Suggested Solutions

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response Questions

18 September 2024
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 **22** printed pages.

Section A

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

1 **(a)** A bomb calorimeter and a Styrofoam cup calorimeter are both tools used in thermodynamics to measure heat changes during a chemical reaction. However, they differ significantly in their design, operation, and the type of reactions they measure.

Fig. 1.1 shows a simplified diagram of a bomb calorimeter which can be used for the accurate determination of heat changes during the combustion of alkanes.

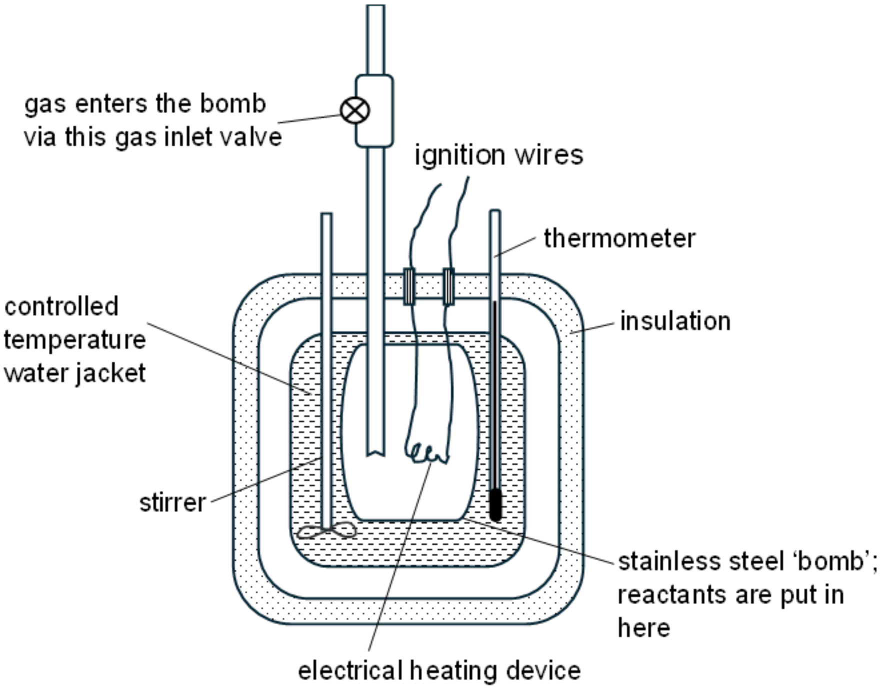


Fig. 1.1

The combustion process takes place at constant volume and the reaction is initiated via the electrical heating device which ignites the mixture.

(i) State one reason why the conditions inside the bomb calorimeter are considered non-standard. [1]

The pressure is high inside the bomb calorimeter and hence, is different from standard conditions, which is defined as 1 atm.

(ii) Suggest a reason why the Styrofoam cup calorimeter would be unsuitable to be used to measure heat changes during the combustion of alkanes. [1]

Styrofoam cup calorimeter would be unsuitable in this case because the combustion reaction involve gases and they would escape from the cup.

(b) The heat capacity of a bomb calorimeter, C_{cal}, is the amount of heat required to raise the temperature of the calorimeter by 1 °C, and it can be calculated using a fuel which the heat change is known.

In an experiment to calculate C_{cal}, 2.00 g of liquid hexane is ignited with oxygen gas which is required to be in 20% excess.

A temperature change of 12.6 °C is recorded.

Under the conditions of the experiment, 1.00 mol of hexane releases 4254 kJ of energy when combusted.

(i) Write an equation for the complete combustion of hexane. [1]

$CH_3(CH_2)_4CH_3(l) + \frac{19}{2}O_2(g) \rightarrow 6CO_2(g) + 7H_2O(l)$

(ii) Calculate the number of moles of oxygen gas needed to ensure the excess and hence, the volume occupied by this same amount of oxygen gas at a temperature of 298 K and a pressure of 1.00 atm, assuming ideal gas behaviour. [2]

Amount of hexane present $= \frac{2.00}{86.0}$
$= 0.023256$ mol

Amount of oxygen gas needed to ensure the 20% excess
$= 0.023256 \times \frac{19}{2} \times 1.2$
$= 0.26512$ mol

Let V = volume of O_2 gas introduced

Using the ideal gas equation,
$pV = nRT$
$V = \frac{nRT}{P}$
$V = \frac{0.26512 \times 8.31 \times 298}{101325}$
$V = 0.0064794\ m^3$
$\approx 0.00648\ m^3$

(iii) Calculate the heat capacity of the bomb calorimeter, C_{cal}, in kJ K^{-1}. [2]

Amount of heat energy released = 0.023256 × 4254 = 98.930 kJ

$C_{cal} = \frac{98.930}{12.6} = 7.85\ kJ\ K^{-1}$

(iv) When the experiment is repeated with 2.00 g of butane, the temperature change recorded is 12.3 °C. Calculate the heat change per mole of butane combusted.

If you were unable to calculate a value for C_{cal} in **(b)(iii)**, use 6.50 kJ K^{-1}.
[2]

Amount of heat released = 7.8516 × 12.3 = 96.575 kJ

Amount of butane used = $\frac{2.00}{58.0}$ = 0.034483 mol

Heat change for butane = $\frac{96.575}{0.034483}$ = 2800.7 kJ mol^{-1}
≈ 2800 kJ mol^{-1}

(c) **(i)** Halogenoalkanes, R−X, undergo substitution reactions with *nucleophiles*.

Define what a *nucleophile* is. [1]

A nucleophile is an electron pair donor which is attracted to an electron deficient atom or region of low electron density.

Table 1.1 shows the melting points of two metal nitrites which have different structure and bonding.

