



DUNMAN HIGH SCHOOL

Preliminary Examination

Year 6

H2 CHEMISTRY

Paper 3 Free Response Questions

9729/03

25 September 2025

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.

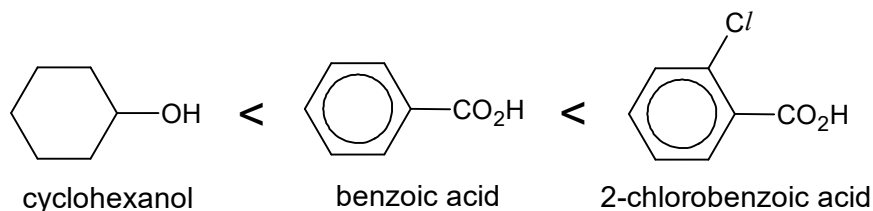
For Examiner's Use	
Section A	
1	20
2	20
3	20
Section B	
4 / 5	20
Total	80

This document consists of **22** printed pages.

Section A

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

- 1 (a) The order of increasing Brønsted-Lowry acidity of cyclohexanol, benzoic acid and 2-chlorobenzoic acid is shown. Explain this order.



[3]

Cyclohexanol is the least acidic because its conjugate base, is destabilised by the electron-donating effect of the cyclohexyl/alkyl group,



which intensifies the negative charge on the oxygen in the conjugate base.

Both 2-chlorobenzoic acid and benzoic acid are more acidic than cyclohexanol because their conjugate bases are resonance-stabilised by the delocalisation of negative charge over two highly electronegative oxygen atoms.

In 2-chlorobenzoic acid, presence of electron withdrawing *Cl* atom helps to disperse the negative charge, making its conjugate base (2-chlorobenzoate ion) more stable than benzoate.

Hence, 2-chlorobenzoic dissociates to the largest extent and cyclohexanol to the least extent.

- (b) BF_3 acts as a Lewis acid in its reaction with dimethylether, CH_3OCH_3 , to form product **P**.

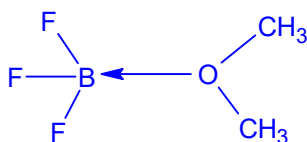
- (i) Describe how BF_3 acts as a Lewis acid in this reaction.

[1]

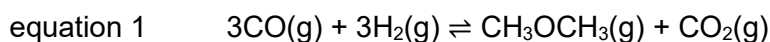
The electron deficient B atom in BF_3 accepts the (lone) electron pair from O in CH_3OCH_3 .

- (ii) Draw a structure for **P** to show the bonding present.

[1]



- (c) Dimethylether, CH_3OCH_3 , can be formed from the reaction between carbon monoxide, CO , and hydrogen, H_2 , as shown by equation 1.



A mixture of CO and H_2 was introduced into a 10 m^3 sealed vessel at 500 K . The initial total pressure was 40 atm .

After dynamic equilibrium was established at 500 K, the total pressure in the vessel decreased to 28 atm.

- (i) Write an expression for the equilibrium constant, K_p , for this reaction, and state its units. [1]

$$K_p = \frac{P_{\text{CH}_3\text{OCH}_3} P_{\text{CO}_2}}{(P_{\text{CO}})^3 (P_{\text{H}_2})^3} \quad \text{units: atm}^{-4} \text{ OR Pa}^{-4}$$

- (ii) *Use of the Data Booklet is relevant to this question.*

The amount of CH_3OCH_3 at equilibrium was found to be 732 mol. Show that the equilibrium partial pressure of CH_3OCH_3 in the sealed vessel is 3 atm. [1]

$$pV = nRT$$

$$p = nRT/V$$

$$\text{partial pressure of CH}_3\text{OCH}_3 \text{ at equilibrium} = \frac{732 \times 8.31 \times 500}{10} = 304146 \text{ Pa}$$

$$= \frac{304146}{101325} = 3.0017 \text{ atm}$$

$$= 3 \text{ atm (shown)}$$

OR

$$n = pV/RT$$

$$\text{total moles of gases at equilibrium} = \frac{28 \times 101325 \times 10}{8.31 \times 500} = 6828.2 \text{ mol}$$

$$\text{partial pressure of CH}_3\text{OCH}_3 \text{ at equilibrium} = \frac{732}{6828.2} \times 28 = 3.0017 \text{ atm}$$

$$= 3 \text{ atm (shown)}$$

- (iii) At equilibrium, it was found that 60% of the CO had been converted to the products. Calculate the equilibrium partial pressures of CO and H_2 in atm. Hence, determine the value of K_p for the reaction. [3]

Let the initial partial pressure of CO be x.

	3CO(g)	$+ 3\text{H}_2\text{(g)}$	\rightleftharpoons	$\text{CH}_3\text{OCH}_3\text{(g)}$	$\text{CO}_2\text{(g)}$
initial / atm	x	$40 - x$		0	0
change / atm	$-0.6x$	$-0.6x$		+3	+3
equilibrium/ atm	$0.4x$	$40 - 1.6x$		3	3



$$\text{Change in partial pressure of CO} = (3)(3) = 9 \text{ atm}$$

$$\therefore 0.6x = 9 \text{ atm}$$

$$x = 15 \text{ atm}$$

$$\text{Equilibrium partial pressure of CO} = 0.4x$$

$$= 0.4(15)$$

$$= 6.0 \text{ atm}$$

OR

$$(0.4x) + (40 - 1.6x) + 3 + 3 = 28$$

$$x = 15 \text{ atm}$$

$$\text{Equilibrium partial pressure of H}_2 = 28 - 6 - 3 - 3$$

$$= 16.0 \text{ atm}$$

$$K_p = \frac{P_{\text{CH}_3\text{OCH}_3} P_{\text{CO}_2}}{(P_{\text{CO}})^3 (P_{\text{H}_2})^3}$$

$$= \frac{(3)(3)}{(6)^3 (16)^3}$$

$$= 1.02 \times 10^{-5} \text{ atm}^{-4}$$

- (iv) The volume of the vessel is reduced from 10 m³ to 5 m³ and the system is allowed to reach equilibrium.

