separate experiments were carried out using initial $[\text{butanal}] = 0.100 \text{ mol dm}^{-3}$ with different NaBH_4 concentrations. The results of Experiment 1 using $[\text{NaBH}_4] = 1.0 \text{ mol dm}^{-3}$ are shown in Fig 4.1.

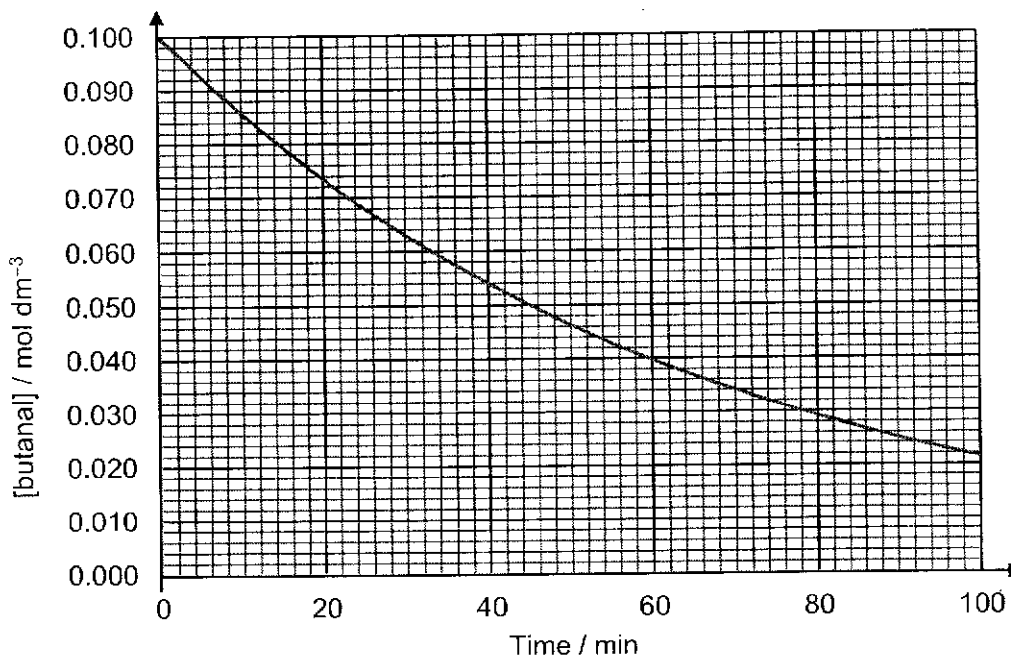


Fig 4.1

- (i) Using Fig 4.1, show that the reaction is first order with respect to [butanal]. [1]
- (ii) Experiment 2 was carried out using $[\text{NaBH}_4] = 1.5 \text{ mol dm}^{-3}$. It was found that the reaction is first order with respect to $[\text{NaBH}_4]$.

Experiment	initial [butanal] / mol dm ⁻³	initial $[\text{NaBH}_4]$ / mol dm ⁻³
1	0.100	1.0
2	0.100	1.5

Plot on the same axes given in Fig 4.1, the graph you would expect to obtain for Experiment 2, showing the time taken for [butanal] to decrease to 12.5 % of its initial concentration.

[2]

(iii) Using Fig. 4.1, determine the initial rate of Experiment 1.

[2]

(iv) Experiment 3 was carried out using $0.050 \text{ mol dm}^{-3}$ butanal and 1.0 mol dm^{-3} NaBH_4 .

Predict and explain how

- the half-life of butanal in Experiment 3
- the initial rate of Experiment 3

would compare with Experiment 1.

.....

[2]

(v) NaBH_4 produces hydride ions, :H^- , used in the reduction of aldehydes to alcohols. The following shows the mechanism to reduce butanal to butan-1-ol.

Complete the mechanism in Fig. 4.2. Show relevant partial charges and draw curly arrows to show the movement of electron pairs in both steps.

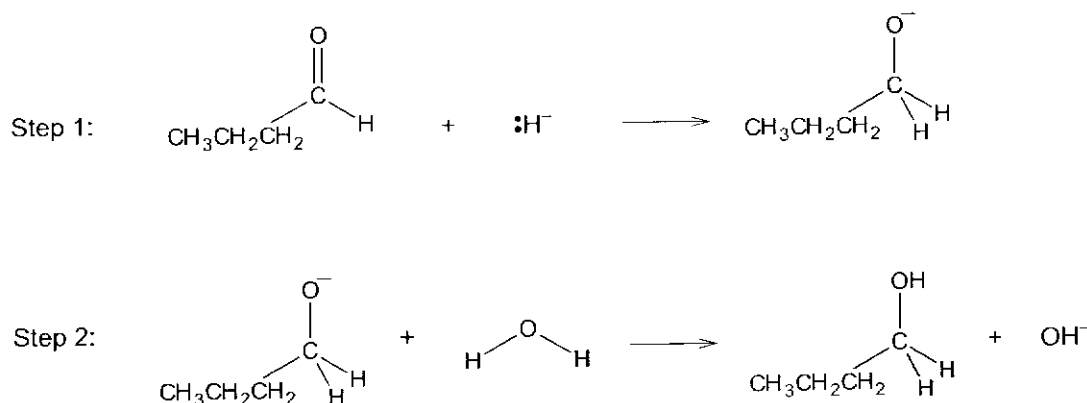
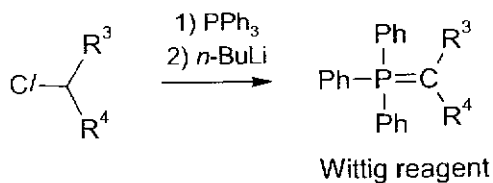


Fig. 4.2

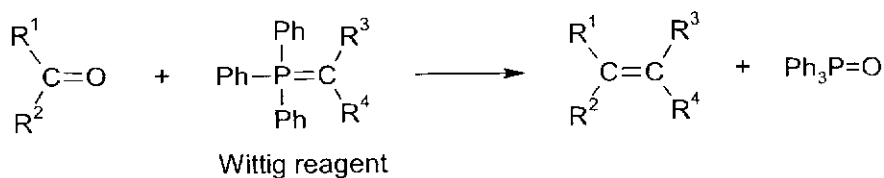
[2]

- (b) The Wittig reaction is a chemical reaction of an aldehyde or a ketone with a Wittig reagent to give an alkene.

A Wittig reagent is first prepared by reacting an alkyl halide with triphenylphosphine, PPh_3 , followed by a strong base such as *n*-butyllithium, *n*-BuLi. [Ph = phenyl, R = alkyl or H]



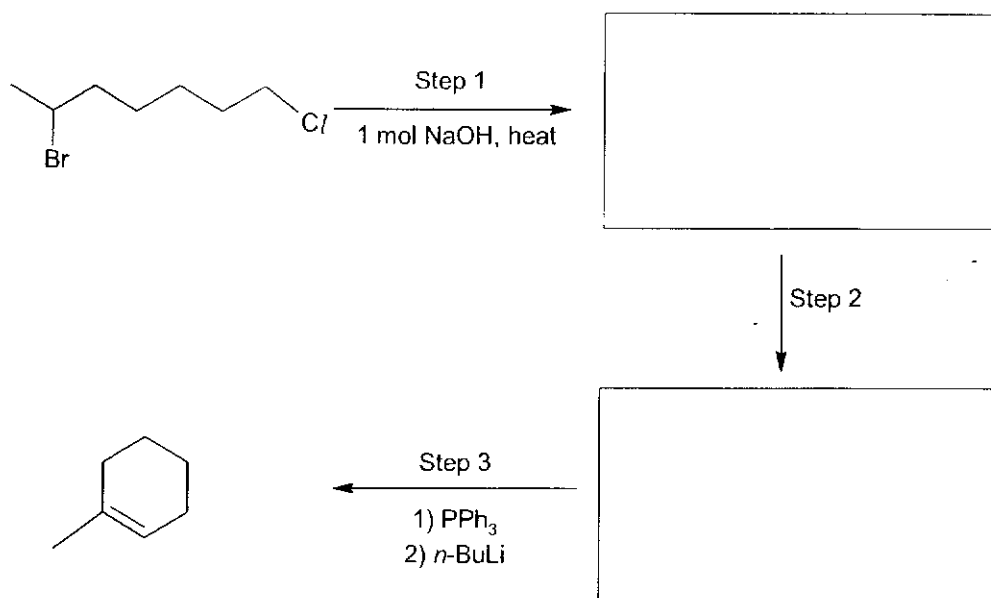
The Wittig reagent is then used to synthesise an alkene from an aldehyde or a ketone.



