Suggested Solutions

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response Questions

21 September 2022

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. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use	
Section A	
1	**20**
2	**20**
3	**20**
Section B	
4 / 5	**20**
Total	**80**

This document consists of **23** printed pages.

Section A

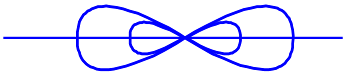
Answer **all** the questions from this section.

1 **(a)** Alkynes is a class of organic compounds with the general formula, C_nH_{2n-2}.

(i) Describe what is meant by sp hybridisation with reference to one carbon atom in ethyne, C_2H_2. Draw the hybrid orbitals of the carbon atom.

[2]

One 2s and one 2p atomic orbitals are mixed to form two 2sp hybrid orbitals that are degenerate / of equal energy.



(ii) Use relevant radius values from the *Data Booklet* to calculate the bond length of a single carbon-hydrogen bond. Show your working clearly.

[1]

From the *Data Booklet,*
single covalent radius of hydrogen = 0.037 nm
single covalent radius of carbon = 0.077 nm

Bond length = sum of covalent radii
= 0.037 nm + 0.077 nm = 0.114 nm

(iii) Table 1.1 shows the carbon-hydrogen bond length in ethene and ethyne.

Table 1.1

molecule	carbon-hydrogen bond length/ nm
ethene	0.109
ethyne	0.106

With reference to Table 1.1, state which carbon-hydrogen bond is stronger. Use the concept of hybridisation to explain the difference in bond length of the carbon-hydrogen bond between these two molecules.

[2]

The carbon-hydrogen bond of ethyne is stronger.

The sp hybridised carbon atom in ethyne has a higher percentage s character than the sp^2 hybridised carbon atom in ethene. Hence, the extent of orbital overlap between the sp hybridised carbon atom and H atom is greater, resulting in a shorter bond length.

(iv) Write a balanced equation for the complete combustion of propyne, C_3H_4.

[1]

$C_3H_4 + 4O_2 \rightarrow 3CO_2 + 2H_2O$

(v) A sample of propyne was burned in excess oxygen. When the remaining gases were passed through aqueous sodium hydroxide, the gas volume was reduced by 0.450 dm^3. Calculate the mass of propyne in the sample.

Assume all gas volumes were measured at r.t.p.

[2]

Since carbon dioxide is the only acidic gas, volume of CO_2 = 0.450 dm^3

$3CO_2 \equiv C_3H_4$

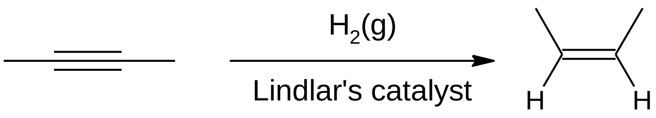
By volume ratio, volume of C_3H_4 = 0.150 dm^3

$$\text{Moles of } C_3H_4 = \frac{0.15}{24} = 0.00625 \text{ mol}$$

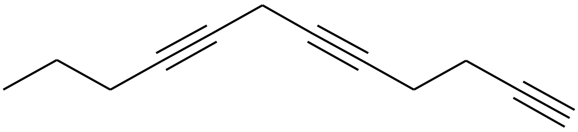
$$\text{Mass of } C_3H_4 = 0.00625 \times ((4 \times 1.0) + (3 \times 12.0)) = 0.250 \text{ g}$$

(b) The use of hydrogen gas with Lindlar's catalyst is a selective method which reduces alkynes to form the *cis*-isomer of alkenes.

As an example, but-2-yne, C_4H_6, can be reduced to give *cis*-but-2-ene only.

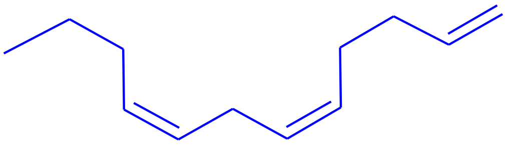


Suggest the structure of the alkene formed when compound **A** is reduced with the use of Lindlar's catalyst.

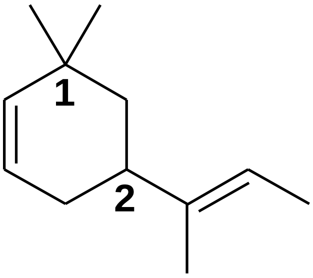


A

[1]



(c) Compound **B** has the following structure.



B

(i) State the isomeric relationship between **B** and your answer in **(b)**.

[1]

<u>Chain / constitutional</u> isomers

(ii) A student made the following deductions about compound **B**:

"*Since carbon atoms labelled **1** and **2** are chiral and there are two carbon-carbon double bonds, compound **B** has 16 possible stereoisomers.*"

Explain where the student has gone wrong in his deductions.

[3]

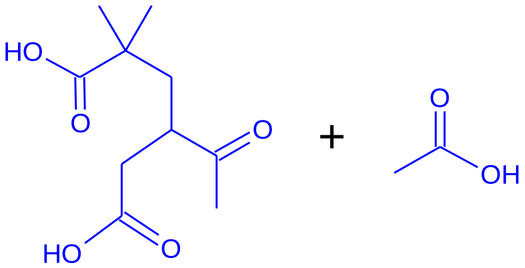
Carbon 1 is not chiral as it is bonded to two identical methyl groups.

For the C=C bond in the ring, only the *cis*-isomer exists. In the presence of a small six-membered ring, the *trans*-isomer will be highly strained and unstable.

With one chiral centre and one C=C bond not located in a ring, there is a total of $2^2 = 4$ possible stereoisomers for compound B.

(iii) Draw all the organic products that are formed when compound **B** is heated with acidified potassium manganate(VII).