Explain the effect this will have on the partial pressures of the individual gases and the composition of the reaction mixture.

[2]

A reduction in volume causes partial pressures of all gas components at equilibrium to double, position of equilibrium shifts to the right, favouring the side with fewer moles of gaseous particles, to reduce the pressure. At new equilibrium, the mixture contains more moles of products, CH₃OCH₃ and CO₂ and less moles of the reactants, CO and H₂ than that before the reduction in volume.

- (d) NH₃ is commonly used as a nucleophile in organic chemistry. In some instances, it adds to the C=C bond as shown in Fig. 1.1.

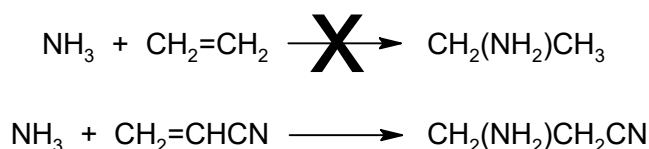


Fig. 1.1

- (i) Suggest reasons to explain Fig. 1.1.

Use concepts of electronegativity and electronic effects in your answer.

[2]

Ethene is non-polar.

There are no electron deficient sites in ethene to attract the NH₃ nucleophile
OR NH₃ is a nucleophile and is repelled by the electron-rich C=C bond in ethene.

Due to presence of electronegative N / electron-withdrawing -CN group, electron density is withdrawn away from the C=C bond. This causes the carbon of the terminal alkene to be electron deficient, hence susceptible to nucleophilic attack by NH₃.

Ammonia or primary amines react with aldehydes and ketones to produce imines as shown in Fig. 1.2.

The reaction is carried out at carefully controlled pH of between 4 and 5. In Fig. 1.2, R_1 , R_2 and R_3 represent alkyl groups or hydrogen atoms.

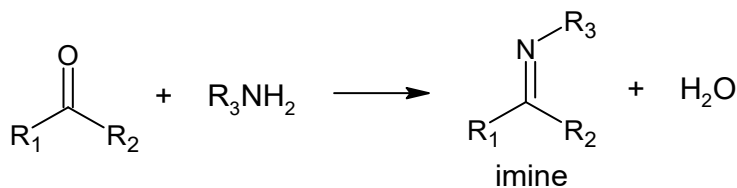
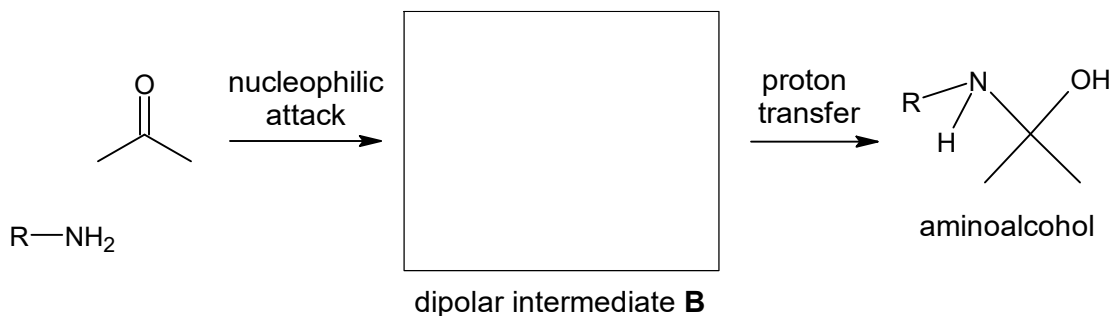


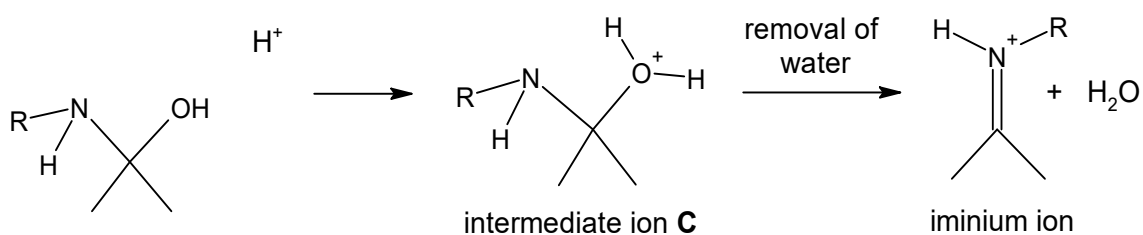
Fig. 1.2

The mechanism for the formation of an imine between a primary amine and propanone is shown in Fig. 1.3.

Stage 1: Formation of aminoalcohol



Stage 2: Formation of iminium ion intermediate



Stage 3: Formation of imine via deprotonation

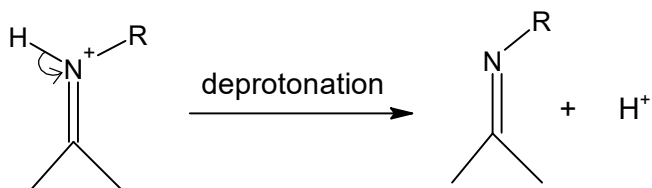
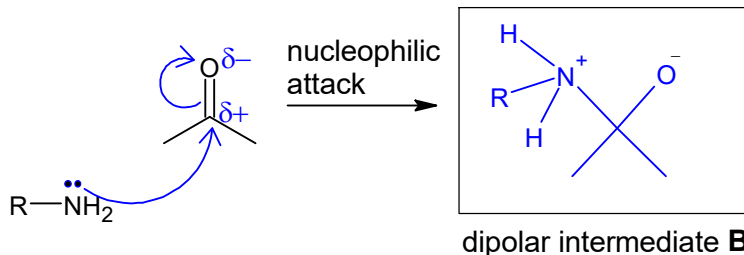


Fig. 1.3

(ii) Complete the mechanism for the formation of **B** in Fig. 1.3 by

- adding curly arrows, a lone pair and a dipole to show how the nucleophilic attack occurs between the primary amine and propanone.
- drawing the structure of the dipolar intermediate **B** in the box provided.