Table 1.1

metal nitrite	melting point/ °C
$AgNO_2$	140
KNO_2	441

Fig. 1.2 shows a general structure of $AgNO_2$.

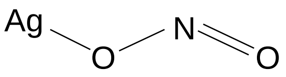
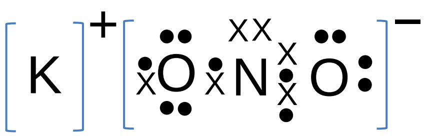


Fig. 1.2

(ii) Draw a 'dot-and-cross' diagram to show the type of bonding present in KNO_2. [1]



(iii) With consideration of the difference in bonding between KNO_2 and $AgNO_2$, explain why R−X react with KNO_2 to form alkyl nitrites, R−ONO, while R−X react with $AgNO_2$ to form nitroalkanes, $R{-}NO_2$, as the major product.

[R: alkyl group]

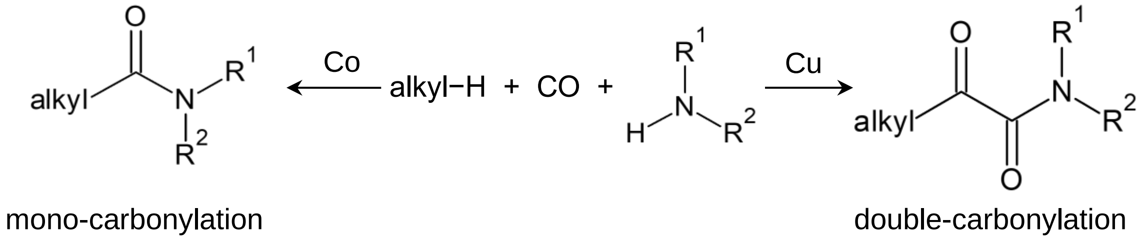
[2]

KNO_2 is predominantly ionic and one of the oxygen atoms have a negative charge. Nucleophilic attack through this negatively charged oxygen atom on the alkyl halides mainly gives RONO.

In contrast, $AgNO_2$ is a covalent compound and both O and N atoms carry lone pair of electrons. Since N is less electronegative than O, the lone pair of electrons of N is more readily available for bond formation. Hence, RNO_2 is the major product.

(d) Carbonylation reactions are chemical reactions in which a carbon monoxide (CO) molecule is incorporated into an organic molecule.

Fig. 1.3 shows metal-controlled mono- and double-carbonylation reactions of alkanes with amines to prepare alkyl amides and alkyl α-ketoamides respectively. The choice of the Co or Cu catalyst precursor was the key to producing a switch in the reaction selectivity.



[R: alkyl group or H atom]

Fig. 1.3

(i) State the type of reaction common to both carbonylation reactions seen in Fig. 1.3. [1]

Addition

Fig. 1.4 shows a reaction scheme which includes the carbonylation reactions shown in Fig. 1.3.

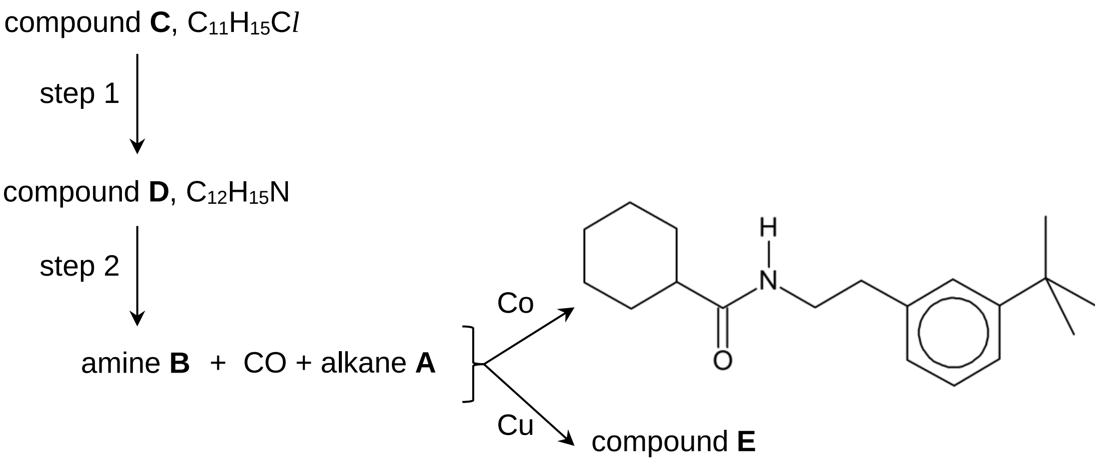
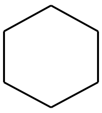
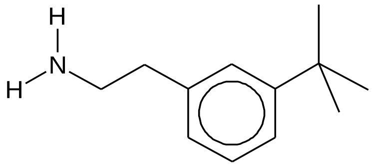
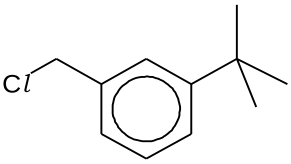
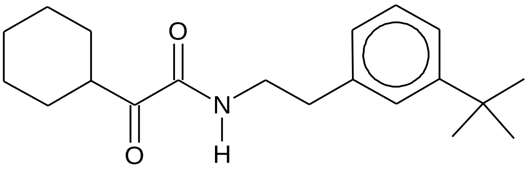


Fig. 1.4

(ii) With reference to Fig. 1.4, draw the structures of

- alkane **A**,
- amine **B**,
- compounds **C** and **E**.