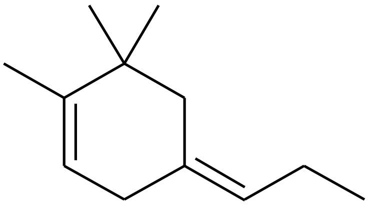
[1]



Marker's Comments

Typical mistakes include:
- Oxidation of the C=C bond to aldehyde functional group instead of carboxylic acid functional group
- Missing ethanoic acid as one of the organic products
- Missing methyl groups or carbon atoms
- Five bonds around carbon in C=O of the ketone functional group

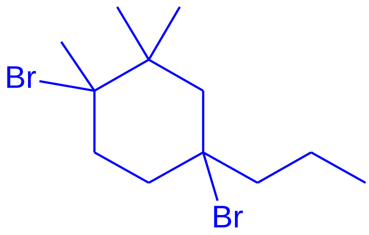
(d) Compound **C** is an isomer of compound **B**.



C

Draw the structure of the major product formed when compound **C** is reacted with excess HBr(g). Explain your answer.

[2]



The tertiary carbocation is more stable than the secondary carbocation formed as there are more electron–donating alkyl groups to disperse the positive charge on each carbon atom.

(e) Lithium aluminium hydride, $\text{LiA}l\text{H}_4$, is a reducing agent commonly used in organic chemistry.

(i) Assuming $\text{LiA}l\text{H}_4$ as a source of hydride (H^-) ions, suggest why the reduction of alkynes using $\text{LiA}l\text{H}_4$ is likely **not** a suitable method.

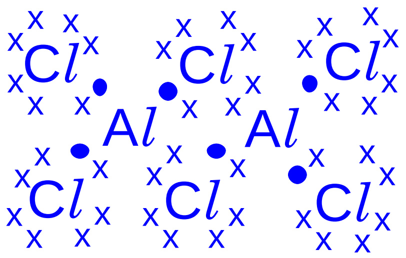
[1]

The π electrons / triple bond / C≡C bond in alkynes will repel the negatively charged H^-.

(ii) $\text{LiA}l\text{H}_4$ can be synthesised from aluminium chloride, which exists as a dimer, $\text{A}l_2\text{C}l_6$, at room temperature.

Draw a dot-and-cross diagram to illustrate the bonding present in $\text{A}l_2\text{C}l_6$.

[1]



(iii) When heated, $\text{LiA}l\text{H}_4$ decomposes to $\text{LiA}l$(s) as one of its products. $\text{LiA}l$(s) has a melting point of 718 °C. It can conduct electricity when in solid and molten states.

Suggest the structure of $\text{LiA}l$(s) and describe the bonding present.

[2]

Giant metallic structure.
Strong electrostatic forces of attraction between lattice of Li^+ and $\text{A}l^{3+}$/ positively-charged ions and the sea of delocalised electrons.

[Total: 20]

2 **(a)** 1,2–diols are common precursors used in many pharmaceuticals, agrochemicals, and natural products.

Fig. 2.1 shows a *pinacol coupling reaction* which involves the *homo–coupling** of a carbonyl compound to produce a symmetrically substituted 1,2–diol.

**Two identical molecules react to form a different one*.

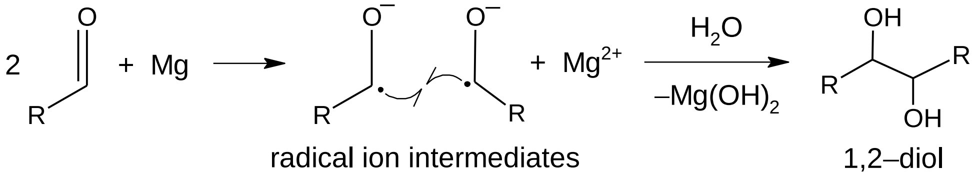


Fig. 2.1

The first step is single electron transfer involving the carbonyl group, which generates radical ion intermediates that couple via carbon–carbon bond formation to give a 1,2–diol.

(i) State the role of magnesium in the first step of Fig. 2.1 and give a reason for its suitability in this reaction. [2]

Magnesium is functioning as a reducing agent in the first step.
It is suitable due to its relatively low ionisation energies/ low electronegativity.

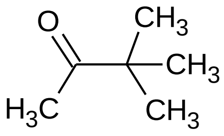
(ii) It is possible to synthesise a desired unsymmetrical diol using methods similar to the *pinacol coupling reaction* but a mixture of diols will be obtained.

Explain why a mixture of diols is formed. Suggest why this is unfavourable other than a low yield of the desired diol. [2]

Two different carbonyl compounds have to be used to synthesise an unsymmetrical diol. In the process, two different radical ion intermediates will be formed and different combinations of these radicals will couple to form a mixture of (three) diols.
Obtaining a mixture of diols is unfavourable as the separation of the diols to yield the desired one would be complex.

The pinacol coupling can be followed up by a *pinacol rearrangement* to convert the 1,2–diol to a carbonyl compound.

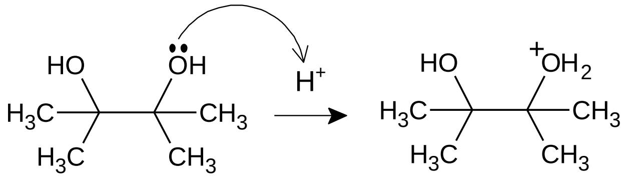
Pinacolone is a carbonyl compound that can be produced via the *pinacol rearrangement* and it has the following structure.



pinacolone

Fig. 2.2 shows the first step of the *pinacol rearrangement* to form pinacolone using pinacol as the starting reactant.