- (i) Draw the structural formulae of the two isomers formed when butanone reacts with ethyl chloride, $\text{CH}_3\text{CH}_2\text{Cl}$, in a Wittig reaction. Identify the type of isomerism shown.

[2]

- (ii) 1-methylcyclohexene can be obtained in the following reaction scheme. Wittig reaction is used in step 3.

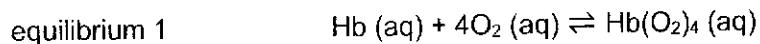


Draw the structures of the intermediate compounds in the boxes provided and state the reagent and conditions required in Step 2.

[3]

[Total :14]

- 5 (a) Haemoglobin (Hb) is a protein in red blood cells that carries oxygen from the lungs to the rest of the body. Each Hb molecule can bind up to four molecules of oxygen.



- (i) Write an expression for K_c of equilibrium 1.

[1]

The proportion of oxygen carrying sites in all red blood cells that are occupied by oxygen molecules is known as oxygen saturation. Fig. 5.1 shows how oxygen saturation varies with increasing partial pressure of oxygen (p_{O_2}) for a healthy adult.

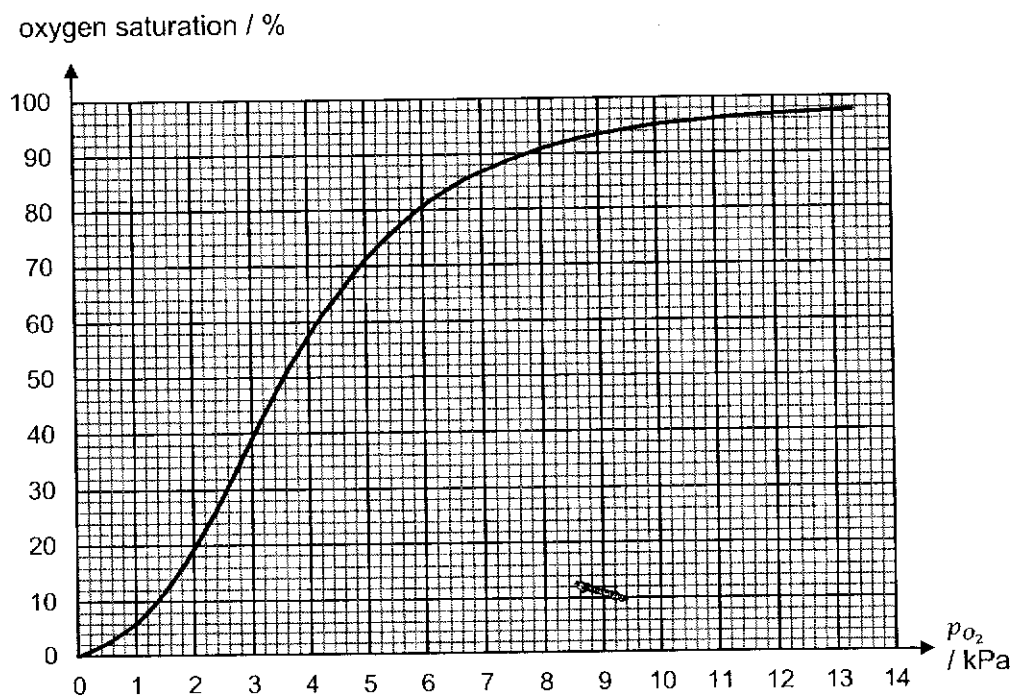


Fig. 5.1

Table 5.1 shows the representative p_{O_2} values at different regions of the circulatory system in a healthy adult. The p_{O_2} value at the lungs is always 13.3 kPa, leading to an oxygen saturation of 98 %.

Table 5.1

	Lungs	Resting tissue	Exercising tissue
p_{O_2} / kPa	13.3	5.3	2.4
oxygen saturation / %	98		

- (ii) The quantity of oxygen transported to a specific tissue depends on the difference in oxygen saturation between the lungs and that tissue.

Complete Table 5.1 and compare the relative quantities of oxygen that is transported from the lungs to resting and exercising tissues.

.....

[2]

- (iii) Explain how the shape of the graph at low p_{O_2} in Fig. 5.1 shows that the binding of one oxygen molecule facilitates the binding of subsequent oxygen molecules to Hb.

.....

[1]

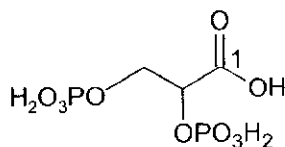
A conventional measure for haemoglobin binding affinity is the P_{50} value, the partial pressure of oxygen that results in 50 % oxygen saturation. This is equivalent to having an equal concentration of Hb and $Hb(O_2)_4$.

- (iv) Use Fig. 5.1 to determine the P_{50} value of a healthy adult.
[1]

- (v) At the P_{50} value, the concentration of oxygen in blood is $1.40 \times 10^{-3} \text{ mol dm}^{-3}$. Calculate the value of K_c for equilibrium 1.

[2]

- (b) 2,3-DPG is a substance found in red blood cells that increases the P_{50} value to promote the release of oxygen to body tissues.



2,3-DPG

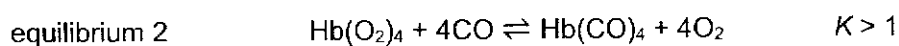
- (i) Draw all the hybrid atomic orbitals around the carbon labelled 1 in 2,3-DPG.

[1]

- (ii) Suggest the structure of a functional group isomer of 2,3-DPG that still contains two phosphonic acid groups, $-OPO_3H_2$.

[1]

- (c) Carbon monoxide competes with oxygen molecules for binding with haemoglobin.



- (i) State the type of reaction described in equilibrium 2.

.....[1]

- (ii) Comment on the relative affinity of CO and O_2 for haemoglobin.

.....

[1]

(iii) State the sign of ΔG^\ominus for equilibrium 2. Briefly explain your answer.

.....
.....
.....[1]

(iv) Explain why the treatment for carbon monoxide poisoning is to administer pure oxygen.

.....
.....
.....[2]

The red colour of meat is due to haem, an iron(II) complex. Browning of meat by cooking arises from the oxidation of iron(II) to iron(III).

(v) Explain what is meant by the term *complex*.

.....
.....
.....[1]

(vi) Suggest why the colour of iron(II) and iron(III) complexes differ.

.....
.....
.....[1]

(vii) To maintain the red colour of fresh meat, meat is stored in a carbon monoxide environment.

Deduce the impact of carbon monoxide binding on the iron(III)–iron(II) reduction potential in haem.