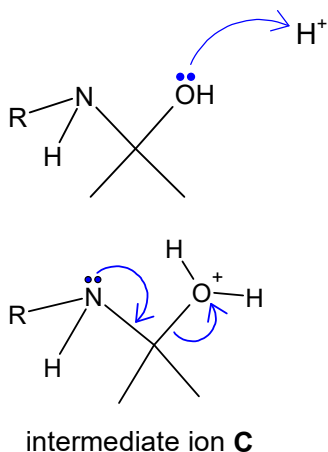
[2]



(iii) Complete the mechanism for stage 2 in Fig. 1.3 by

- adding a curly arrow and a lone pair to show protonation of the aminoalcohol.
- adding a lone pair and curly arrows on intermediate ion **C** to show how the iminium ion is formed.

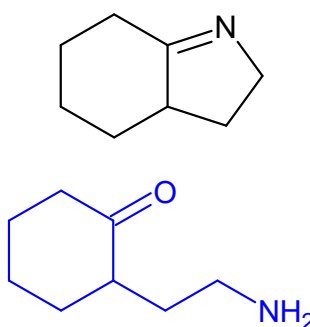
[2]



(iv) By considering stage 1, suggest why the reaction is slower at pH lower than 4. [1]

At pH < 4, the primary amine is protonated and does not have a lone pair of electrons available for nucleophilic addition. This leads to a slower rate of reaction as there is lower concentration of amine available.

(v) Suggest the reactant used to form the following product by a similar reaction to that shown in Fig. 1.2.



[1]

[Total: 20]

- 2 (a) Phenylamine can be made in the laboratory using the method given below.

Nitrobenzene is heated under reflux with a mixture of tin and concentrated hydrochloric acid.

Once the reaction mixture has cooled, concentrated sodium hydroxide solution is added until the mixture is alkaline. Pure phenylamine can be obtained from this mixture.

The reaction between tin and concentrated hydrochloric acid produces SnCl_2 and H_2 gas. Nitrobenzene then reacts with SnCl_2 , in the presence of concentrated hydrochloric, to form $\text{C}_6\text{H}_5\text{NH}_3^+$ and $[\text{SnCl}_6]^{2-}$ ions.

- (i) Describe the roles of tin and concentrated hydrochloric acid when they are added together to form SnCl_2 and H_2 gas. Explain your answer in terms of electron transfer.

[2]

Tin acts as a reducing agent while concentrated hydrochloric acid as an oxidising agent in the reaction.

Electrons are lost from tin and gained by concentrated hydrochloric acid.

- (ii) Construct a half-equation for the formation of $\text{C}_6\text{H}_5\text{NH}_3^+$ from nitrobenzene. State symbols are **not** required.

[1]



- (iii) Using the relevant theory of acids and bases, explain how the phenylamine can be recovered from the mixture by adding concentrated sodium hydroxide solution.

[1]

$\text{C}_6\text{H}_5\text{NH}_3^+$ loses a proton to OH^- to obtain $\text{C}_6\text{H}_5\text{NH}_2$ via a Brønsted-Lowry acid-base reaction.

OR

OH^- gains a proton from $\text{C}_6\text{H}_5\text{NH}_3^+$ to obtain $\text{C}_6\text{H}_5\text{NH}_2$ via a Brønsted-Lowry acid-base reaction.

- (iv) Describe a simple chemical test you could carry out to confirm the presence of phenylamine in the product. State what you would observe.

[2]

Add $\text{Br}_2(\text{aq})$ to the mixture.

The presence of phenylamine will result in the decolourisation of orange $\text{Br}_2(\text{aq})$ and the formation of a white precipitate.

- (b) (i) Table 2.1 gives the $\text{p}K_{\text{b}}$ values of some nitrogen-containing compounds at 25 °C.

Table 2.1

name	structure	$\text{p}K_{\text{b}}$
phenylamine	$\text{C}_6\text{H}_5\text{NH}_2$	9.40

phenylalanine	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$	4.87 (α -amino group)
propylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	3.46

Explain the relative basicities of the compounds in Table 2.1 in terms of their structures.

[3]

$\text{C}_6\text{H}_5\text{NH}_2$ is the least basic as the lone pair of electrons on N delocalises into the benzene ring and is the least available for donation / dative bonding with a proton.

The α -amino group in phenylalanine is less basic than propylamine as the electron-withdrawing $-\text{CO}_2\text{H}$ group / electron-withdrawing oxygen atoms decreases the electron density on the N atom, making the lone pair of electrons on N less available for donation / dative bonding with a proton.

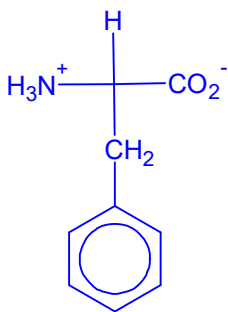
Propylamine is more basic than the α -amino group in phenylalanine as the electron-donating alkyl / propyl group increases the electron density on the N atom, making the lone pair of electrons on N more available for donation / dative bonding with a proton.

- (ii) Use Table 2.2 to draw the predominant species of phenylalanine at pH 8.

Table 2.2

name	structure	$\text{p}K_{\text{a}}$ at 25 °C	
		α -carboxyl group	α -amino group
phenylalanine	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$	1.83	9.13

[1]



- (c) Arecoline, $\text{C}_8\text{H}_{13}\text{NO}_2$, is a compound found in the Taiwanese betel nut.

Arecoline has three different functional groups, does not display cis-trans isomerism and does not contain a chiral centre. It contains a six-membered ring comprising one nitrogen and five carbon atoms.

Table 2.3 shows the organic products formed, and other information, when arecoline and compound **F**, $\text{C}_8\text{H}_{15}\text{NO}_2$, are added to different reagents under specific conditions.

Table 2.3

test	reactant	reagents and conditions	organic products formed	other information
1	arecoline	excess H_2 / Ni	F , $\text{C}_8\text{H}_{15}\text{NO}_2$	F contains one chiral centre.
2	arecoline	2,4-DNPH	no reaction	
3	arecoline	$\text{Na}_2\text{CO}_3(\text{aq})$	no reaction	
4	arecoline	ethanoyl chloride	no reaction	
5	arecoline	excess CH_3Cl in ethanol, heat	G , $\text{C}_9\text{H}_{16}\text{NO}_2\text{Cl}$	G is an ionic compound.
6	F	excess $\text{HCl}(\text{aq})$, heat	H , $\text{C}_7\text{H}_{14}\text{NO}_2^+$, and J	
7	F	excess acidified KMnO_4 , heat	H only	effervescence observed.