Step 1:



pinacol

Fig. 2.2

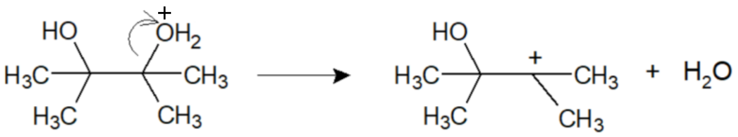
(iii) Below describes the remaining three steps of the *pinacol rearrangement* to form pinacolone.

- Step 2 involves the removal of water from the intermediate in Step 1 in Fig. 2.2 to form a carbocation.
- Step 3 involves the shifting of an adjacent methyl group to the positively charged carbon to form another carbocation.
- Step 4 involves the deprotonation of the −OH group in the carbocation in Step 3 to form pinacolone.

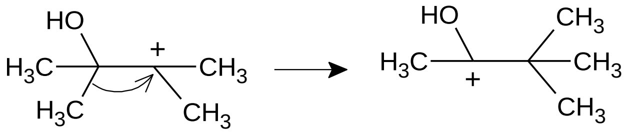
Using the information provided, draw Steps 2 to 4 of the mechanism for the formation of pinacolone via *pinacol rearrangement*.

Show all charges and show the movement of electron pairs by using curly arrows. [3]

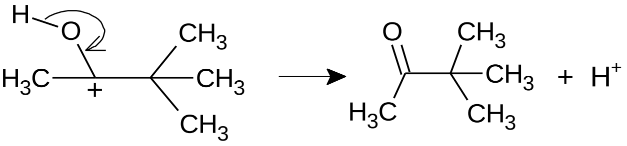
Step 2:



Step 3:

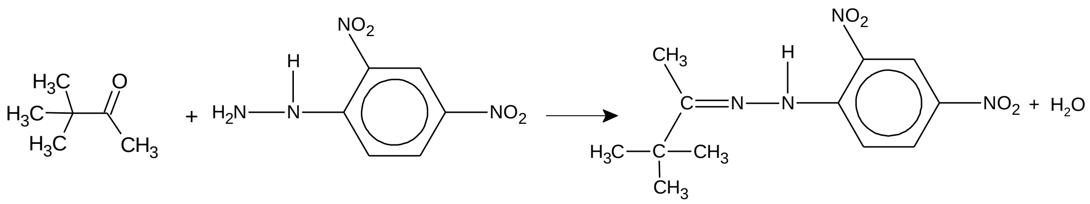


Step 4:

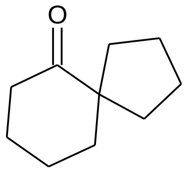


(iv) Suggest a simple chemical test that you could carry out to confirm the formation of pinacolone from pinacol. State the observations you would make and write a balanced equation for the reaction. [2]

Add 2,4–DNPH to the reaction mixture.
The formation of an orange ppt indicates the formation of pinacolone.

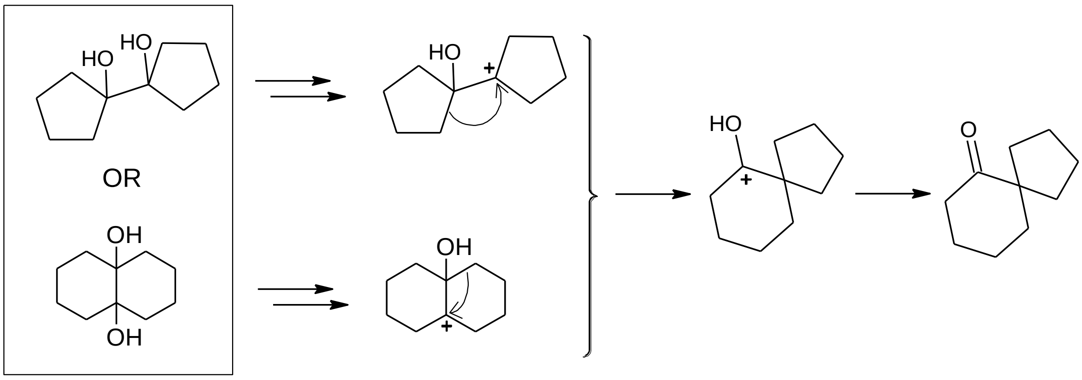


(v) Compound **X** is a product formed from *pinacol rearrangment*.



compound **X**

Draw the structure of the 1,2-diol responsible for producing **X**. [1]



1,2-diol

(b) A research team in Kanazawa University was successful in selectively synthesising one species of 1,2-diol from an aldehyde and a ketone as the starting materials. The key to the success was a newly developed copper catalyst that could distinguish between the two different carbonyl compounds.

Fig. 2.3 shows the structure of the copper catalyst with N-heterocyclic carbene (NHC) as one of the ligands.

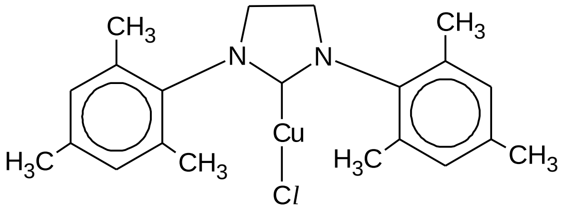
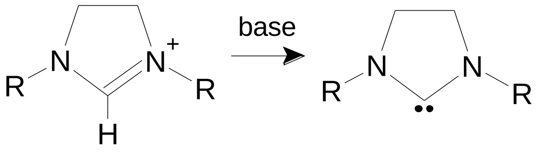


Fig. 2.3

Bases can be used to prepare the NHC ligand, as shown in Fig. 2.4.



R = bulky substituent NHC

Fig. 2.4

(i) Define the term *ligand*. [1]

A ligand is a neutral molecule or an anion containing at least one atom with a lone pair of electrons that can be donated into low lying vacant orbital of metal atom/ion to form a coordinate bond.