.....
.....
.....[2]

- (d) (i) State the conditions under which real gases behave like ideal gases.
[1]

- (ii) Fig. 5.2 shows how the compressibility factor, Z , of 1 mol of oxygen gas changes with pressure.

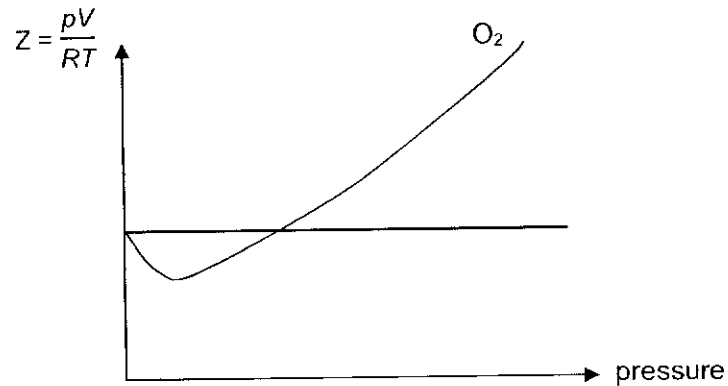


Fig. 5.2

On Fig. 5.2, sketch how the compressibility factor, Z , of 1 mol of carbon monoxide will change with pressure.

[1]

- (e) (i) When $\text{NaOH}(\text{aq})$ is added dropwise to a $0.100 \text{ mol dm}^{-3}$ solution of iron(II) nitrate, a green precipitate starts to form when pH reaches 6.95.

Calculate the K_{sp} value of the sparingly soluble salt.

[3]

- (ii) The green precipitate turns brown on contact with air. Using the *Data Booklet*, write a balanced equation to account for the observation made.

.....[1]

[Total: 24]

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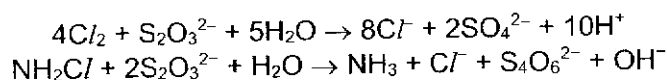
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To prepare an aquarium tank, a water conditioner containing sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is added to the tank to remove both the aqueous chlorine and chloroamine present in tap water.

Sodium thiosulfate reacts with chlorine and chloroamine respectively as shown in the reactions below.



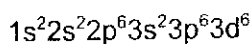
- (i) Calculate the volume of $0.010 \text{ mol dm}^{-3}$ sodium thiosulfate solution that would be required to prepare a tank containing 360 dm^3 of water. [3]

$$\begin{aligned} \text{moles of } \text{Cl}_2 \text{ present} &= 3.24 \times 10^{-5} \times 360 = 1.167 \times 10^{-2} \text{ mol} \\ \text{moles of } \text{NH}_2\text{Cl} \text{ present} &= 3.88 \times 10^{-5} \times 360 = 1.397 \times 10^{-2} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{moles of } \text{S}_2\text{O}_3^{2-} \text{ to react with } \text{Cl}_2 &= \frac{1}{4} \times 1.167 \times 10^{-2} = 0.002916 \text{ mol} \\ \text{moles of } \text{S}_2\text{O}_3^{2-} \text{ to react with } \text{NH}_2\text{Cl} &= 2 \times 1.397 \times 10^{-2} = 0.02794 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Volume of } \text{S}_2\text{O}_3^{2-} \text{ required} &= \frac{0.002916 + 0.02794}{0.010} \\ &= 3.09 \text{ dm}^3 \end{aligned}$$

- (ii) State the full electronic configuration of iron in $\text{Fe}_3(\text{PO}_4)_2$. [1]

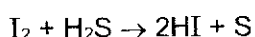


(b) The direct reaction of hydrogen with chlorine gives hydrogen chloride. However, hydrogen chloride is produced industrially by treatment of halide salts with sulfuric acid. On the other hand, hydrogen iodide, HI, is produced by the reaction of iodine with hydrogen sulfide or with hydrazine.

- (i) Explain briefly why it is not industrially viable to produce HCl through the direct reaction of hydrogen with chlorine. [1]

Reaction of hydrogen and chlorine is explosive to handle.

- (ii) Write a balanced equation showing the formation of HI from iodine and hydrogen sulfide. Hence, with reference to the *Data Booklet*, show that the reaction is spontaneous. [2]



$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}} = 0.54 - 0.14 = +0.40 \text{ V} > 0$$

Since $E^\ominus_{\text{cell}} > 0$, the redox reaction is spontaneous under standard conditions.

- (iii) Explain why the $\text{p}K_{\text{a}}$ values decrease from HCl to HI. [2]

Down the group, size of halogen atoms increases. Hence, bond length of H-X increases and H-X bond strength decreases down the group. It is therefore easier to break the H-X bond to dissociate H^+ and halide ions in aqueous solution. Acid strength increases from HCl to HI, K_{a} values therefore increases and $\text{p}K_{\text{a}}$ decreases.

(c) In an experiment, a sample of chloride ions was vapourised and passed through an electric field. Analysis revealed that a beam of $^{37}\text{Cl}^-$ gives an angle of deflection of -1.0° .

- (i) State the angle of deflection for a beam of deuterium nuclei in the same experimental set-up.

(D is deuterium, ^2_1H)

[1]

$$\text{Angle of deflection} \propto \frac{\text{charge}}{\text{mass}}$$

$$\frac{\text{charge}}{\text{mass}} \text{ of } ^{37}\text{Cl}^- = -\frac{1}{37}$$

$$\frac{\text{charge}}{\text{mass}} \text{ of } ^2\text{D}^+ = +\frac{1}{2}$$

$$\begin{aligned} \text{Angle of deflection of deuterium nuclei} &= +1.0 \div \frac{1}{37} \times \frac{1}{2} \\ &= +18.5^\circ \end{aligned}$$

- (ii) Under identical conditions, a beam of particles, **Z**, each having 32 times the mass of a proton, was deflected by an angle of -2.3° . Given that the proton number of **Z** is 16, deduce the identity of **Z**.

[2]

Since proton number of **Z** is 16, **Z** is a sulfur ion.

Let charge of **Z** be q .

$$\mathbf{Z}: -2.3^\circ \propto \frac{q}{32}$$

$${}^{37}\text{Cl}^-: -1.0^\circ \propto -\frac{1}{37}$$

$$\frac{-2.3}{-1.0} = \frac{q}{32} \div -\frac{1}{37}$$

$$q = -2 \text{ (nearest whole number)}$$

Hence the identity of **Z** is S^{2-} .

[Total: 12]

- 2 The electrochemical oxidation of benzylic alcohols to the corresponding aldehydes via a two-phase electrolysis system was reported in 2007. An example is shown in Fig. 2.1.

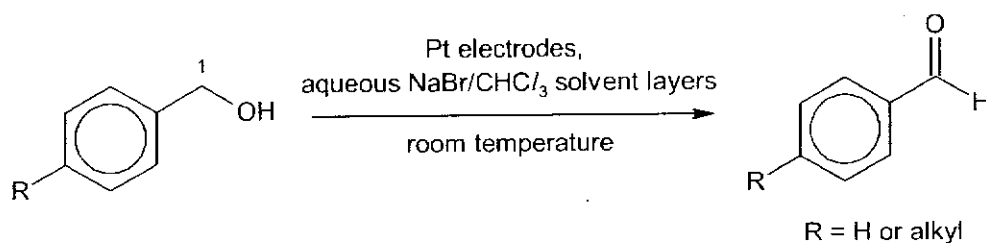


Fig. 2.1

- (a) State the reagents and conditions for the conversion of benzylic alcohols to the corresponding aldehydes in a school laboratory.