[4]

alkane **A**	amine **B**
	
compound **C**	compound **E**
	

(iii) With reference to Fig. 1.4, identify the reagents and conditions for steps 1 and 2. [2]

step 1: KCN or NaCN in ethanol, heat under reflux
step 2: $\text{LiA}l\text{H}_4$ in dry ether, room temperature

[Total: 20]

2 **(a)** Describe the reactions, if any, of the chlorides $NaCl$, $AlCl_3$ and PCl_5 with water. Write an equation for any reaction and state the pH of the resultant mixtures. [3]

$NaCl$

Dissolves readily in water to form hydrated ions in a neutral solution.

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

pH = 7

$AlCl_3$

Dissolves in water with partial hydrolysis to give an acidic solution.

$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$

pH = 3

PCl_5

Undergoes complete hydrolysis in water to form a strongly acidic solution.

$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$

pH = 2

(b) In 1849, the German chemist Adolf Kolbe reported his investigations into the electrolysis of aqueous solutions of sodium salts of carboxylic acids, using inert platinum electrodes. The reaction occurring at the anode is described by the equation shown below.

$$2RCO_2^- \rightarrow R\text{–}R + 2CO_2 + 2e^-$$

R can be any alkyl group.

(i) Identify the substances liberated at the cathode during the electrolysis. [1]

H_2 and OH^-

(ii) Calculate the volume of CO_2 gas produced at the anode at room temperature and pressure when a current of 0.100 A is passed through the electrolytic cell for 45.0 minutes. [2]

$Q = (0.1)(45 \times 60) = 270$ C

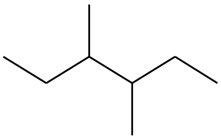
moles of e^- = 270 / 96500 = 0.0027979 mol

$CO_2 \equiv e^-$

moles of CO_2 = 0.0027979 mol

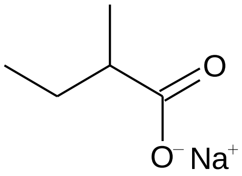
volume of CO_2 = 0.0027979 × 24 = 0.0672 dm^3

3,4-dimethylhexane is produced from the Kolbe electrolysis of the aqueous solution of the sodium salt of a carboxylic acid.



3,4-dimethylhexane

(iii) Draw the structure of the salt used to produce 3,4-dimethylhexane.
Give the systematic name of the salt. [2]



sodium 2-methylbutanoate

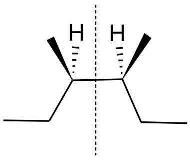
There are three different types of 3,4-dimethylhexane molecule.

- molecule **X** rotates plane polarised light to the right.
- molecule **Y** rotates plane polarised light to the left.
- molecule **Z** has no effect on plane polarised light.

(iv) Deduce the isomeric relationship between molecules **X** and **Y**. Explain your reasoning. [1]

X and **Y** are a pair of enantiomers as they rotate plane polarised light in opposite directions.

(v) Draw the 3-dimensional structure of molecule **Z**, showing its stereochemical formula. Hence, explain why **Z** has no effect on plane polarised light. [2]



internal plane of symmetry

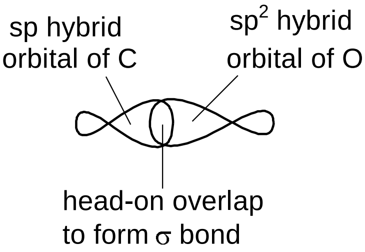
Molecule **Z** has an internal plane of symmetry and is thus an achiral molecule which is optically inactive.

(c) The carbon atom in CO_2 is sp hybridised.

(i) Explain what is meant by sp hybridisation with reference to the carbon atom in CO_2. [1]

The C atom in CO_2 has its 2s orbital mixed with one of its three 2p orbitals to form two degenerate sp hybrid orbitals.

(ii) Draw a labelled diagram to show how orbitals overlap to form one of the carbon–oxygen sigma bonds in CO_2.
Assume that the oxygen atoms in CO_2 are sp^2 hybridised. [1]



(iii) Explain the overall polarity of a CO_2 molecule by reference to its shape. [1]

CO_2 is linear around the C atom so the dipole moments of the C=O bonds are equal and opposite such that they cancel out. Hence CO_2 has no overall dipole moment and is a non-polar molecule.

(d) The half-life of a second-order reaction with respect to a reactant A can be calculated using the formula in Fig. 2.1.

$$t_{\frac{1}{2}} = \frac{1}{k[A]_t}$$

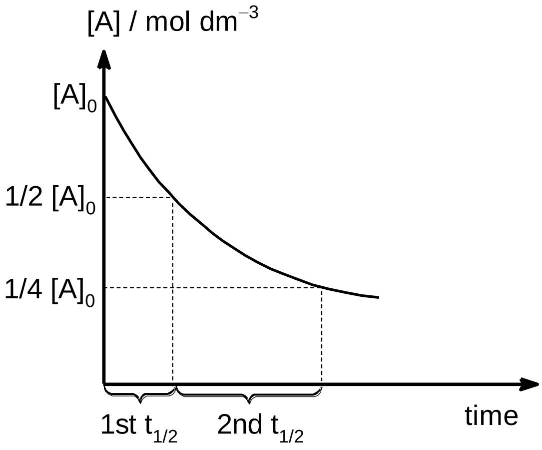
k is the rate constant at a specific temperature.
$[A]_t$ is the concentration of reactant A at time t.

Fig. 2.1

(i) State how **successive** half-lives vary for a second-order reaction as the concentration of reactant A decreases over time.

Hence, sketch a concentration of reactant A versus time graph for a second-order reaction. Label clearly two **successive** half-lives on the graph. [2]

successive half-lives increase for a second-order reaction



The decomposition of nitrogen dioxide to nitric oxide and oxygen is known to follow second-order kinetics.

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

The rate constant, k, for the decomposition at 300 °C is 0.54 mol^{-1} dm^{3} s^{-1}.

(ii) At 300 °C, a sample of NO_2 in a closed container took 46.3 s for its concentration to decrease to one-fourth of its original value.