(ii) State the oxidation number of Cu in Fig. 2.3. [1]

+1

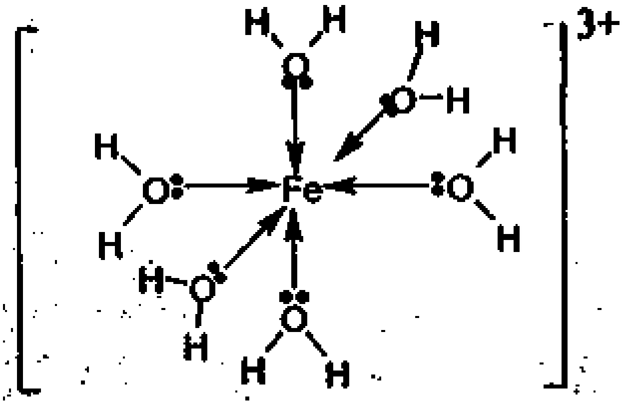
(iii) Coordination number is defined as the number of dative bonds formed between ligands and the central metal atom or ion.

State the coordination number of Cu in Fig. 2.3. [1]

2

(c) **(i)** Hexaaquairon(III) ions, $[Fe(H_2O)_6]^{3+}$, are pale violet.

Draw the structure of hexaaquairon(III) ion, showing the arrangement of the ligands in the structure. [1]



(ii) Explain why hexaaquairon(III) ions are coloured. [3]

In the presence of water ligands in the hexaaquairon(III) ions, the d orbitals of the Fe^{3+} ion are split into two groups of different energy levels.

When white light shines on the complex, a d electron is promoted to a higher energy vacant or partially filled d orbital.

During the transition, the d electron absorbs wavelength of light from the visible spectrum.

The light energy not absorbed/transmitted, which is complementary to the wavelength of light absorbed, gives the transition metal complex its colour.

(iii) When a few drops of KSCN(aq) are added to 5 cm^3 of Fe^{3+}(aq), followed by a few drops of KF(aq), the solution changes colour from violet to deep-red to colourless.

Identify the type of reaction occurring and explain the sequence of colour changes observed. [3]

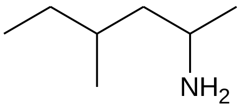
In both reactions, ligand exchange has taken place.

When a few drops of KSCN are added to Fe^{3+}, the stronger SCN^- ligand replaces the weaker H_2O ligand, and hence the colour of the solution changes from violet to deep red.

When a few drops of KF are added to the resultant solution from the first part, the solution changes colour from deep red to colourless as the stronger F^- ligand replace the weaker SCN^- ligands.

[Total: 20]

3 **(a)** Compound **Y** is a banned performance–enhancing stimulant. Usain Bolt lost one of his three gold medals from the 2008 Olympics because one of his relay team members tested positive for this drug.



Y

Compound **Y** may be prepared by the three–step synthesis shown in Fig. 3.1. Other products of each step are not shown.

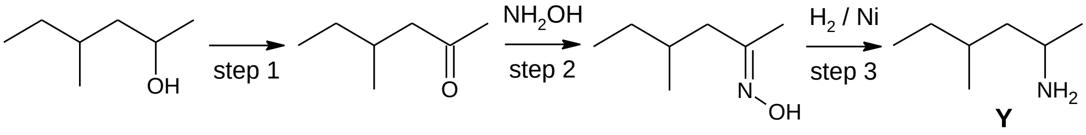


Fig. 3.1

(i) Name the starting organic material in step 1 of Fig. 3.1. [1]

4–methylhexan–2–ol

(ii) Deduce the identity of the other product formed in step 2 of Fig. 3.1. [1]

H_2O

(b) A student suggested that compound **Y** could be prepared directly from the starting material in step 1 by reacting it with phosphorus pentachloride, PCl_5, followed by ammonia, NH_3.

(i) State the property of ammonia that makes this a possible synthesis route for compound **Y**. [1]

There is a lone pair of electrons on the nitrogen atom which allows NH_3 to act as a nucleophile.

(ii) A second student suggested that the first student's proposal might work better if the reaction with ammonia was carried out in the presence of acid.

Explain if the second student's suggestion is correct. [1]

The second student is wrong. The lone pair of electrons on the nitrogen atom will not be available as it would have been used to form dative bond with the acid in the acid-base reaction.

(iii) Thionyl chloride, $SOCl_2$, can be used as a replacement for PCl_5 in the reaction mentioned in **(b)**. $SOCl_2$ is difficult to handle safely and is similar to PCl_5 in terms of reactivity and cost.

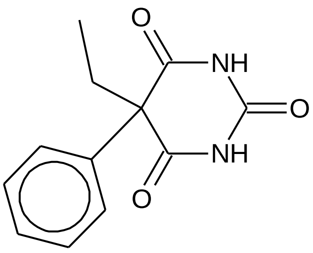
Suggest an advantage of using $SOCl_2$ instead of PCl_5. [1]

Both the by–products, SO_2 and HCl, are gases hence are easily separated from the chloroalkane product.

$R\text{–}OH + PCl_5 \rightarrow R\text{–}Cl + POCl_3(l) + HCl(g)$

$R\text{–}OH + SOCl_2 \rightarrow R\text{–}Cl + SO_2(g) + HCl(g)$

(c) Phenobarbital is a drug used in the treatment of seizures.



phenobarbital

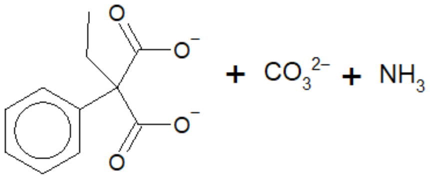
(i) Comment on the basicity of phenobarbital.