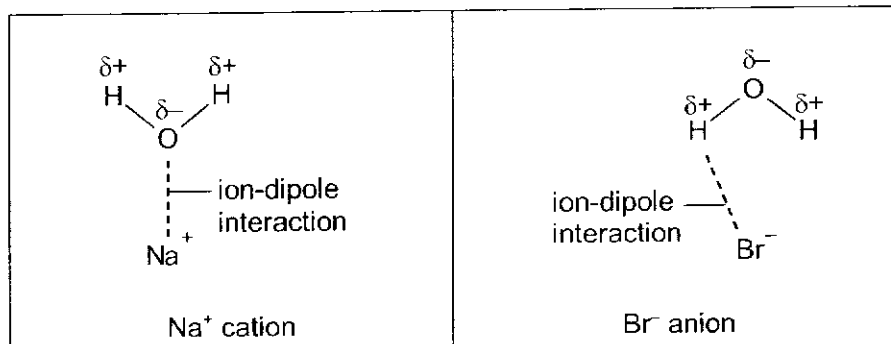
[1]

$\text{K}_2\text{Cr}_2\text{O}_7$ in dilute H_2SO_4 , heat with immediate distillation

- (b) The two-phase electrolysis system comprises the aqueous NaBr and organic CHCl_3 layers.

- (i) Draw simple diagrams to illustrate how a water molecule can be attached to a sodium cation, and to a bromide anion in the aqueous layer. Label each diagram to show the type of interaction involved.

[2]



- (ii) Predict and explain which layer the benzylic alcohols would predominantly dissolve in. [2]

Layer predominantly dissolved in: CHCl_3 / Organic layer

Explanation: The less extensive hydrogen bonds formed between benzylic alcohol and water molecules (due to the non-polar benzene ring interfering with the hydrogen bonding between the $-\text{OH}$ group of benzylic alcohol and water molecules) will not release sufficient energy to overcome the more extensive hydrogen bonds between water molecules.

- (c) (i) Describe the change in oxidation state of the benzylic carbon, labelled 1 in Fig. 2.1, when the alcohol is oxidised to the corresponding aldehyde. [1]

The oxidation state of the benzylic carbon increases from -1 in benzyl alcohol to $+1$ in benzaldehyde.

- (ii) In experiment 1 where $\text{R} = \text{H}$ in Fig. 2.1, one mole of benzylic alcohol is oxidised to give 96 % yield of aldehyde.

Using your answer in (c)(i), determine the charge, in Faraday, required to yield the aldehyde. [1]

Since oxidation state of benzylic carbon increases from -1 to $+1$, 2 moles of electrons are lost per mole of benzylic alcohol.

Charge required per mole of benzylic alcohol oxidised = 2F

Charge required for yield of benzaldehyde = $2 \times 0.96 = 1.92 \text{ F}$

- (iii) Current efficiency describes the efficiency with which charge is transferred in an electrolysis system and is given by the equation below.

$$\text{current efficiency} = \frac{\text{charge required}}{\text{charge passed}} \times 100\%$$

In experiment 1, 5.5 F of charge is passed per mole of benzylic alcohol.

Using your answer in (c)(ii), calculate the current efficiency of experiment 1. [1]

Current efficiency = $1.92 / 5.5 \times 100\% = 34.9 \%$

- (iv) Some data obtained from experiments 2 and 3 are shown in Table 2.1.

Table 2.1

Experiment No.	R group in Fig. 2.1	Current efficiency / %
2	$-\text{CH}_3$	42.5
3	$-\text{C}(\text{CH}_3)_3$	64.0

Using the data provided in Table 2.1, deduce the relationship between the electronic effect of the R group on the benzene ring and the current efficiency of the electrochemical process.

[1]

The stronger the electron donating effect of the R group, the greater the current efficiency.

- (v) Hence, suggest how you would expect the current efficiency when $R = -OCH_3$ to compare with that when $R = -CH_3$. Explain your reasoning.

[1]

The current efficiency when $R = -OCH_3$ will be greater than that when $R = -CH_3$. $-OCH_3$ exerts a stronger electron donating effect than $-CH_3$ as the lone pair of electrons on O can delocalise into the benzene ring via resonance effect while $-CH_3$ exerts an electron donating inductive effect.

- (d) In the two-phase electrolysis system, two platinum electrodes are placed in the upper aqueous NaBr layer and the bromide ions are oxidised at the anode.

State the polarity of the anode and quote relevant values from the *Data Booklet* to explain the preferential production of bromine at the electrode.

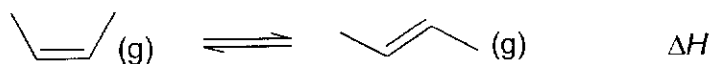
[2]

The anode is the positive electrode.

Since $E^\ominus(Br_2/Br^-) = +1.07\text{ V}$ is less positive than $E^\ominus(O_2/H_2O) = +1.23\text{ V}$, Br^- will be preferentially oxidised at the anode to produce bromine.

[Total: 12]

- 3 (a) The cis-trans isomerisation of but-2-ene in the gas phase is promoted by transition metal catalysts.



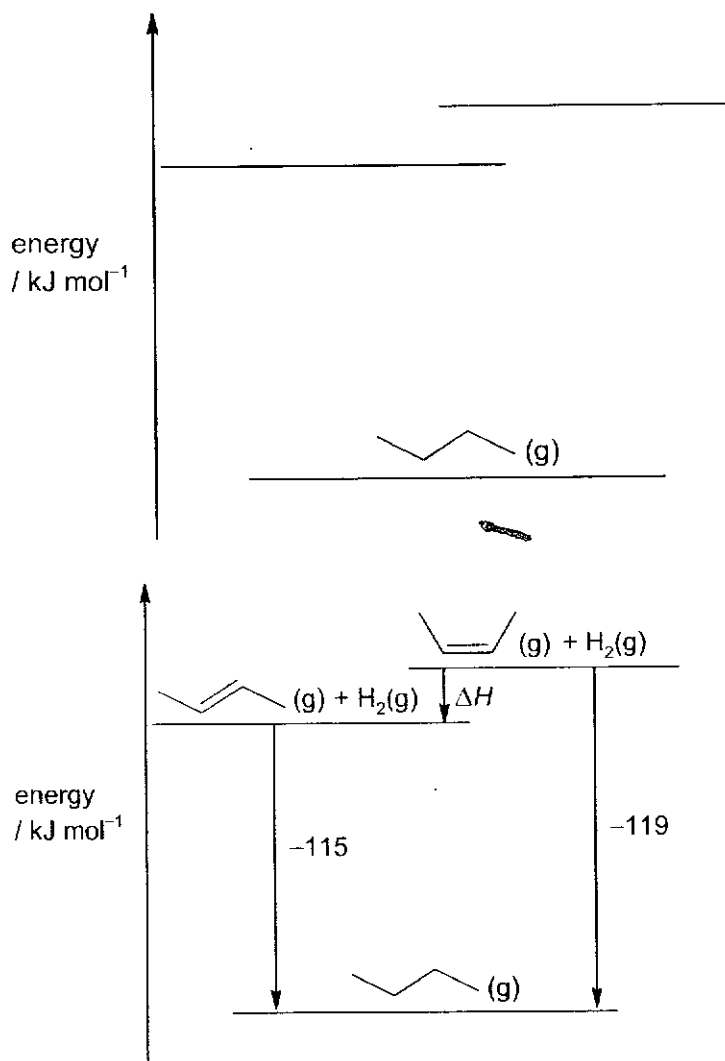
- (i) Complete the energy diagram below by drawing arrows to show how the enthalpy changes in Table 3.1 can be used to determine ΔH , the enthalpy change of conversion of cis-but-2-ene to trans-but-2-ene in the gas phase.