Use the formula in Fig. 2.1 to determine the original concentration, in mol dm^{-3}, of NO_2 in the container. [2]

Let the original $[NO_2]$ be c mol dm^{-3}, then $[NO_2]$ after 1st half-life = $c/2$ mol dm^{-3}.

1st half-life = $\frac{1}{kc}$

2nd half-life = $\frac{2}{kc}$

total time taken = $\frac{3}{kc} = \frac{3}{0.54c} = 46.3$

$\Rightarrow c = 0.120$ mol dm^{-3}

(iii) Nitrogen dioxide has significant environmental consequences if emitted into the atmosphere.

Describe and explain with the aid of suitable equations, the role of NO_2 in the oxidation of atmospheric sulfur dioxide. [2]

NO_2 acts as a homogeneous catalyst.

NO_2 oxidises SO_2 to SO_3 while itself is reduced to NO:
$NO_2 + SO_2 \rightarrow SO_3 + NO$

NO is rapidly re–oxidised to NO_2 by oxygen, thus regenerating the catalyst:
$NO + \frac{1}{2}O_2 \rightarrow NO_2$

[Total: 20]

3 **(a)** **(i)** Describe the distribution of mass and charges within an atom with reference to its structure. [1]

An atom is made up of a positively charged nucleus surrounded by negatively charged electrons. The protons and neutrons in the nucleus make up the mass of the atom while electrons are negligible in mass.

(ii) In two separate experiments a beam of electrons and a beam of protons, travelling at the same velocity, passed through an electric field.

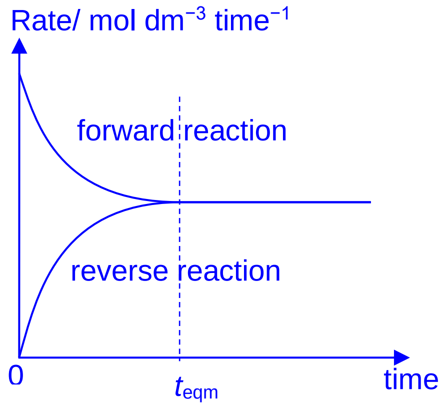
State two ways in which the behaviour of electrons would differ from that of protons. [1]

Electrons are deflected in a direction opposite to that of protons. The angle of deflection for electrons is larger (or deflected to a greater extent).

(b) When dinitrogen tetroxide, N_2O_4, and nitrogen monoxide, NO, are mixed in a 1:2 ratio in a 1 dm^3 sealed container, the two gases react slowly to form dinitrogen trioxide, N_2O_3.

$$N_2O_4(g) + 2NO(g) \rightleftharpoons 2N_2O_3(g) \qquad \Delta H^{\ominus} = -26\ \text{kJ mol}^{-1}$$

(i) Sketch a graph showing how the rates of the forward and reverse reactions change from the time the two gases are mixed (t = 0) to the time **after** the reaction reaches equilibrium ($t = t_{eqm}$). Label your two lines clearly. [2]



(ii) State and explain how the position of equilibrium might change when

- temperature is increased,
- the container is compressed. [2]

With an increase in temperature, by Le Chatelier's Principle, position of equilibrium shifts left so as to decrease the temperature by favouring the endothermic reverse reaction that absorbs heat.

Total pressure increases when the container is compressed. By Le Chatelier's Principle, position of equilibrium shifts right to decrease the total pressure by reducing the total moles of gas molecules.

(c) Describe and explain the relative ease of hydrolysis of the following three organochlorine compounds.

C_6H_5Cl $\qquad$ $C_6H_5CH_2Cl$ $\qquad$ CH_3COCl

[3]

Ease of hydrolysis: $C_6H_5Cl < C_6H_5CH_2Cl < CH_3COCl$

The sp^2 C–Cl bond in CH_3COCl breaks most readily. The sp^2 C atom has the greater partial positive charge as it is bonded to electronegative O and Cl atoms. This attracts a nucleophile strongly for hydrolysis to happen.

The sp^3 C atom in $C_6H_5CH_2Cl$, has a smaller partial positive charge than the sp^2 C atom in CH_3COCl as it is bonded to one electronegative Cl atom only.

In C_6H_5Cl, the relatively stronger sp^2 C–Cl bond has partial double bond character due to side-on overlap of the π electron cloud of the benzene ring and the p orbital of Cl. The lone pair of electrons on Cl can delocalise into the benzene ring to form a delocalised π electron cloud.

(d) Compounds **Q** and **R** are chiral compounds with molecular formula $C_9H_{10}O_3$. **Q** effervesces with aqueous sodium carbonate but not **R**.

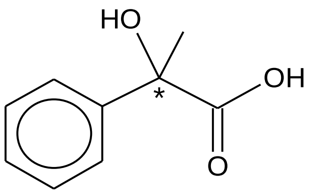
Q can react with PCl_5(s) to form compound **S**, $C_9H_8OCl_2$. **Q** does not react when heated with acidified $KMnO_4$. When **Q** is reacted with limited Cl_2(g) under ultraviolet light, compound **T**, $C_9H_9O_3Cl$, is the only product formed.

When concentrated HNO_3 is added to **R**, compound **U**, $C_9H_8O_7N_2$, is formed. **R** forms a yellow precipitate with alkaline aqueous iodine but does not react with Tollens' reagent. When **R** is heated with concentrated H_2SO_4, compound **V** is formed.