[1]

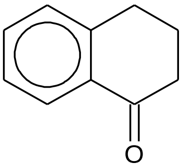
In each –CONH group, the lone pair of electrons on the nitrogen atom is not available to form a dative bond with a proton as it is delocalised into the adjacent C=O bond. Therefore, phenobarbital is not a basic (or is a neutral) drug.

(ii) Predict the products of the alkaline hydrolysis of phenobarbital.

[2]



(d) 1–tetralone is used in the synthesis of propranolol, a drug used in the treatment of high blood pressure.

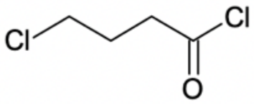


1-tetralone

Benzene can be used to make 1–tetralone.

(i) Suggest the structure of an organic reagent that could form 1–tetralone from benzene in a single step.

[1]



(ii) Explain why benzene does not undergo addition reactions.

[1]

The extra stability associated with the delocalisation of six π electrons in the continuous overlapping p–orbitals is destroyed if benzene undergoes addition reactions.

(e) Organic drug synthesis processes often involve alkali metals.

Alkali metals react with water as shown in the equation, where **M** represents the alkali metal.

$$\mathbf{M}(s) + H_2O(l) \rightarrow \mathbf{M}OH(aq) + \tfrac{1}{2}H_2(g) \qquad \Delta H_r^{\ominus}$$

For each of the alkali metals, Table 3.1 shows:

- the standard enthalpy change of atomisation, $\Delta H_{at}^{\ominus}$,
- the standard enthalpy change of hydration, $\Delta H_{hyd}^{\ominus}$,
- the first ionisation energy, 1st IE,
- the standard enthalpy change of reaction between alkali metal and water, $\Delta H_r^{\ominus}$.

Table 3.1

alkali metal	$\Delta H_{at}^{\ominus}$ (**M**) / kJ mol^{-1}	$\Delta H_{hyd}^{\ominus}$ (**M**$^+$) / kJ mol^{-1}	1st IE (**M**) / kJ mol^{-1}	$\Delta H_r^{\ominus}$ (**M**) / kJ mol^{-1}
Li	+160	–519	+519	–222
Na	+109	–406	+495	–184
K	+90	–322	+418	–196
Rb	+86	–301	+402	–195
Cs	+79	–276	+376	–203

(i) Define the term *standard enthalpy change of hydration*.

[1]

Standard enthalpy change of hydration of an ion is the energy released when one mole of the gaseous ion is hydrated at standard conditions / 298 K and 1 bar.

(ii) Explain the trend in the standard enthalpy change of hydration, $\Delta H_{hyd}^{\ominus}$, down the group.

[2]

The magnitude of $\Delta H_{hyd}^{\ominus}$ of an ion depends on its charge density. The charge density of the ions decreases as the ionic radii increases down the group.
The lower the charge density of the ion, the weaker the ion–dipole interactions formed between the ion and water molecules. Less energy will be evolved and hence, $\Delta H_{hyd}^{\ominus}$ will be less exothermic.

(f) **(i)** Use relevant data from Table 3.1 to calculate the enthalpy change for the following reaction.

$$Na(s) \rightarrow Na^+(aq) + e^-$$

[1]

$$\begin{tikzcd}
Na(s) \arrow[r] \arrow[d, "\Delta H_{at}^{\ominus}"'] & Na^+(aq) + e^- \\
Na(g) \arrow[r, "1^{st}\ IE"'] & Na^+(g) + e^- \arrow[u, "\Delta H_{hyd}^{\ominus}"']
\end{tikzcd}$$

enthalpy change = (+109) + (+495) + (–406) = +198 kJ mol^{-1}

(ii) Using relevant data from Table 3.1 and your answer in **(f)(i)**, draw an energy cycle to determine the enthalpy change of **reaction 1**.

reaction 1 $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$

Show your working clearly.

[2]

$$\begin{tikzcd}
2Na(s) + 2H_2O(l) \arrow[rr, "2 \text{ x } \textbf{(f)(i)}"] \arrow[dr, "2 \text{ x } (-184)"'] & & 2Na^+(aq) + 2e^- + 2H_2O(l) \arrow[dl, "\text{reaction 1}"] \\
& 2Na^+(aq) + 2OH^-(aq) + H_2(g) &
\end{tikzcd}$$

Enthalpy change of reaction 1 = –(2 x 198) + [2 x (–184)]
= –764 kJ mol^{-1}

(iii) There is particular interest in lithium as an energy source due to its low density.

Use relevant data form Table 3.1 to calculate the energy change per gram of lithium for the reaction between lithium and water.

[1]

Energy change per gram of lithium = –222 ÷ 6.9 = –32.2 kJ g^{-1}

(g) Lithium carbonate undergoes thermal decomposition in a similar way to Group 2 carbonates, though a much higher temperature is required.

Explain why the reaction occurs at high temperatures. Refer to the signs of ΔH, ΔS and ΔG in your answer.

[2]

$$\Delta G = \Delta H - T\Delta S$$

$\Delta H_{decomposition} > 0$ since heat is required to break the chemical bonds during decomposition.

$\Delta S_{decomposition} > 0$ since CO_2 gas is produced.

Production of CO_2 gas results in the products being more disordered than the reactants.

At high T, the negative $-T\Delta S$ outweighs the positive ΔH, hence $\Delta G < 0$.

The decomposition reaction is spontaneous.

(h) Group 2 metals undergo reaction with water in a similar way to alkali metals.

However, magnesium and barium have different reactivities when added separately to water.

Use relevant $E^\ominus$ values from the *Data Booklet* to explain the difference in the reactivity of magnesium and barium with water.