Label each level with the appropriate formulae.

Table 3.1

gaseous alkene	enthalpy change of hydrogenation / kJ mol^{-1}
cis-but-2-ene	-119
trans-but-2-ene	-115

[2]



- (ii) Use the energy diagram in (a)(i) to calculate a value for ΔH . [1]

$$\Delta H = -119 - (-115) = -4 \text{ kJ mol}^{-1}$$

- (iii) Comment on the difference in stability of the cis-trans isomers of but-2-ene. Use the concept of steric effects in your answer. [1]

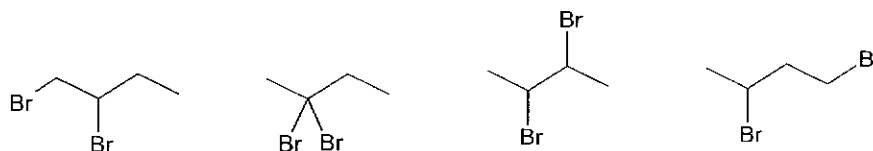
Cis-but-2-ene is less stable than trans-but-2-ene because the methyl / $-\text{CH}_3$ groups being on the same side of the $\text{C}=\text{C}$ bond are in close proximity and will experience steric repulsion between their electron clouds.

- (iv) Using your answer in (a)(ii), calculate ΔS for the conversion of cis-but-2-ene to trans but-2-ene at equilibrium at 355 K. [1]

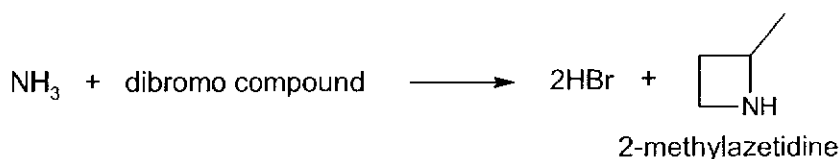
$$\begin{aligned} \text{Since } \Delta G = \Delta H - T\Delta S = 0 \text{ at equilibrium, } \Delta S &= \Delta H / T \\ &= -4000 / 355 \\ &= -11.3 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

- (b) But-2-ene reacts with hydrogen bromide to form 2-bromobutane.

- (i) Draw the structures of the four dibromo compounds that could be formed when 2-bromobutane reacts with bromine in ultraviolet light. Ignore any stereoisomers formed. [2]



2-methylazetidine can be synthesised by reacting ammonia with a dibromo compound.



- (ii) Using your answer in (b)(i) or otherwise, name the dibromo compound that reacted with ammonia to form 2-methylazetidine. [1]

1,3-dibromobutane

- (iii) Describe and explain the relative basicity of ammonia and 2-methylazetidine. [2]

2-methylazetidine is more basic than ammonia.

The electron donating alkyl groups attached to N in 2-methylazetidine increases the electron density of the N atom, making the lone pair of electrons on N more available for donation.

(c) Magnesium, silicon and sulfur are Period 3 elements.

- (i) On Fig. 3.1, sketch a graph of melting point against electronegativity for each of the three elements.

[1]

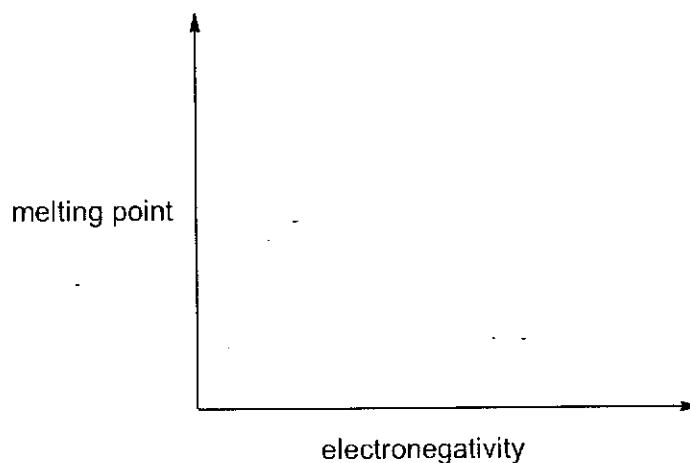
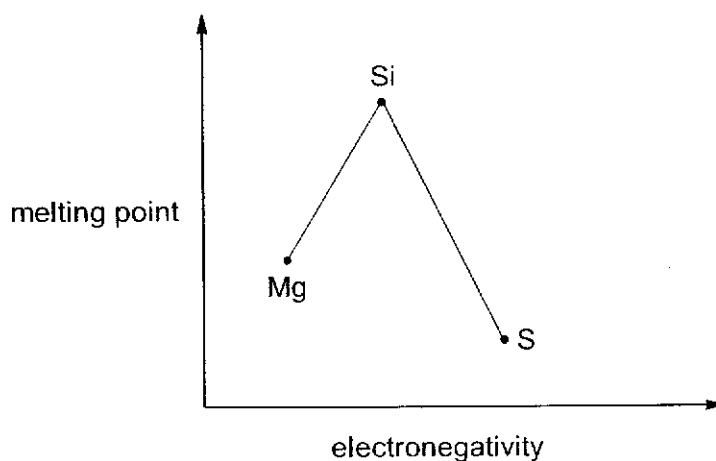


Fig. 3.1



- (ii) Explain the variation in melting point for the three elements.

[2]

Silicon has a giant molecular structure. It has the highest melting point as the largest amount of energy is required to break the strong and extensive covalent bonds between Si atoms.

Magnesium has a giant metallic structure while sulfur has a simple molecular structure. More energy is required to overcome the strong electrostatic forces of attraction between the Mg^{2+} cations and sea of delocalised electrons than the weak instantaneous dipole-induced dipole interactions between sulfur molecules. Hence magnesium has a higher melting point than sulfur.

[Total: 13]

- 4 (a) Sodium boron hydride, NaBH_4 , is commonly used in the pharmaceutical industries as a selective reducing agent. Aqueous NaBH_4 is used to reduce butanal to butan-1-ol.

The reaction kinetics between butanal using excess of NaBH_4 is studied. The concentration of butanal was determined at regular intervals as the reaction progressed.

Two separate experiments were carried out using initial $[\text{butanal}] = 0.100 \text{ mol dm}^{-3}$ with different NaBH_4 concentrations. The results of Experiment 1 using $[\text{NaBH}_4] = 1.0 \text{ mol dm}^{-3}$ are shown in Fig 4.1.