For each of the seven tests, state the type of reaction occurring, if any. For each compound, state what the information in Table 2.3 tells you about the functional groups it contains. Include your reasoning.

Suggest possible structures for **F**, **G**, **H** and **J**. Hence deduce a possible structure for arecoline.

[10]

test	type of reaction	functional group
1	reduction	arecoline contains alkene / $\text{C}=\text{C}$ bond or ketone or aldehyde
2	no reaction	ketone and aldehyde are absent
3	no reaction	carboxylic acid is absent
4	no reaction	alcohol, primary and secondary amine are absent
5	nucleophilic substitution	G , $\text{C}_9\text{H}_{16}\text{NO}_2\text{Cl}$, is a quaternary ammonium salt while arecoline contains a tertiary amine

6	acid hydrolysis	<p>F, $C_8H_{15}NO_2$, contains an ester</p> <p>H, $C_7H_{14}NO_2^+$, contains the carboxylic acid and protonated amine / quaternary ammonium group</p> <p>J contains an alcohol group</p>
7	acid hydrolysis and oxidation	J contains a primary alcohol group

J = CH_3OH / methanol

arecoline	F , $C_8H_{15}NO_2$	G , $C_9H_{16}NO_2Cl$	H , $C_7H_{14}NO_2^+$
 OR 			

[Total: 20]

- 3 (a)** Aqua regia (a mixture of 25% nitric acid and 75% hydrochloric acid by volume) is highly corrosive. Only noble metals like iridium are inert to this solution. A 5 g sample of platinum–iridium alloy required 24.6 cm^3 of aqua regia for complete reaction. Platinum was completely oxidised to platinum(IV) ions by nitric acid and 0.5 g of the remaining metal was recovered.

- (i) Find the percentage of each metal in the alloy.

[1]

Only Pt was oxidised during the reaction, Ir remains inert.

\therefore 0.5 g of metal was recovered, the metal was Ir
percentage by mass of Ir in sample

$$\frac{0.5}{5} \times 100$$

$$= 10\%$$

Percentage by mass of Pt in sample

$$= (100 - 10)\%$$

$$= 90\%$$

- (ii) Aqua regia was prepared using 5.0 mol dm^{-3} nitric acid. Assuming that the reaction between the sample and aqua regia is complete, calculate the number of moles of nitric acid reacted per mole of platinum.

[2]

volume of HNO_3 used

$$= 0.25 \times 24.6$$

$$= 6.15 \text{ cm}^3$$

amount of HNO_3 reacted

$$= 0.00615 \times 5$$

$$= 0.03075 \text{ mol}$$

amount of Pt reacted

$$= \frac{4.5}{195.1}$$

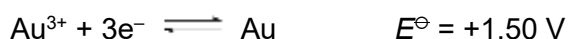
$$= 0.02306 \text{ mol}$$

$$\therefore \text{mole ratio of } \text{HNO}_3 : \text{Pt} = 1.33 : 1$$

- (b) Gold is typically an inert metal and it does not dissolve in either hydrochloric acid or nitric acid alone. It will dissolve in aqua regia because of the unique combined action of the two acids.

In aqua regia, nitric acid converts gold to its ionic form, Au^{3+} , and hydrochloric acid provides a source of chloride which reacts with the gold cations to form stable tetrachloroaurate(III) complex, AuCl_4^- .

The standard reduction potential of Au^{3+} to Au is given below.



- (i) With the use of relevant data from the *Data Booklet*, explain why hydrochloric acid alone cannot dissolve gold.

[1]



$$E_{\text{cell}}^\ominus = 0.00 - (+1.50)$$

$$= -1.50 \text{ V} < 0, \text{ hence reaction is not spontaneous.}$$

- (ii) Gold has the chemical properties of a typical transition element.
Explain why gold can be considered a transition element.

[1]

Gold is a d-block element that forms one or more stable ions with a partially filled d subshell.

- (iii) Another method of extracting gold from low-grade ore involves converting the gold to a water-soluble dicyanoaurate(I) anionic complex, $[\text{Au}(\text{CN})_2]^-$.

Explain why the gold complex ion, AuCl_4^- in (b), is coloured while the dicyanoaurate(I) complex ion, $[\text{Au}(\text{CN})_2]^-$, is colourless.

[4]

AuCl_4^- : d^8 configuration for Au^{3+}

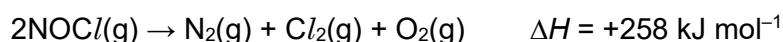
In the presence of Cl^- ligands, the d orbitals of Au^{3+} are split into two groups of different energy levels.

When white light shines on the complex, a d electron from lower energy level undergoes d–d electronic transition and is promoted to a higher energy vacant or partially filled d orbital. The colour of the solution is the complementary colour of the light absorbed.

$\text{Au}(\text{CN})_2^-$: d^{10} configuration for Au^+ / fully filled d subshell and hence no d–d electronic transition is possible.

- (c) Freshly prepared aqua regia decomposes quickly and one of the decomposition products, nitrosyl chloride, NOCl , is a yellow gas.

Nitrosyl chloride can further decompose into nitrogen, chlorine and oxygen, as shown in the equation below.



- (i) Define the term *bond energy of N=O bond*.

[1]

Energy required to break 1 mol of gaseous N=O bond to form its gaseous N and O atoms.

- (ii) Using data from the *Data Booklet*, calculate the bond energy of N=O bond in NOCl .