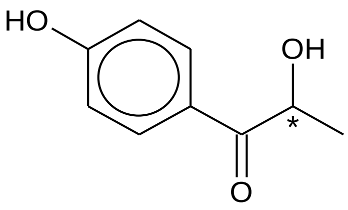
Suggest possible structures for **Q**, **R**, **S**, **T**, **U** and **V**. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [11]

Evidence	**Type of Reaction**	**Deduction**
Q and **R** has molecular formula $C_9H_{10}O_3$.	-	C : H ratio is ≈ 1 : 1 Benzene ring present in **Q** and **R**.
Q and **R** are chiral compounds.	-	**Q** and **R** contains at least one chiral carbon and has no internal plane of symmetry.
Q effervesces with aqueous sodium carbonate but not **R**.	Acid-base OR Acid-carbonate	–COOH group present in **Q** and absent in **R**. With three O atoms in its molecular formula, only one –COOH group is present.
Q can react with PCl_5(s) to form compound **S**, $C_9H_{10}OCl_2$.	Nucleophilic substitution	–COOH group in **Q** forms –COCl in **S**. Since 2 Cl atoms are substituted in **Q** to form **S**, **Q** has an alcohol group but not phenol. **S** is also a chloroalkane.
Q does not react when heated with acidified $KMnO_4$.	Oxidation	Since **Q** cannot be oxidised, **Q** has a tertiary alcohol in the side-chain. OR the C atom bonded directly to the benzene ring has no H atoms attached (no side-chain oxidation).

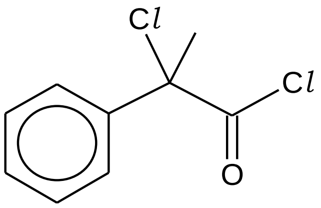
When **Q** is reacted with limited Cl_2(g) under ultraviolet light, compound **T** is the only product formed.	Free radical substitution	The H atoms in alkyl groups of **Q** are identical. OR One set of equivalent H atoms present. **T** is a halogenoalkane.
When concentrated HNO_3 is added to **R**, compound **U**, $C_9H_8O_7N_2$, is formed.	Electrophilic Substitution	Two NO_2 groups are substituted on **R**, phenol group present. Two –NO_2 groups are in 2,4 positions relative to the phenol group.
R forms a yellow precipitate with alkaline aqueous iodine.	Oxidation	**R** has –CH(OH)CH_3 and/or –$COCH_3$ in its structure.
R does not react with Tollens' reagent.	Oxidation	Aldehyde group absent in **R**.
When **R** is heated with concentrated H_2SO_4, compound **V** was formed.	Elimination	Alcohol group present in **R**. A H atom and the –OH group are attached to adjacent C atoms. C=C bond present in V.



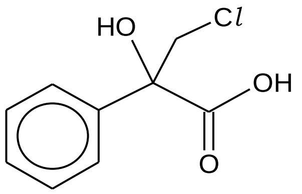
Q



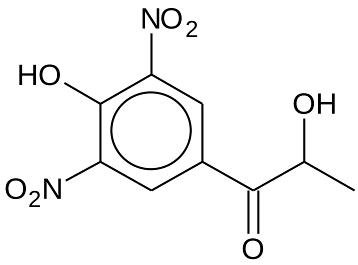
R



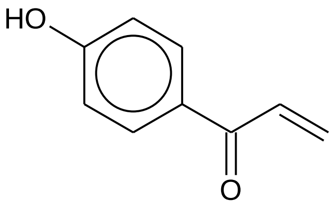
S



T



U



V

[Total: 20]

Section B

Answer **one** question from this section.

4 This question explores the chemistry of magnesium and nickel compounds.

(a) The Grignard reagent is an organometallic reagent containing magnesium attached to an alkyl group and a halogen. CH_3MgBr is an example of a Grignard reagent.

Fig. 4.1 shows the reaction of CH_3MgBr with propanal to produce compound **X** which forms butan-2-ol when treated with a dilute acid.

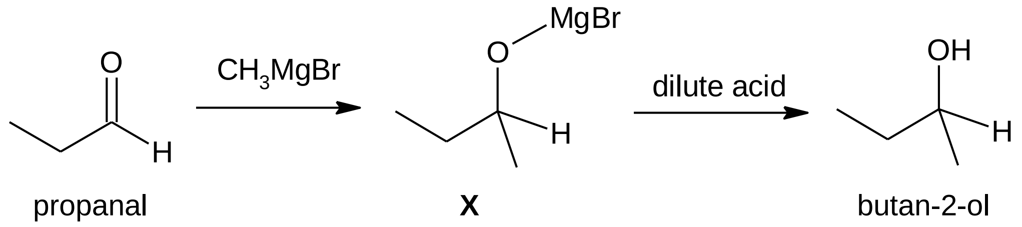


Fig. 4.1

(i) Explain why propanal cannot be converted to butan-2-ol using lithium aluminium hydride or sodium borohydride. [1]

The reduction of propanal using $LiA\mathit{l}H_4$ or $NaBH_4$ will produce a primary alcohol, propan-1-ol instead.

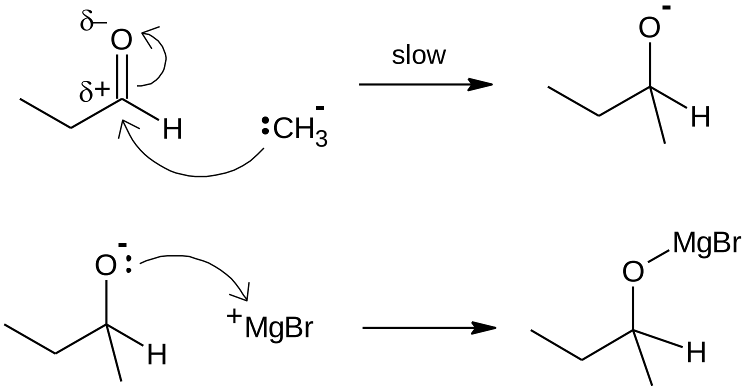
OR $LiA\mathit{l}H_4$ or $NaBH_4$ are reducing agents that do not add additional carbon atoms.