[1]

Barium is more reactive than magnesium.

$$Mg^{2+} + 2e^- \rightleftharpoons Mg \qquad E^\ominus = -2.38V$$

$$Ba^{2+} + 2e^- \rightleftharpoons Ba \qquad E^\ominus = -2.90V$$

$E^\ominus$ (Ba^{2+}/Ba) is more negative than $E^\ominus$ (Mg^{2+}/Mg). Therefore, the reducing power of barium is greater compared to magnesium.

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Alcohol is widely used in the preparation of aldehydes and ketones. The electrolysis of alcohols to carbonyl compounds is reported. A simplified diagram of the cell set-up is shown in Fig. 4.1.

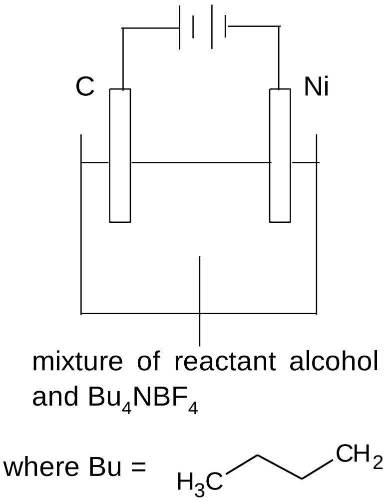
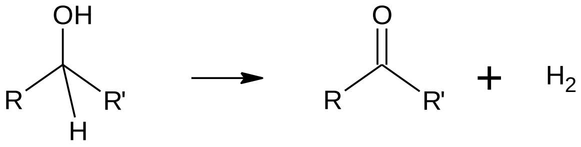


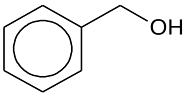
Fig. 4.1

The overall equation for the electrolysis of alcohol is shown.



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

(i) Write a balanced equation that shows the complete combustion of benzyl alcohol.

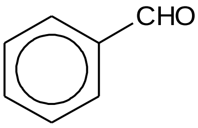


benzyl alcohol

[1]

$C_6H_5CH_2OH + \frac{17}{2}O_2 \rightarrow 7CO_2 + 4H_2O$

(ii) Draw the structure of the product formed when benzyl alcohol is electrolysed. [1]



(iii) State and explain at which electrode does the conversion of the reactant alcohol take place. You should state the element that the electrode is made of. [2]

Carbon. Since the electrolysis of alcohol to form carbonyl compound is an oxidation process, it will occur at the anode.

(iv) Suggest the role of Bu_4NBF_4 in the set-up in Fig. 4.1. [1]

Electrolyte.

(v) A constant current of 800 mA is delivered at room temperature over 10 minutes. By considering the change in the oxidation state of the reactive carbon, calculate the number of moles of carbonyl compound formed from the electrolysis given that the yield of this conversion is 90%. [3]

$Q = \frac{800}{1000} \times 10 \times 60 = 480 \text{ C}$

Since no. of moles of alcohol: no.of moles of e^- is 1:2,

No. of moles of alcohol used $= \frac{Q}{2F}$

$= \frac{480}{2 \times 96500}$

$= 2.487 \times 10^{-3}$ mol

No. of moles of carbonyl formed $= 0.9 \times 2.487 \times 10^{-3}$

$= 2.24 \times 10^{-3}$ mol (3sf)

(vi) Anodising aluminium is another useful application of electrochemical method. Describe how anodising of aluminium is achieved. [2]

An electrolytic cell with the aluminium that is to be anodised being the anode is set up. The electrolyte used is either H_2SO_4 or chromic acid. At the anode, H_2O is preferentially discharged to form O_2. The discharged O_2 reacts with the aluminium anode to form a protective layer of Al_2O_3.

(b) Iodine-based reagents are commonly used in organic synthesis owing to their unique chemical properties which are linked to their physical properties such as ionic radius and ionisation energy.

(i) State what is meant by the *first ionisation energy of iodine*. [1]

The first ionisation energy of iodine is the amount of energy absorbed by one mole of gaseous iodine atoms to remove one mole of electrons to form one mole of gaseous singly positively charged iodine cations.

(ii) State and explain the variation of atomic radius down Group 17. [2]

Atomic radius increases down the group.
The number of electronic shells and shielding effect increase and each successive element has its valence electrons located in a shell with a higher principal quantum number, *n*. Hence, valence electrons are increasingly further away from the nucleus despite the increase in nuclear charge.

(iii) Hydrofluoric acid and sodium fluoride can be used to form an acidic buffer.

Explain how an acidic buffer controls the pH of a solution.

[1]

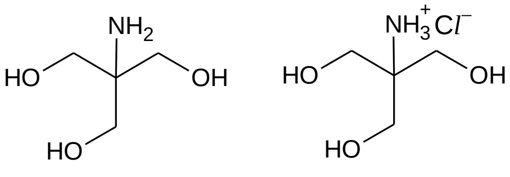
A buffer resists pH changes when small amounts of acid or base is added to the solution. When a small amount of acid is added, the conjugate base will neutralise the added acid. When a small amount of base is added, the weak acid will neutralise the added base.

(iv) Predict and explain if hydroiodic acid and sodium iodide can be used to form an acidic buffer.

[1]

Since hydroiodic acid is a strong acid, it will not be able to form an acidic buffer with sodium iodide.

(c) Tris buffer is a biochemical buffer used in COVID–19 vaccines. The structure of Tris and Tris–HC*l* is shown below. The K_b of Tris is 1.05×10^{-6} mol dm^{-3}.



Tris Tris-HC*l*

A Tris buffer is formed by mixing 200 cm^3 of 1.50 mol dm^{-3} Tris with 200 cm^3 of 1.66 mol dm^{-3} Tris–HC*l*.

(i) Calculate the pH of the Tris buffer.