[2]

$$\begin{aligned} \text{Enthalpy change of decomposition} &= \sum \text{BE}_{\text{rxt}} - \sum \text{BE}_{\text{pdt}} \\ +258 &= [2\text{BE}(\text{N}=\text{O}) + 2\text{BE}(\text{N}-\text{Cl})] - [\text{BE}(\text{N}\equiv\text{N}) + \text{BE}(\text{Cl}-\text{Cl}) + \text{BE}(\text{O}=\text{O})] \\ +258 &= [2\text{BE}(\text{N}=\text{O}) + 2(+310)] - [(+944) + (+244) + (+496)] \\ \text{BE}(\text{N}=\text{O}) &= +661 \text{ kJ mol}^{-1} \end{aligned}$$

- (iii) The boiling points of NOCl and NOF are -5.6°C and -72.4°C respectively. Suggest a reason for the difference in their boiling points.

[2]

Both NOCl and NOF have simple molecular structure with permanent dipole–permanent dipole interactions between molecules. NOCl has a larger and hence more polarisable electron cloud than NOF . Hence more energy is required to overcome the stronger instantaneous dipole–induced dipole interaction between NOCl molecules.

- (iv) Copper(II) oxide, CuO , is a common catalyst used for the decomposition of NOCl . Suggest the type of catalyst CuO acts as and describe its mode of action.

[3]

Heterogeneous catalyst. Reactant molecules diffuse towards the catalyst surface and are adsorbed onto the active sites at the surface. Intramolecular bonds within the reactant molecules are weakened, thus lowering the activation energy. The adsorption process increases the concentration of the reactant molecules on the catalyst surface. Product molecule desorbs and diffuses away from the catalyst surface.

(d) Use of the Data Booklet is relevant to this question.

A student wanted to study the following reaction.



He first sets up an electrochemical cell which comprises of Au^{3+}/Au and Ni^{2+}/Ni half-cells prepared under standard conditions.

When the reaction begins, $[\text{Au}^{3+}]$ starts to decrease while $[\text{Ni}^{2+}]$ increases. In the study of electrochemical cells, the *Nernst equation*, given below, can be applied to determine the cell potential under non-standard conditions.

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0592}{n} \log_{10} Q$$

where n is the number of moles of electrons transferred, Q is the reaction quotient

given by $\frac{[\text{Ni}^{2+}]^3}{[\text{Au}^{3+}]^2}$ and $E^{\ominus}_{\text{cell}}$ is the standard cell potential.

- (i) Using the $E^{\ominus}(\text{Au}^{3+}/\text{Au})$ given in (b), calculate the new E_{cell} using the Nernst equation, when $[\text{Au}^{3+}]$ and $[\text{Ni}^{2+}]$ are 0.02 mol dm^{-3} and 2.47 mol dm^{-3} respectively.

[2]

$$E^{\ominus}_{\text{cell}} = +1.50 - (-0.25) = +1.75 \text{ V}$$

$$E_{\text{cell}} = +1.75 - \frac{0.0592}{6} \log_{10} \frac{(2.47)^3}{(0.02)^2} = +1.70 \text{ V}$$

- (ii) Suggest and explain what happens to E_{cell} value of the electrochemical cell when the mass of nickel electrode is increased.

[1]

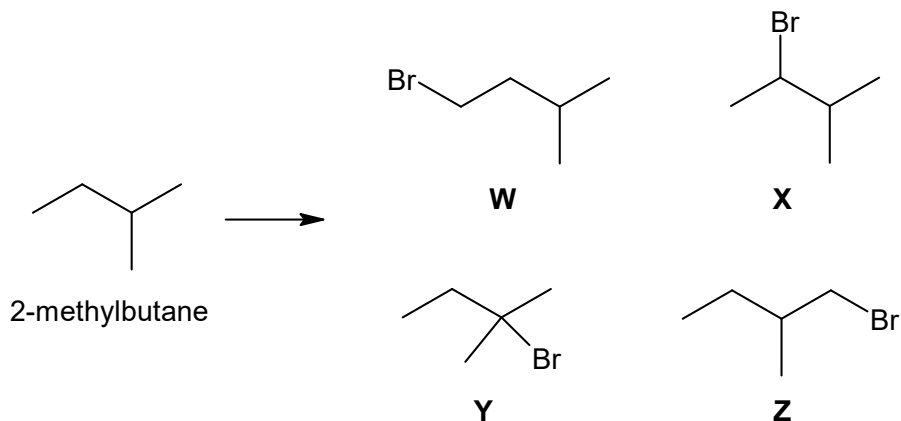
There is no change to the E_{cell} value as the increase in mass of Ni electrode will not affect the equilibrium position of $\text{Ni}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Ni}$

[Total: 20]

Section B

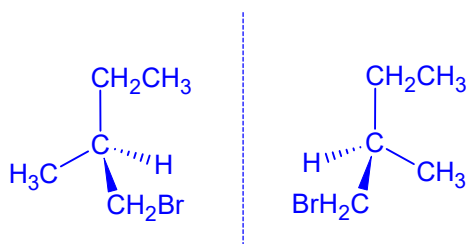
Answer **one** question from this section.

- 4 2-methylbutane reacts with bromine in the presence of UV light to give a mixture of products. There are four possible monobromoalkanes, **W** to **Z**, that can be formed.



- (a) (i) Draw both stereoisomers of **Z**.

[1]



- (ii) Name and draw the mechanism for the formation of **W** from 2-methylbutane using curly arrows.

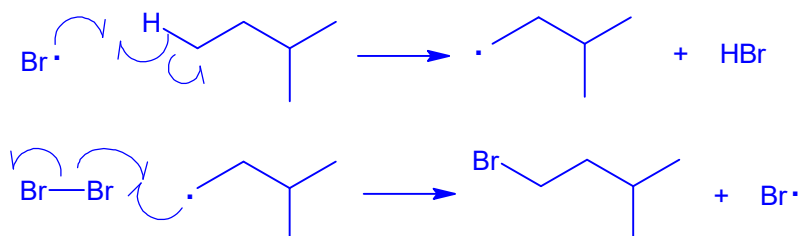
[3]

Name of mechanism: Free radical substitution

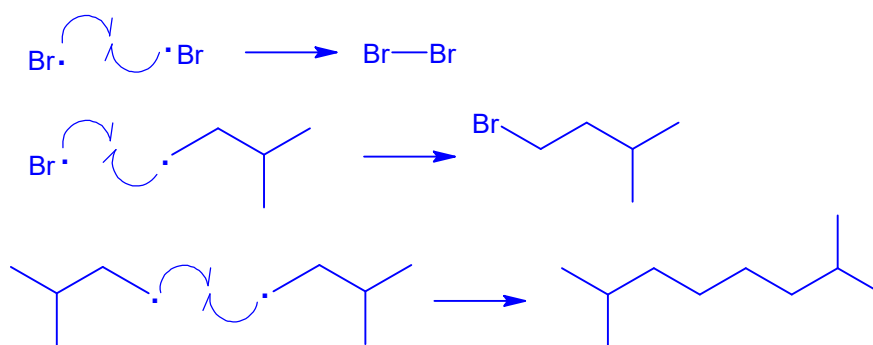
Initiation



Propagation



Termination



Empirical evidence has shown that different types of carbons have a different relative probability of being substituted by bromine. These probabilities can be found in Table 4.1.