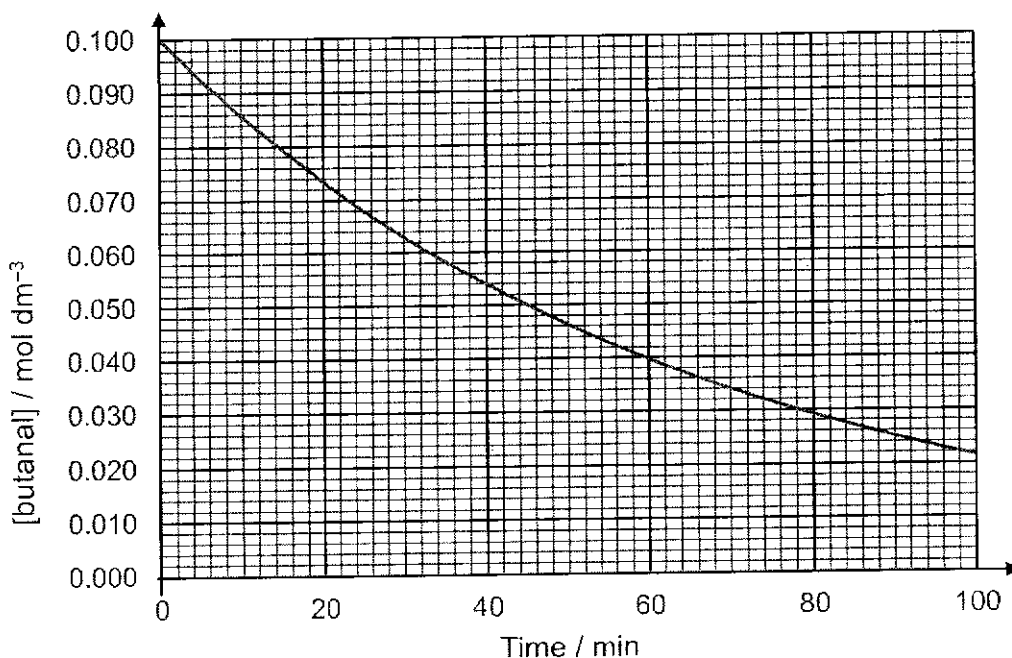


Fig 4.1

- (i) Using Fig 4.1, show that the reaction is first order with respect to [butanal]. [1]
- $t_{1/2}$ from $0.100 \text{ mol dm}^{-3}$ butanal to $0.050 \text{ mol dm}^{-3}$ butanal is about 45 min.
 $t_{1/2}$ from $0.080 \text{ mol dm}^{-3}$ butanal to $0.040 \text{ mol dm}^{-3}$ butanal is about 45 min.
- Since $t_{1/2}$ is constant at 45 min, reaction is first order with respect to [butanal].
- (ii) Experiment 2 was carried out using $[\text{NaBH}_4] = 1.5 \text{ mol dm}^{-3}$. It was found that the reaction is first order with respect to $[\text{NaBH}_4]$.

Experiment	initial [butanal] / mol dm ⁻³	initial $[\text{NaBH}_4]$ / mol dm ⁻³
1	0.100	1.0
2	0.100	1.5

Plot on the same axes given in Fig 4.1, the graph you would expect to obtain for Experiment 2, showing the time taken for [butanal] to decrease to 12.5 % of its initial concentration.

[2]

Half-life for Experiment 2 = $\frac{2}{3} \times 45 = 30$ min

When $[\text{NaBH}_4]$ increases 1.5 times, rate also increases 1.5 times, time taken is 1.5 times shorter.

(iii) Using Fig. 4.1, determine the initial rate of Experiment 1.

[2]

$$\text{Gradient} = \frac{0.10 - 0.00}{0 - 65} = -1.53 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$$

$$\text{initial rate} = |\text{gradient}| = 1.53 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$$

(iv) Experiment 3 was carried out using $0.050 \text{ mol dm}^{-3}$ butanal and 1.0 mol dm^{-3} NaBH_4 .

Predict and explain how

- the half-life of butanal in Experiment 3
- the initial rate of Experiment 3

would compare with Experiment 1.

[2]

No change since concentration of NaBH_4 used is in large excess.

$$\text{rate} = k[\text{butanal}][\text{NaBH}_4]$$

$$= k' [\text{butanal}] \text{ where } k' = k[\text{NaBH}_4]$$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[\text{NaBH}_4]}$$

$t_{1/2}$ does not depend on the change in concentration of butanal.

Comparing experiments 1 and 3, $[\text{butanal}]$ is halved while $[\text{NaBH}_4]$ is kept constant. Since order of reaction with respect to butanal is one, initial rate of experiment 3 is halved.

(v) NaBH_4 produces hydride ions, $:\text{H}^-$, used in the reduction of aldehydes to alcohols. The following shows the mechanism to reduce butanal to butan-1-ol.

Complete the mechanism in Fig. 4.2. Show relevant partial charges and draw curly arrows to show the movement of electron pairs in both steps.

[2]

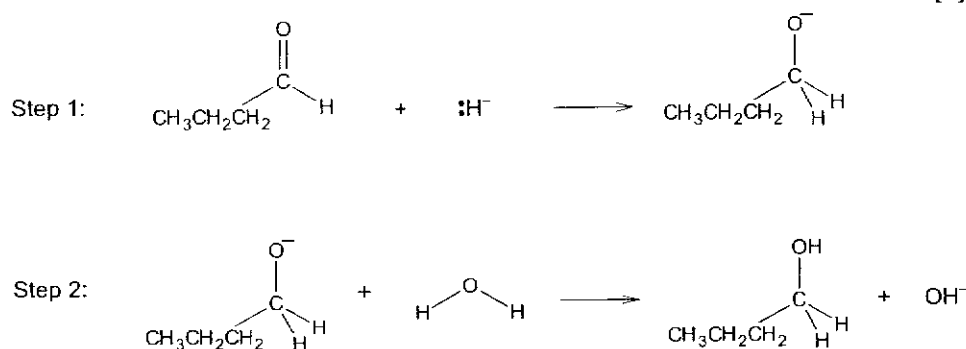
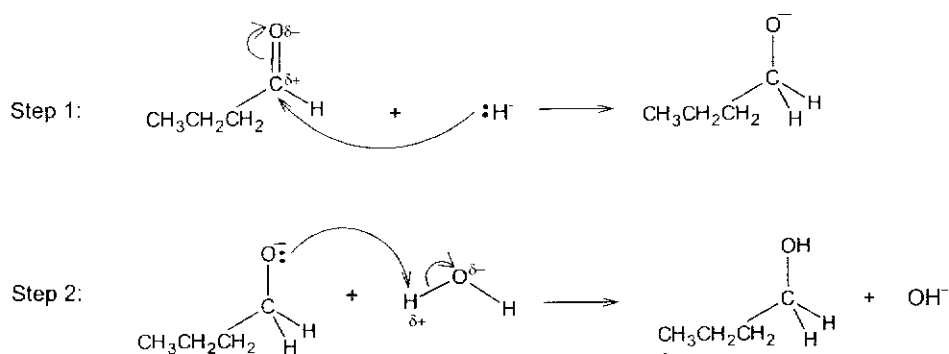
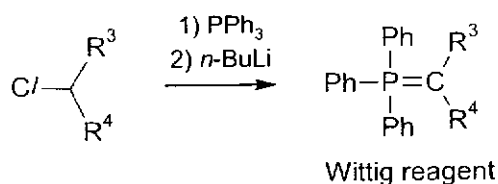


Fig. 4.2

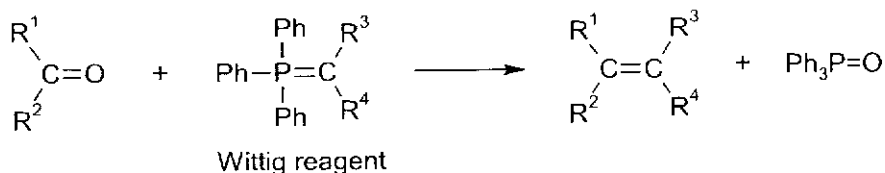


- (b) The Wittig reaction is a chemical reaction of an aldehyde or a ketone with a Wittig reagent to give an alkene.