(ii) The reaction between propanal and CH_3MgBr is a nucleophilic addition reaction which proceeds via the following two steps.

- In the slow step, the nucleophile $:CH_3^-$ attacks the electrophilic carbon in propanal, forming a reactive intermediate.
- This reactive intermediate then reacts with ^+MgBr to form **X**.

Use the information provided to draw the mechanism for this reaction.

In your answer, indicate the movement of electron pairs with curly arrows, and show any relevant lone pairs and partial charges. [3]



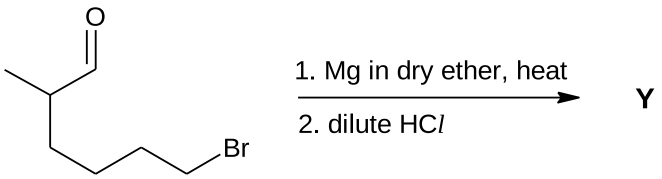
(iii) With reference to your answer in **(a)(ii)**, explain why the resultant product mixture is optically inactive. [2]

Propanal is trigonal planar around the electrophilic carbon. In step 1, there is an equal probability of the nucleophile attacking the carbonyl carbon from the top and bottom of the plane, forming two enantiomers of equal quantities. Hence, an optically inactive racemic mixture is formed.

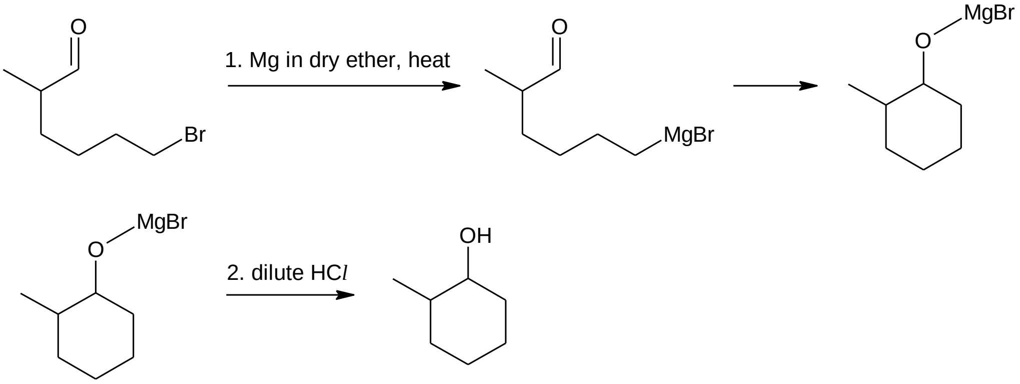
(iv) The synthesis of Grignard reagents involves heating a bromoalkane with magnesium metal in dry ether. An example is shown below.

$$CH_3CH_2Br + Mg \rightarrow CH_3CH_2MgBr$$

Using this information and Fig. 4.1, draw the structure of the organic product **Y** of the following reaction.

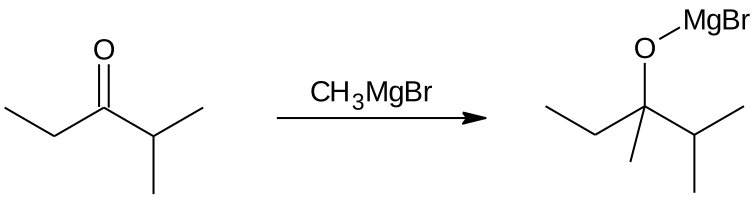


[1]



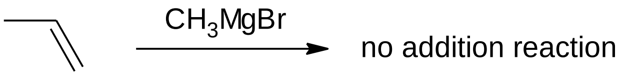
Y

(v) The reaction between CH_3MgBr and 2-methylpentan-3-one occurs at a slower rate as compared to the reaction of CH_3MgBr in Fig. 4.1.



2-methylpentan-3-one

In contrast, CH_3MgBr does not undergo addition reaction with propene.



propene

By comparing to the reaction of CH_3MgBr in Fig. 4.1, suggest reasons to explain each observation above. Use the concepts of electronegativity, electronic and steric effects in your answer. [3]

Reaction between CH_3MgBr and 2-methylpentan-3-one:

- 2-methylpentan-3-one has an additional electron-donating alkyl group compared to propanal. Hence, its carbonyl carbon is less electron deficient / less electrophilic and is less susceptible towards nucleophilic attack.

- The presence of the bulkier alkyl group in 2-methylpentan-3-one sterically hinders the approach of the nucleophile, reducing the rate of reaction.

No addition reaction between CH_3MgBr and propene:

- No electronegativity difference between the carbon atoms in the C=C bond. Hence, there is no electron deficient site for the nucleophile to attack.

(b) Nickel is widely used in the production of stainless steel and many other metal alloys.

(i) ^{78}Ni is a known isotope of nickel with a *relative isotopic mass* of 78.

A sample of nickel contains 3 isotopes of nickel. Table 4.1 shows the identity of these isotopes and their relative abundance in the sample.

Table 4.1

isotope	relative abundance / %
^{58}Ni	75.4
^{60}Ni	22.5
^{78}Ni	2.1

Define the term *relative isotopic mass* and calculate the relative atomic mass of nickel in the sample. Leave your answer to 2 decimal places. [2]

The relative isotopic mass of an isotope is the ratio of the mass of one atom of the isotope to $\frac{1}{12}$ of the mass of an atom of carbon–12.

Relative atomic mass of Ni in the sample

$= \frac{75.4}{100} \times 58 + \frac{22.5}{100} \times 60 + \frac{2.1}{100} \times 78 = 58.87$ (to 2 d.p.)