Table 4.1

type of carbon	relative probability of substitution
primary	1
secondary	62
tertiary	1640

- (iii) By considering the number of H atoms on each carbon, and information in Table 4.1, predict the relative proportions of **W**, **X**, **Y** and **Z** in the product mixture.

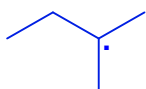
[1]

$$\text{W:X:Y:Z} = 3 : (2 \times 62) : 1640 : 6 = 3 : 124 : 1640 : 6$$

The reaction of 2-methylbutane and bromine gas also forms a mixture of side-products with a molecular formula of $\text{C}_{10}\text{H}_{22}$.

- (iv) Use Table 4.1 to deduce the identity of the most stable alkyl radical present in the reaction mixture. Draw its structure using skeletal formula.

[1]



- (v) Hence name the $\text{C}_{10}\text{H}_{22}$ product that is formed in the highest proportion.

[1]

3,3,4,4-tetramethylhexane

- (b) Fig. 4.1 shows a 2-step synthesis to obtain 2-methylbutan-2-ol from **X**.

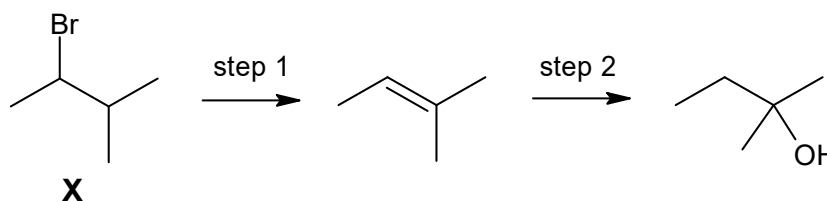


Fig. 4.1

- (i) State the reagents and conditions required for each step.

[2]

step 1: alcoholic NaOH, heat

step 2: cold, concentrated H₂SO₄, followed by H₂O and heat

OR

H₂O(g), heat in presence of concentrated H₃PO₄ catalyst at high temperature and pressure

Each step in the synthesis forms a mixture of products as there is more than one possible region for each reaction to occur. The term *regioselectivity* refers to the preference for a chemical reaction to occur at a specific region of a molecule to give the major product.

- (ii) Explain if each step in Fig. 4.1 is regioselective for the intended product. Your answer should refer to the relative stability of relevant products or intermediates.

Hence conclude if the synthesis will give a good yield of 2-methylbutan-2-ol.

[2]

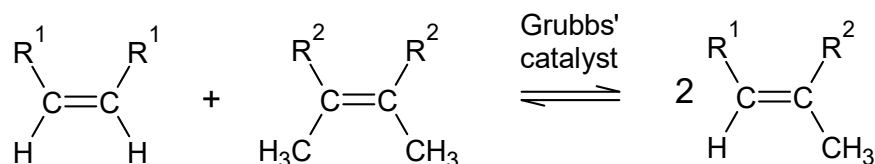
For step 1, the tri-substituted alkene is the major product as it is lower in energy / more stable than the di-substituted alkene.

OR the more substituted alkene is more stable and hence it is the major product of step 1.

For step 2, the tertiary carbocation leading to 2-methylbutan-2-ol is more stable than the secondary carbocation leading to 3-methylbutan-2-ol as the positive charge is dispersed to a greater extent by more electron-donating alkyl groups. Hence 2-methylbutan-2-ol is the major product.

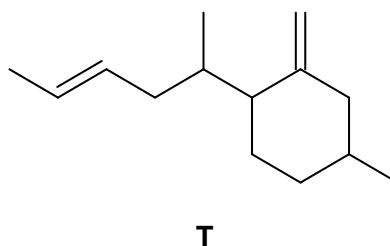
The two-step synthesis is likely to give a good yield of 2-methylbutan-2-ol as each step is regioselective for the intended product.

- (c) Alkene metathesis allows the redistribution of alkene fragments.



The reaction only involves the breaking and forming of C=C bonds.

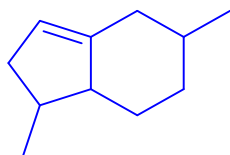
Compound **T** is shown. When compound **T** undergoes alkene metathesis, an intramolecular reaction occurs to form a small hydrocarbon and a product containing two rings.



Predict the small hydrocarbon and the product formed in this reaction.

[2]

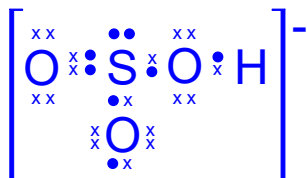
Propene, CH₃CH=CH₂



(d) Sodium bisulfite, NaHSO_3 , is commonly used as a food preservative.

- (i) Given that the bisulfite ion contains a O–H covalent bond, draw a dot-and-cross diagram to show the bonding in a bisulfite ion, HSO_3^- .

[1]

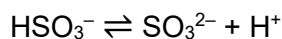


- (ii) Hence state the shape and bond angle around the sulfur atom within the bisulfite ion. Explain your answer using the Valence Shell Electron Pair Repulsion Theory.

[2]

There are 3 bond pairs and 1 lone pair around the central S atom. According to VSEPR theory, the 4 electron pairs are arranged as far apart as possible around the central S atom to minimise repulsion. Since bond pair-bond pair repulsion is weaker than bond pair-lone pair repulsion, the ion has a trigonal pyramidal shape around the central S atom and a bond angle of 107° .