A Wittig reagent is first prepared by reacting an alkyl halide with triphenylphosphine, PPh_3 , followed by a strong base such as *n*-butyllithium, *n*-BuLi.
[Ph = phenyl, R = alkyl or H]

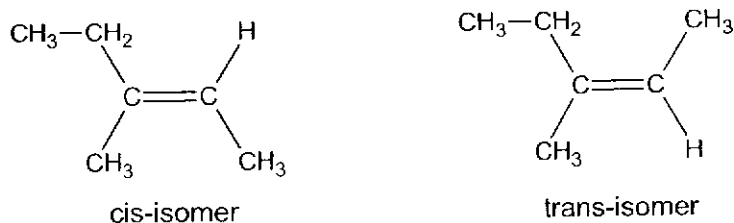


The Wittig reagent is then used to synthesise an alkene from an aldehyde or a ketone.



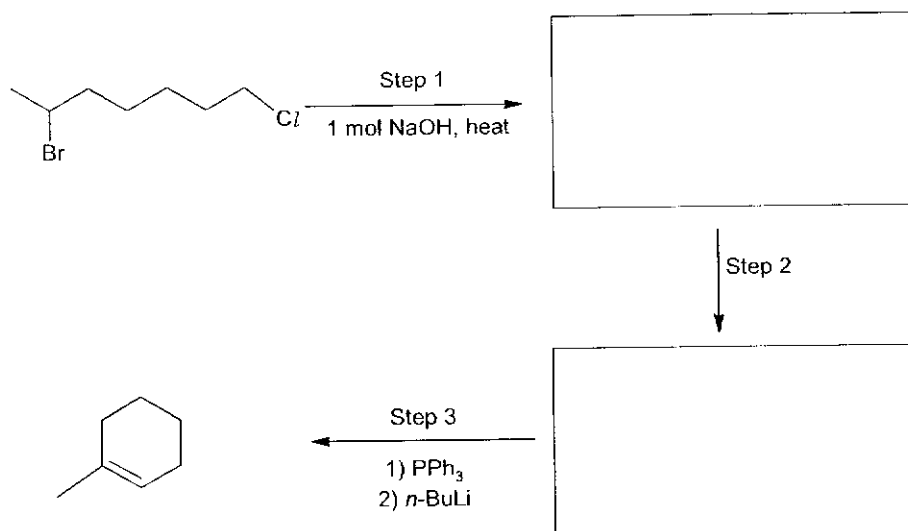
- (i) Draw the structural formulae of the two isomers formed when butanone reacts with ethyl chloride, $\text{CH}_3\text{CH}_2\text{Cl}$, in a Wittig reaction. Identify the type of isomerism shown.

[2]



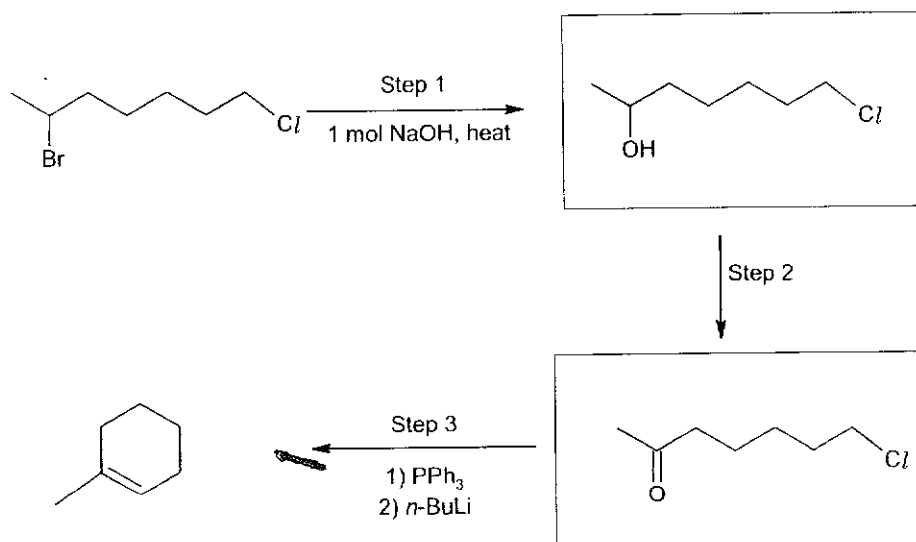
cis-trans isomerism

- (ii) 1-methylcyclohexene can be obtained in the following reaction scheme. Wittig reaction is used in step 3.



Draw the structures of the intermediate compounds in the boxes provided and state the reagent and conditions required in Step 2.

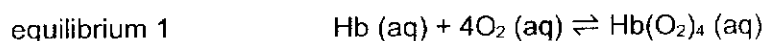
[3]



Step 2: KMnO₄/dilute H₂SO₄, heat under reflux

[Total :14]

- 5 (a) Haemoglobin (Hb) is a protein in red blood cells that carries oxygen from the lungs to the rest of the body. Each Hb molecule can bind up to four molecules of oxygen.



- (i) Write an expression for K_c of equilibrium 1.

[1]

$$K_c = \frac{[\text{Hb(O}_2)_4]}{[\text{Hb}][\text{O}_2]^4}$$

The proportion of oxygen carrying sites in all red blood cells that are occupied by oxygen molecules is known as oxygen saturation. Fig. 5.1 shows how oxygen saturation varies with increasing partial pressure of oxygen (p_{O_2}) for a healthy adult.

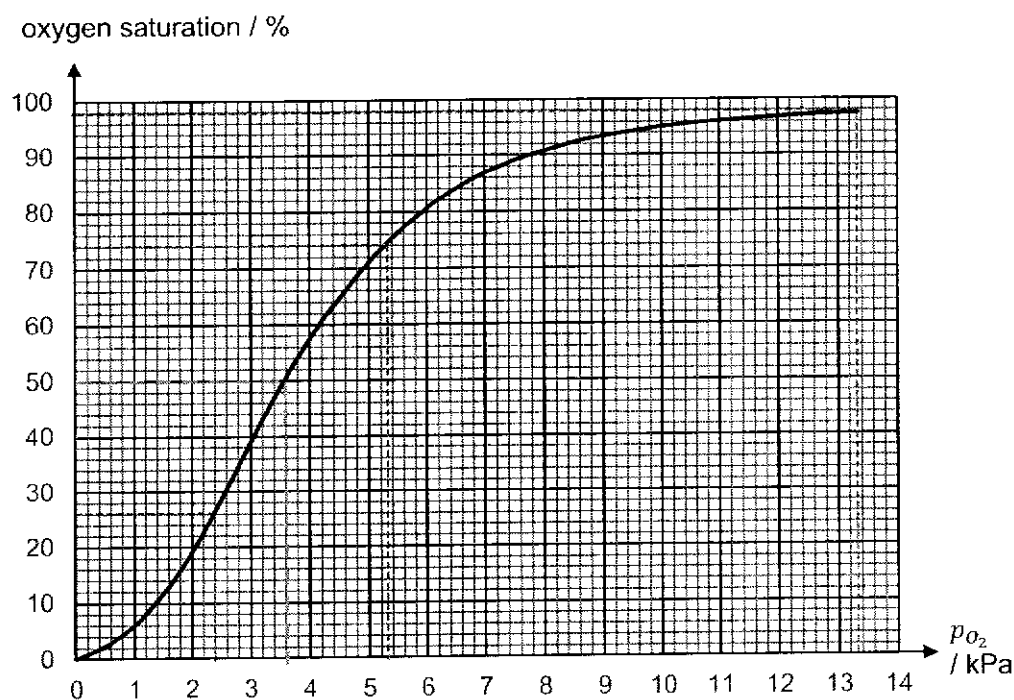


Fig. 5.1

Table 5.1 shows the representative p_{O_2} values at different regions of the circulatory system in a healthy adult. The p_{O_2} value at the lungs is always 13.3 kPa, leading to an oxygen saturation of 98 %.