(ii) Elemental nickel can be oxidised by nitric acid, HNO_3. Nitrous oxide, NO, is produced as one of the products of this reaction.

In an experiment, 5 g of nickel was reacted with excess nitric acid. At the end of the reaction, 1.36 dm^3 of NO gas was collected at room temperature and pressure.

Using appropriate calculations, determine the final oxidation state of nickel at the end of the reaction. [2]

Let the final oxidation state of nickel be +*n*.

Oxidation half equation: $Ni \rightarrow Ni^{n+} + ne^-$
Reduction half equation: $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$

Amount of NO gas produced = $\frac{1.36}{24}$ = 0.056667 mol
Amount of electrons transferred = 0.056667 × 3 = 0.17 mol

Amount of nickel used = $\frac{5}{58.7}$ = 0.085179 mol

Using the oxidation half equation, $\frac{\text{amount of electrons transferred}}{\text{amount of nickel used}} = \frac{n}{1} = \frac{0.17}{0.085179}$
Hence, $n = 1.9958 \approx 2$
The final oxidation state of nickel is +2.

(c) Magnesium carbonate and nickel(II) hydroxide are sparingly soluble salts. Table 4.2 shows their K_{sp} values at 25 °C.

Table 4.2

salt	solubility product, K_{sp}
$MgCO_3$	6.82×10^{-6}
$Ni(OH)_2$	5.84×10^{-16}

(i) 1 dm³ saturated solutions of $MgCO_3$ and $Ni(OH)_2$ are evaporated to dryness. Using appropriate calculations, show that the saturated solution containing $MgCO_3$ will produce a larger mass of solid after being evaporated to dryness. [2]

M_r of $MgCO_3$ = 84.3, M_r of $Ni(OH)_2$ = 92.7

$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$
$K_{sp} = [Ni^{2+}][OH^-]^2$

$[Ni(OH)_2]$ present in saturated solution = $[Ni^{2+}]$ in saturated solution
$= \sqrt[3]{\frac{5.84\times10^{-16}}{4}}$
$= 5.26563 \times 10^{-6}$ mol dm^{-3}

Mass of $Ni(OH)_2$ present in saturated solution = $5.26563 \times 10^{-6} \times 1 \times 92.7$
$= 4.88 \times 10^{-4}$ g (to 3 s.f.)

$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$
$K_{sp} = [Mg^{2+}][CO_3^{2-}]$

$[MgCO_3]$ present in saturated solution = $[Mg^{2+}]$ in saturated solution
$= \sqrt{6.82 \times 10^{-6}}$
$= 0.0026115$ mol dm^{-3}
Mass of $MgCO_3$ present in saturated solution
$= 0.0026115 \times 1 \times 84.3$
$= 0.220$ g (to 3 s.f.) $> 4.88 \times 10^{-4}$ g (shown)

(ii) State and explain how the solubility of $Ni(OH)_2$ in water would compare with its solubility in solutions of higher pH. [1]

$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^{-}(aq)$ – (1)

A higher concentration of OH^{-} exists at higher pH. Due to the presence of the common ion, the position of equilibrium (1) shifts left to reduce the concentration of OH^{-}. Hence, the solubility of $Ni(OH)_2$ in solutions of higher pH would be lower than that in water.

(d) When heated to a sufficiently high temperature, nickel(II) carbonate decomposes to give nickel(II) oxide.

Using appropriate data from the *Data Booklet*, suggest with reasoning, how the decomposition temperature of nickel(II) carbonate will compare to that of barium carbonate. [3]

Cationic radius of Ni^{2+} = 0.069 nm
Cationic radius of Ba^{2+} = 0.135 nm

Since Ni^{2+} has a smaller cationic radius than Ba^{2+}, it has a higher charge density and polarising power. This means that it is able to polarise the electron cloud of the carbonate anion to a greater extent. The C-O bond in $NiCO_3$ is weakened to a greater extent and less energy is required to break this C-O bond. Hence, the thermal decomposition temperature of $NiCO_3$ is lower.

[Total: 20]

5 **(a)** The nickel−iron battery is a rechargeable battery which uses Fe(s) and NiO(OH)(s) as its electrodes, and aqueous potassium hydroxide as its electrolyte.

During a typical discharge, Fe forms $Fe(OH)_2$ while NiO(OH) forms solid $Ni(OH)_2$ respectively. The standard cell potential measured during this discharging process is +1.40 V.

(i) Define *standard cell potential*. [1]

The standard cell potential, $E^\ominus_{cell}$, is the maximum potential difference between two half−cells under standard conditions.

(ii) Write half–equations for the reactions taking place, in an alkaline medium, at the anode and cathode during the discharging process.
Include state symbols. [2]

Anode: $Fe(s) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) + 2e^-$
Cathode: $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$

(iii) Using the information from **(a)** and your answer in **(a)(ii)**, calculate $\Delta G^\ominus_{cell}$ and comment on its significance in the discharging process. [2]

$$\begin{aligned}\Delta G^\ominus_{cell} &= -nFE^\ominus_{cell}\\ &= -2(96500)(+1.40)\\ &= -270 \text{ kJ mol}^{-1}\end{aligned}$$

Since $\Delta G^\ominus_{cell} < 0$, the discharging process is spontaneous.

(iv) The standard electrode potential of the $Fe(OH)_2$/Fe half−cell is measured against a standard hydrogen electrode. A reading of −0.88 V is obtained from the voltmeter.