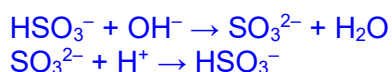
The bisulfite ion is a weak acid with a $\text{p}K_a$ value of 6.97.



An aqueous mixture containing bisulfite ions, $\text{HSO}_3^-(\text{aq})$, and sulfite ions, $\text{SO}_3^{2-}(\text{aq})$, can act as a buffer.

- (iii) Write two equations to describe how a $\text{HSO}_3^-/\text{SO}_3^{2-}$ mixture resists pH change when a small amount of acid or base is added.

[1]



A buffer with pH 7.5 was prepared by mixing 30.0 cm^3 of $0.500 \text{ mol dm}^{-3}$ sodium bisulfite with 20.0 cm^3 of aqueous sodium hydroxide.

- (iv) Calculate the $[\text{SO}_3^{2-}]:[\text{HSO}_3^-]$ ratio of the buffer.

[1]

$$\begin{aligned}\text{pH} &= \text{p}K_a + \lg \frac{[\text{A}^-]}{[\text{HA}]}\end{aligned}$$

$$7.5 = 6.97 + \lg \frac{[\text{SO}_3^{2-}]}{[\text{HSO}_3^-]}$$

$$\frac{[\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = 10^{0.53}$$

$$= 3.39$$

- (v) Hence calculate the concentration of sodium hydroxide used in the preparation of the buffer.

Let the concentration of the sodium hydroxide be $x \text{ mol dm}^{-3}$.

	HSO_3^-	+	OH^-	\rightarrow	SO_3^{2-}	+	$\text{H}_2\text{O(l)}$
Initial / mol	0.015		$0.02x$		0		
Change / mol	$-0.02x$		$-0.02x$		$+0.02x$		
End / mol	$0.015 - 0.02x$		0		$0.02x$		

$$\frac{0.02x}{0.015 - 0.02x} = 3.388$$

$$3.388(0.015 - 0.02x) = 0.02x$$

$$3.388 \times 0.015 = (0.02x)(1 + 3.388)$$

$$0.08776x = 0.05082$$

$$[\text{OH}^-] = 0.579 \text{ mol dm}^{-3}$$

[Total: 20]

- 5 (a) (i) Explain the difference in pH in Table 5.1.

Table 5.1

compound	pH of a 1.0 mol dm ⁻³ solution in water
NaCl	7.0
AlCl ₃	3.0

[2]

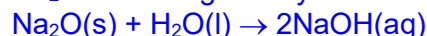
Al³⁺ has a high charge density and polarises (or weakens the O—H bonds in) the surrounding water molecules to a large extent. Hence appreciable hydrolysis occurs to release H⁺ ions and pH is 3.0.

Na⁺ has a relatively low charge density and does not hydrolyse in water. Hence, no H⁺ ions are released and pH is 7.0.

- (ii) With the aid of relevant equation(s), describe what happens when Na₂O, SiO₂ and P₄O₁₀ are separately added to water.

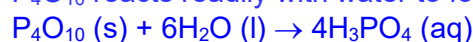
[3]

Na₂O reacts vigorously with water to form a basic solution.



SiO₂ does not dissolve in water due to the strong and extensive covalent bonds between Si and O atoms.

P₄O₁₀ reacts readily with water to form an acidic solution.



- (b) Strontium metal can be obtained by the electrolysis of molten strontium chloride, SrCl₂, using the apparatus shown in Fig. 5.1.

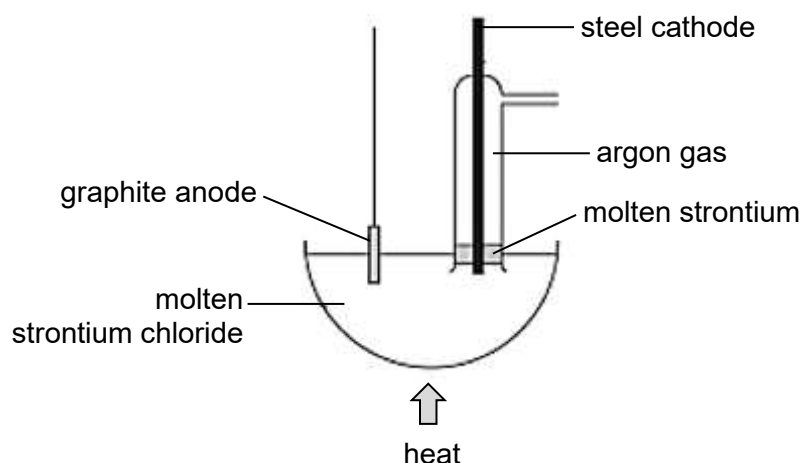
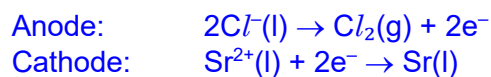


Fig. 5.1

Strontium ions are reduced at the cathode to form molten strontium metal, which is then removed from the set up.

- (i) Write the half-equations, including state symbols, for the reactions at the anode and cathode.

[2]



- (ii) A current of 5.0 A was passed through molten strontium chloride for 45 min.

Calculate the mass of strontium metal formed at the cathode.

[2]

$$\text{quantity of charge passed} = 5.0 \times 45 \times 60 \\ = 13500 \text{ C}$$

$$\text{amount of electrons} = \frac{13500}{96500} = 0.13990 \text{ mol}$$

$$\text{amount of Sr formed} = 0.13990 \div 2 = 0.06995 \text{ mol}$$

$$\text{mass of Sr formed} = 0.06995 \times 87.6 \\ = 6.13 \text{ g}$$

- (c) Cyclohexylamine can be produced from benzene in a three-step synthesis as shown in Fig. 5.2.