Table 5.1

	Lungs	Resting tissue	Exercising tissue
p_{O_2} / kPa	13.3	5.3	2.4
oxygen saturation / %	98	74	26

- (ii) The quantity of oxygen transported to a specific tissue depends on the difference in oxygen saturation between the lungs and that tissue.

Complete Table 5.1 and compare the relative quantities of oxygen that is transported from the lungs to resting and exercising tissues. [2]

The change in oxygen saturation of blood from lungs to resting tissue is 24% whereas that for exercising tissue is 72%. Much more / 3 times the amount of oxygen is being delivered to exercising tissue compared to resting tissue.

- (iii) Explain how the shape of the graph at low p_{O_2} in Fig. 5.1 shows that the binding of one oxygen molecule facilitates the binding of subsequent oxygen molecules to Hb. [1]

The gradient of the graph is less steep at the beginning.

A conventional measure for haemoglobin binding affinity is the P_{50} value, the partial pressure of oxygen that results in 50 % oxygen saturation. This is equivalent to having an equal concentration of Hb and $Hb(O_2)_4$.

- (iv) Use Fig. 5.1 to determine the P_{50} value of a healthy adult. [1]

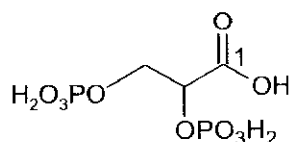
From the graph, $P_{50} = 3.6$ kPa

- (v) At the P_{50} value, the concentration of oxygen in blood is $1.40 \times 10^{-3} \text{ mol dm}^{-3}$. Calculate the value of K_c for equilibrium 1. [2]

At P_{50} , $[Hb] = [Hb(O_2)_4]$

$$K_c = \frac{[Hb(O_2)_4]}{[Hb][O_2]^4} = \frac{1}{[O_2]^4} = \frac{1}{(1.40 \times 10^{-3})^4} = 2.60 \times 10^{11} \text{ mol}^{-4} \text{ dm}^{12}$$

- (b) 2,3-DPG is a substance found in red blood cells that increases the P_{50} value to promote the release of oxygen to body tissues.

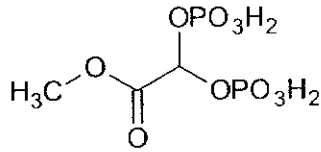


2,3-DPG

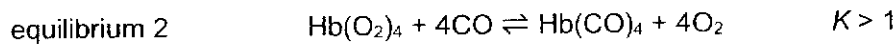
- (i) Draw all the hybrid atomic orbitals around the carbon labelled 1 in 2,3-DPG. [1]



- (ii) Suggest the structure of a functional group isomer of 2,3-DPG that still contains two phosphonic acid groups, $-\text{OPO}_3\text{H}_2$. [1]



- (c) Carbon monoxide competes with oxygen molecules for binding with haemoglobin.



- (i) State the type of reaction described in equilibrium 2. [1]

Ligand exchange

- (ii) Comment on the relative affinity of CO and O_2 for haemoglobin. [1]

CO binds more strongly with haemoglobin since $K > 1$ / the position of equilibrium lies on the right.

- (iii) State the sign of ΔG^\ominus for equilibrium 2. Briefly explain your answer. [1]

Since $K > 1$ and $\Delta G^\ominus = -RT \ln K$, ΔG^\ominus is negative.

- (iv) Explain why the treatment for carbon monoxide poisoning is to administer pure oxygen. [2]

At high $[\text{O}_2]$, the equilibrium 2 shifts left to decrease $[\text{O}_2]$. This removes CO from Hb and increases the oxygen saturation level.

The red colour of meat is due to haem, an iron(II) complex. Browning of meat by cooking arises from the oxidation of iron(II) to iron(III).

- (v) Explain what is meant by the term *complex*. [1]

A complex is formed when a metal ion or atom forms dative / coordinate bonds with surrounding ions or molecules called ligands.

- (vi) Suggest why the colour of iron(II) and iron(III) complexes differ. [1]

The difference in electronic configuration of the metal cation results in a different energy gap between the two groups of d-orbitals.

- (vii) To maintain the red colour of fresh meat, meat is stored in a carbon monoxide environment.

Deduce the impact of carbon monoxide binding on the iron(III)–iron(II) reduction potential in haem. [2]

Since oxidation is disfavoured, the reduction potential is more positive.

- (d) (i) State the conditions under which real gases behave like ideal gases. [1]

High temperature and low pressure

- (ii) Fig. 5.2 shows how the compressibility factor, Z , of 1 mol of oxygen gas changes with pressure.

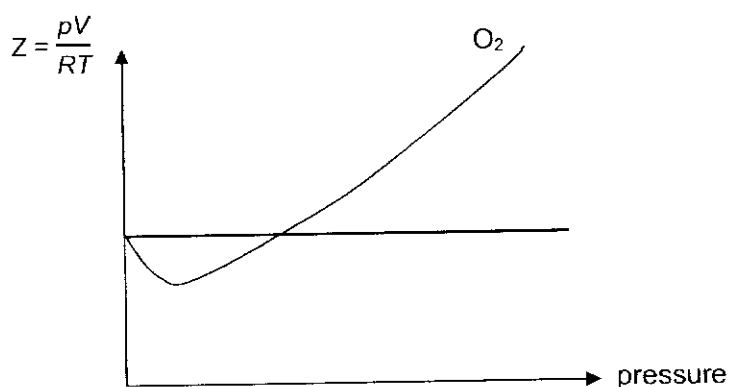
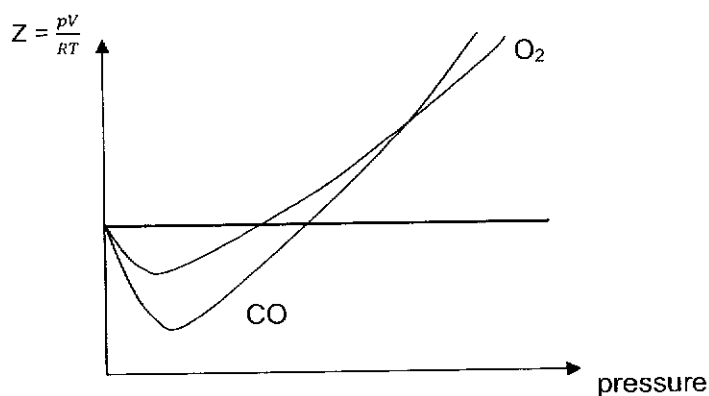


Fig. 5.2

On Fig. 5.2, sketch how the compressibility factor, Z , of 1 mol of carbon monoxide will change with pressure. [1]



- (e) (i) When NaOH(aq) is added dropwise to a $0.100 \text{ mol dm}^{-3}$ solution of iron(II) nitrate, a green precipitate starts to form when pH reaches 6.95.

Calculate the K_{sp} value of the sparingly soluble salt.

[3]

When pH = 6.95,

$$\text{pOH} = 14 - 6.95 = 7.05$$

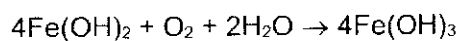
$$[\text{OH}^-] = 10^{-7.05} = 8.91 \times 10^{-8} \text{ mol dm}^{-3}$$

The precipitate is $\text{Fe}(\text{OH})_2$.

$$\begin{aligned} K_{\text{sp}} &= [\text{Fe}^{2+}][\text{OH}^-]^2 \\ &= 0.100 \times (8.91 \times 10^{-8})^2 \\ &= 7.94 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9} \end{aligned}$$

- (ii) The green precipitate turns brown on contact with air. Using the *Data Booklet*, write a balanced equation to account for the observation made.

[1]



[Total: 24]