Calculate the standard electrode potential, $E^\ominus$, for the $NiO(OH)/Ni(OH)_2$ half−cell. [1]

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$
$\Rightarrow +1.40 = E^\ominus_{cathode} - (-0.88)$
$\therefore E^\ominus_{cathode} = +0.52$ V

(v) State and explain the effect on the electrode potential, E, for the $NiO(OH)/Ni(OH)_2$ half−cell when a higher concentration of aqueous potassium hydroxide is used as the electrolyte. [1]

$NiO(OH)(s) + H_2O(l) + e^- \rightleftharpoons Ni(OH)_2(s) + OH^-(aq)$

When $[OH^-]$ increases, by Le Chatelier's Principle, the position of equilibrium shifts to the left to decrease $[OH^-]$, causing $E_{NiO(OH)/Ni(OH)2}$ to be less positive.

(vi) The electrolyte, KOH, is known to slowly degrade over the years and must be replaced to ensure the functionality of the rechargeable battery.

Explain, with the aid of equation(s), how the electrolyte can be degraded with the absorption of atmospheric carbon dioxide gas. [2]

$CO_2 + H_2O \rightarrow H_2CO_3$
$H_2CO_3 + 2KOH \rightarrow K_2CO_3 + 2H_2O$

OR
$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$
$CO_2 + KOH \rightarrow KHCO_3$

When dissolved in water, the carbon dioxide is converted to carbonic acid (H_2CO_3). This carbonic acid neutralises KOH in an acid−base reaction to form potassium carbonate and water.

(b) **(i)** Describe and explain the trend in atomic radius of transition elements. [2]

Atomic radius is relatively invariant across transition elements. Electrons are added to inner/penultimate 3d orbitals. Increase in shielding effect from 3d electrons almost cancels out increase in nuclear charge across transition elements. Effective nuclear charge experienced by valence electrons remains relatively invariant.

(ii) Nickel and iron are both transition elements.

With reference to your answer in **(b)(i)**, suggest why nickel and iron are suitable to be mixed as an alloy. [1]

The similar atomic radii of nickel and iron make it possible for nickel and iron atoms to replace one another in the same solid structure.

(c) Nickel can also be used as a catalyst to convert alkenes into alkanes.

State the type of reaction in this conversion. [1]

Reduction

(d) An especially valuable organoboron intermediate can be prepared by the addition of a dialkylborane, R_2BH, to a carbon−carbon double bond in an alkene. An example of the reaction involving propene is shown in Fig. 5.1.

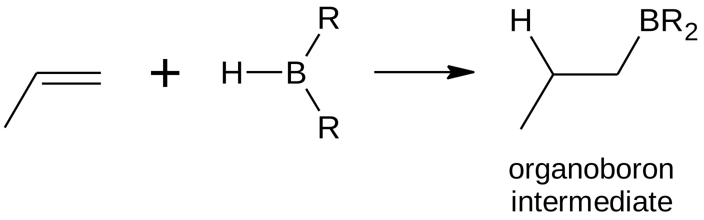


Fig. 5.1

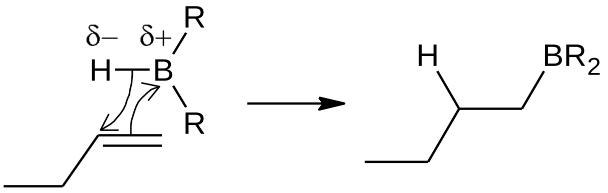
(i) Suggest a reason why the boron is added to the less substituted carbon atom of the C=C bond in Fig. 5.1. [1]

The boron atom is added to the less substituted carbon atom to minimise steric hindrance / because the approach to the more substituted carbon atom is sterically hindered.

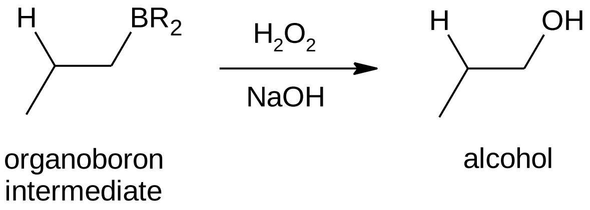
The formation of the organoboron intermediate in Fig. 5.1 occurs via a one-step mechanism. The electron deficient boron and partial negative hydrogen are both **simultaneously** added to the same side of a carbon−carbon double bond. The bond pair of electrons between B and H is used to form the new C−H bond.

(ii) Propose a mechanism for the reaction between but-1-ene and dialkylborane, R_2BH.

Show all relevant dipoles, curly arrows and structure of the organoboron intermediate. [2]



(iii) The organoboron intermediate shown in Fig. 5.1 can be further converted into an alcohol.



With reference to the information in **(d)** and Fig. 5.2, suggest a structure of compound **Z**.

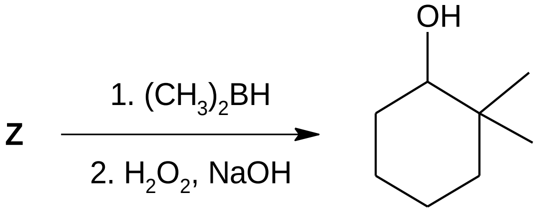
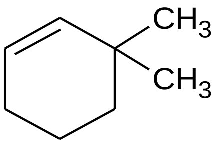


Fig. 5.2

[1]



(e) Propene also undergoes electrophilic addition with hydrogen halides in the form of HCl, HBr and HI.

The hydrogen halides behave differently when heated as shown by the observations given in Table 5.1.

Table 5.1

hydrogen halide	observations
HCl	No visible change even with strong heating
HBr	Strong heating produces brown vapour
HI	Heating produces violet vapour

Explain fully the observations in Table 5.1. [3]

Down the group, H–X bond energy decreases. Covalent bond strength also decreases. Hence, thermal stability decreases.

HCl is most stable and does not decompose on strong heating. HBr is more stable than HI and thus require stronger heating for decomposition.

HBr decomposes to form $Br_2(g)$, the brown vapour, while HI decomposes to form $I_2(g)$, the violet vapour.

[Total: 20]