[2]

K_a of Tris–HC*l* = $\frac{1 \times 10^{-14}}{1.05 \times 10^{-6}}$ = 9.523×10^{-9} mol dm^{-3}

Since equal volume of Tris and Tris–HC*l* is added,
[Tris] = 0.75 mol dm^{-3}
[Tris–HC*l*] = 0.83 mol dm^{-3}

pH = $-\log_{10}(9.523 \times 10^{-9}) + \log_{10}\frac{0.75}{0.83}$
= 7.98 (3sf)

(ii) 25.0 cm^3 of 0.500 mol dm^{-3} HNO_3 is added to 75.0 cm^3 of the Tris buffer prepared.

Calculate the pH of this solution.

[3]

moles of HNO_3 added = $\frac{25}{1000} \times 0.500 = 1.25 \times 10^{-2}$ mol

New moles of Tris = $(\frac{75}{1000} \times 0.75) - 1.25 \times 10^{-2} = 0.04375$ mol

New moles of Tris-HC*l* = $(\frac{75}{1000} \times 0.83) + 1.25 \times 10^{-2} = 0.07475$ mol

$$\text{pH} = -\log_{10}(9.523 \times 10^{-9}) + \log_{10}\frac{0.04375/_{0.10}}{0.07475/_{0.10}} = 7.79 \text{ (3sf)}$$

[Total: 20]

5 **(a)** Fig. 5.1 shows a hydrogen–halogen fuel cell where H_2 gas is supplied to the anode while Br_2, dissolved in an aqueous solution of HBr, is provided to the cathode.

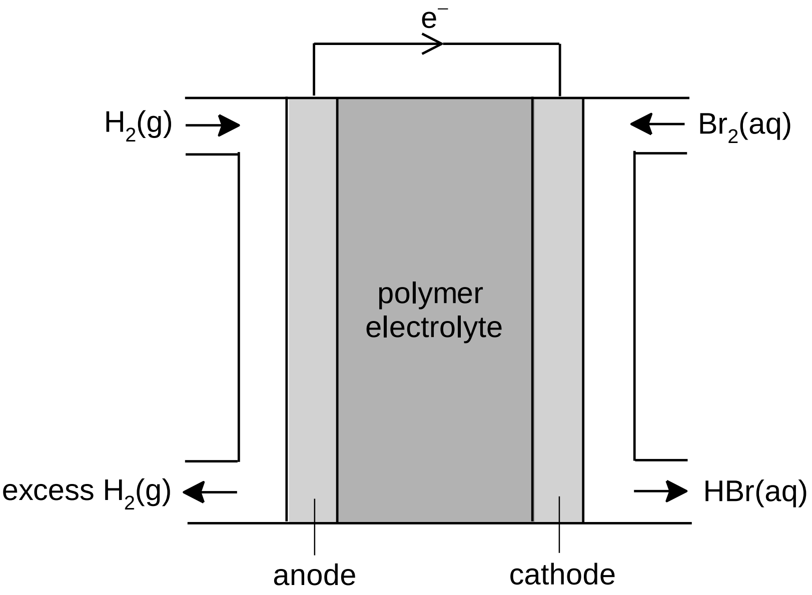


Fig. 5.1

(i) The polymer electrolyte allows the transfer of a simple ion from the anode to the cathode. Use Fig. 5.1 to suggest the identity of the ion and hence construct balanced equations for the reactions occurring at the electrodes.

[2]

Identity of ion: H^+/hydrogen ion/proton
Anode: $H_2 \rightarrow 2H^+ + 2e^-$
Cathode: $Br_2 + 2e^- \rightarrow 2Br^-$

(ii) Use your answer in **(a)(i)** to write the overall equation when current flows and hence use the *Data Booklet* to calculate the standard cell potential, $E^{\ominus}_{cell}$, for this cell.

[2]

Overall: $H_2 + Br_2 \rightarrow 2HBr$
$E^{\ominus}_{cell} = 1.07 - 0.00 = +1.07\ V$

(iii) Use your answer to **(a)(ii)** to calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this electrochemical reaction.

[1]

$\Delta G^{\ominus} = -nFE^{\ominus}_{cell} = -2(96500)(1.07)$
$= -206510\ J\ mol^{-1} = -207\ kJ\ mol^{-1}$

(iv) A similar hydrogen–halogen fuel cell is set up where Cl_2, dissolved in an aqueous solution of HC*l*, is supplied to the cathode.

How would you expect the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this electrochemical reaction to compare with your answer in **(a)(iii)**?

Explain your answer in terms of the difference in relative reactivity of the halogens.

[2]

$\Delta G^{\ominus}$ will be more negative than that in (a)(iii).

Cl_2 is a stronger oxidising agent than Br_2 so the reduction of Cl_2 will take place more readily at the cathode and the electrochemical reaction will be more spontaneous.

(b) The values of two solubility products are given.

$$K_{sp}\ (PbBr_2) = 1.9 \times 10^{-5}\ mol^3\ dm^{-9}$$
$$K_{sp}\ (AgBr) = 5.4 \times 10^{-13}\ mol^2\ dm^{-6}$$

(i) Solid $PbBr_2$ is shaken with water. The remaining solid is filtered off, leaving a saturated solution X. Calculate $[Br^-(aq)]$ in X.

[1]

Let the solubility of $PbBr_2$ be s mol dm^{-3}.

$K_{sp} = [Pb^{2+}][Br^-]^2 = (s)(2s)^2 = 1.9 \times 10^{-5}$
$4s^3 = 1.9 \times 10^{-5}$
$s = 0.016810$
$[Br^-] = 2s = 0.033620 = 0.0336$ mol dm^{-3}

(ii) Drops of dilute aqueous $AgNO_3$ are added to X until AgBr just precipitates. Calculate $[Ag^+(aq)]$ in the resulting solution when AgBr just precipitates.