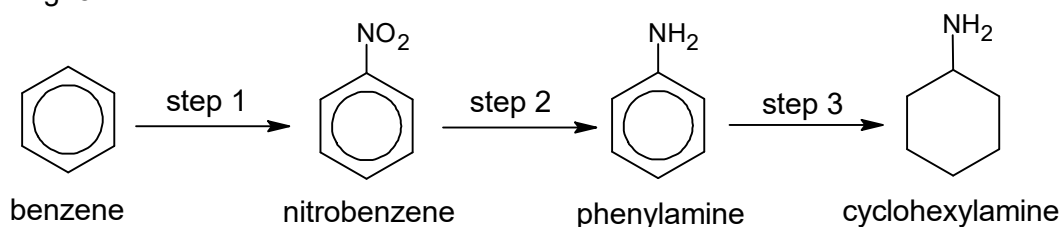


Fig. 5.2

- (i) Name and draw the mechanism for step 1. Include all relevant lone pairs, curly arrows and charges. Include the structure of the organic intermediate.

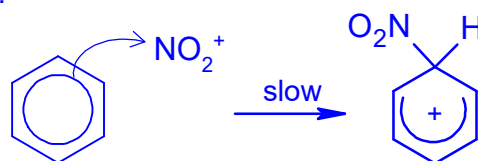
[3]

Electrophilic substitution

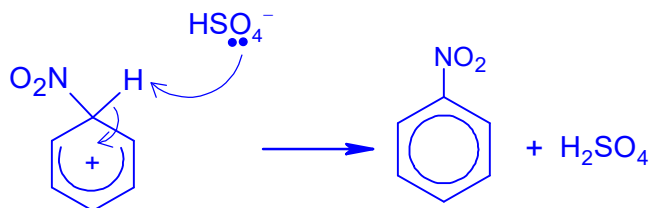
Generation of the electrophile, NO_2^+ :



Step 1:



Step 2:



In step 3, phenylamine is converted to cyclohexylamine using hydrogen gas dissolved in supercritical carbon dioxide in the presence of rhodium catalyst supported on alumina. This was carried out at high temperature and pressure.

- (ii) By considering the structure of phenylamine, suggest why its conversion to cyclohexylamine requires the use of a catalyst.

[1]

The reaction has a very high activation energy as phenylamine is resonance-stabilised / has delocalised π electrons in the ring.

- (d) Glycine, $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$, is a naturally occurring α -amino acid.

It can be synthesised using bromomethane as shown in Fig. 5.3.

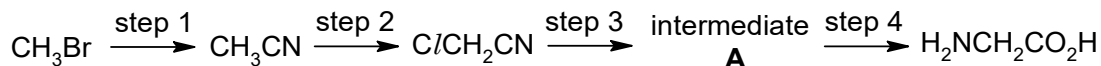


Fig. 5.3

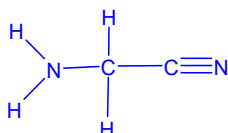
- (i) State the reagents and conditions required for step 1.

[1]

KCN in ethanol, heat (under reflux)

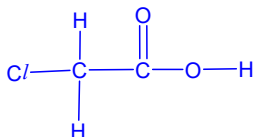
- (ii) Draw the **displayed** structural formula of intermediate **A** and state the reagents and conditions required for step 3.

[2]



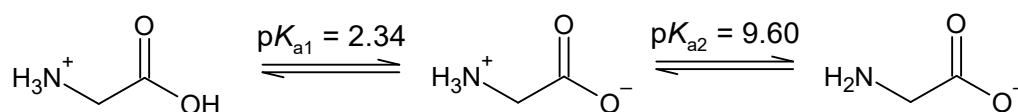
excess NH_3 (in ethanol), heat in a sealed tube

OR



dilute H_2SO_4 , heat

- (e) Protonated glycine acts as a dibasic weak acid.



A student adds small portions of $0.125 \text{ mol dm}^{-3}$ NaOH(aq) to 25.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ protonated glycine. The student uses a pH meter to measure the pH of the mixture.

- (i) Calculate the pH of $0.100 \text{ mol dm}^{-3}$ protonated glycine. You may ignore the effect of $\text{p}K_{\text{a}2}$ on the pH.

[1]

$$[\text{H}^+] = \sqrt{10^{-2.34} \times 0.100} = 0.021380 \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(0.021380) = 1.67$$

- (ii) Calculate the volume of NaOH required to reach the first equivalence point.

[1]

$$\text{amount of protonated glycine} = \frac{25.0}{1000} \times 0.100 = 0.00250 \text{ mol}$$

$$\text{amount of NaOH required for 1}^{\text{st}} \text{ equivalence point} = 0.00250 \text{ mol}$$

$$\text{volume of NaOH required} = 0.00250 \div 0.125 = 0.0200 \text{ dm}^3 (= 20.0 \text{ cm}^3)$$

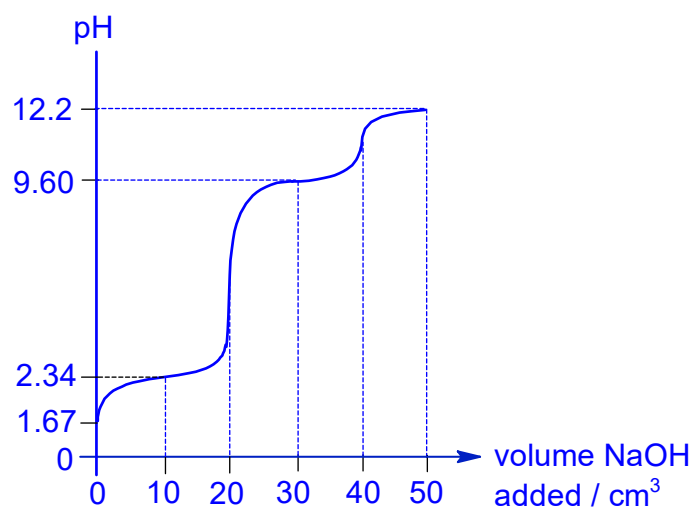
- (iii) Sketch the pH-volume added curve you would expect to obtain when a total of 50 cm^3 of $0.125 \text{ mol dm}^{-3}$ NaOH(aq) is added.

Label the following points on the curve.

- initial pH
- volume required for each equivalence point
- pH and volume at each point of maximum buffering capacity

You may assume that the pH of the solution is 12.2 upon addition of 50 cm^3 of NaOH.

[2]



[Total: 20]