[1]

Ionic product = $K_{sp} = 5.4 \times 10^{-13}$
$[Ag^+][Br^-] = [Ag^+](0.033620) = 5.4 \times 10^{-13}$
$[Ag^+] = 1.6062 \times 10^{-11} = 1.61 \times 10^{-11}$ mol dm^{-3}

(iii) HBr is a strong acid when dissolved in water.

Descibe what you will observe if equal volumes of 0.100 mol dm^{-3} solution of HBr and saturated solution of $PbBr_2$ were mixed. Explain your answer using appropriate calculations.

[2]

Observation: Formation of (white) precipitate.

$[Br^-]$ in mixture = $(0.033620 + 0.100)/2 = 0.06681$ mol dm^{-3}
Ionic product = $[Pb^{2+}][Br^-]^2$
$= (0.016810/2)(0.06681)^2 = 3.75 \times 10^{-5} > 1.9 \times 10^{-5}$ mol^3 dm^{-9}

Since ionic product of $PbBr_2$ will exceed its K_{sp}, white precipitate of $PbBr_2$ will be formed.

(c) Ethene reacts with hydrogen bromide exothermically to produce bromoethane.

$$CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2Br$$

The reaction mechanism has two steps as shown.

step 1 $\quad CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2^+ + Br^-$
step 2 $\quad CH_3CH_2^+ + Br^- \rightarrow CH_3CH_2Br$

(i) State the slow step and hence write the rate equation for the reaction.

[1]

step 1 and rate = $k[CH_2{=}CH_2][HBr]$

(ii) Use your answer in **(c)(i)** and the collision theory to explain the effect on the rate of reaction, if any, of

- decreasing the concentration of hydrogen bromide,
- increasing the temperature of the reaction.

[2]

Rate depends on [HBr] / reaction is first order or non-zero order with respect to HBr as shown by the rate equation. Decreasing the concentration of hydrogen bromide decreases the number of reactant particles per unit volume which decreases the frequency of effective collisions. Hence rate of reaction decreases.

Increasing the temperature of the reaction increases the average kinetic energy of reactant particles. More particles have energy greater than or equal to the activation energy and frequency of effective collisions increases. Rate constant, *k*, increases and hence rate of reaction increases.

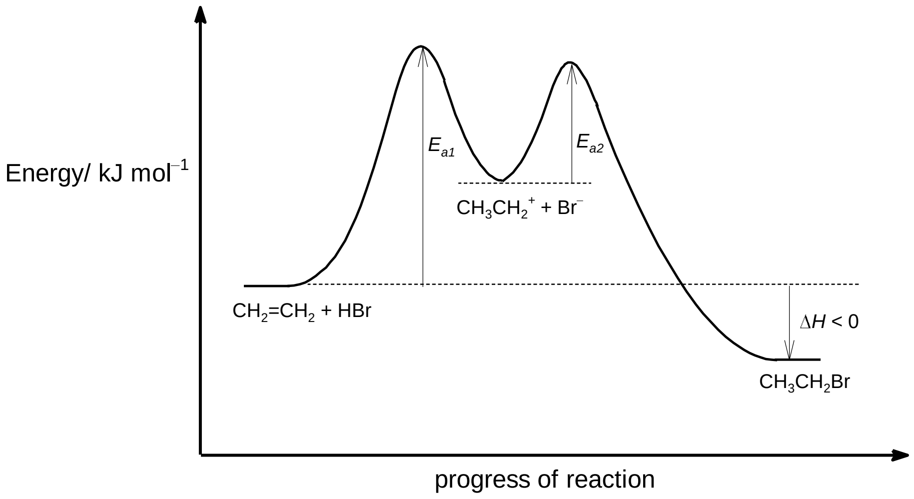
(iii) Use the mechanism to explain the role of $CH_3CH_2^+$.

[1]

$CH_3CH_2^+$ is an intermediate; it is formed in step 1 but consumed in step 2.

(iv) Draw the labelled energy profile diagram for the reaction.

[2]



Note:

- Labelled axes, reactants, intermediate and products
- Two steps with $E_{a1} > E_{a2}$
- Energy level of intermediate higher than reactants
- Overall $\Delta H < 0$

(d) The strength of an acid is measured by its K_a value.

How would you expect the K_a values to compare for the following pairs of acids?

- HF and HC*l*
- CH_3COOH and CF_3COOH
- $[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$

Explain your answer, quoting relevant data from the *Data Booklet* where appropriate.

[3]

- HF and HC*l*

K_a value of HC*l* is **larger** than that of HF.

Since **BE(H–C*l*) = 431 kJ mol^{-1} < BE(H–F) = 562 kJ mol^{-1}**, the **H–C*l* bond is weaker** and **requires less energy to break** than the H–F bond. HC*l* donates H^+ more readily and is a stronger acid with a larger K_a value than HF.

- CH_3COOH and CF_3COOH

K_a value of CF_3COOH is **larger** than that of CH_3COOH.
The presence of three **electron-withdrawing F atoms disperses the negative charge** on the conjugate base of CF_3COOH, making **CF_3COO^- more stable than CH_3COO^-**. CF_3COOH dissociates to a greater extent and is a stronger acid with a larger K_a value than CH_3COOH.

- $[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$

K_a value of $[Fe(H_2O)_6]^{2+}$ is **smaller** than that of $[Al(H_2O)_6]^{3+}$.
Since Fe^{2+} has a **smaller charge and larger ionic radius (0.061 nm)** than Al^{3+} (ionic radius = **0.050 nm**), Fe^{2+} has a **smaller charge density** and polarising power than Al^{3+}. $[Fe(H_2O)_6]^{2+}$ hydrolyses to a smaller extent and is a weaker acid than $[Al(H_2O)_6]^{3+}$.

[Total: 20]