EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2025
General Certificate of Education Advanced Level
Higher 2

CHEMISTRY

Paper 1 Multiple Choice

9729/01

19 September 2025

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, civics group and registration number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this question paper.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **13** printed pages and **3** blank pages.

[Turn Over

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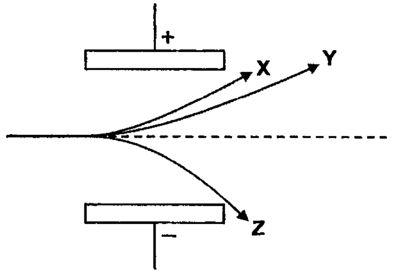
1 Three particles approach an electric field at the same speed. They are deflected as they pass through the electric field.



What could be the identities of particles **X**, **Y** and **Z**?

	X	Y	Z
A	$^{35}_{17}Cl^-$	$^{37}_{17}Cl^-$	$^{23}_{11}Na^+$
B	$^{6}_{3}Li^+$	$^{7}_{3}Li^+$	$^{1}_{1}H^-$
C	$^{37}_{17}Cl^-$	$^{35}_{17}Cl^-$	$^{23}_{11}Na^+$
D	$^{7}_{3}Li^+$	$^{6}_{3}Li^+$	$^{1}_{1}H^-$

Answer: A

Since particles **X** and **Y** are deflected to the positive terminal, they are negatively charged.
Since particle **Z** is deflected to the negative terminal, it is positively charged.

Hence, **X** and **Y** must be Cl^- while **Z** must be Na^+ (either option **A** or **C** is correct).

Between particles **X** and **Y**, the larger angle of deflection of particle **X** indicates that its $\frac{e}{m}$ ratio is larger than that of **Y**. Hence, particle **X** should have a **smaller mass** number than particle **Y** since both **X** and **Y** have the same charge.

Hence, **X** is $^{35}_{17}Cl^-$ while **Y** is $^{37}_{17}Cl^-$.

BP-511

2 Which of the following about calcium and copper is correct?

A The outermost orbital of the atoms of both elements has the same shape.

B Atom of both elements have orbitals of only 2 different shapes of various sizes.

C Atom of both elements have the same number of electrons in the outermost shell.

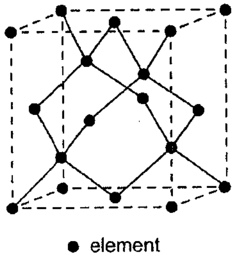
D Both elements form ions of 2+ charge with the electronic configuration of [Ar].

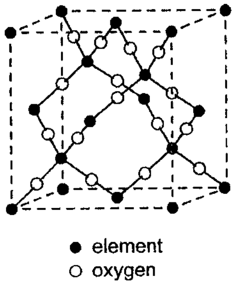
Answer: A

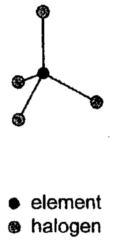
Ca: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$	Cu: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$
Ca^{2+}: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ or [Ar]	Cu^{2+}: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9$ or [Ar] $3d^9$

A ✓: Both atoms have 4s orbital as the outermost filled orbital. Thus, they have the same shape.
B ×: Ca has s and p orbitals (2 different shapes), but Cu has s, p and d orbitals (3 different shapes).
C ×: Ca has 2 electrons in the outmost shell (4s) while Cu has only 1 electron.
D ×: Thus, the ions do not have the same electronic configuration.

3 The following diagrams show the structures of an element, one of its oxides and its halides. What could the element be?







A aluminium **B** carbon **C** phosphorus **D** silicon

Answer: D

Based on the first diagram on the left, the element forms 4 single bonds. Based on the last diagram on the right, the element forms 4 single bonds with the halogen atoms. Hence, it can be concluded that the element is in **<u>Group 14</u>**.

4 The boiling point of water (100 °C) is greater than that of HF (20 °C).
Which statement is a correct explanation of the above?

A Each hydrogen bond formed between water molecules is stronger than that formed between HF molecules.

B There are more atoms in a water molecule than there are in an HF molecule, resulting in stronger intermolecular forces in water.

C There are, on average, more hydrogen bonds between water molecules than there are between HF molecules.

D The water molecule has stronger permanent dipole–dipole interactions than the HF molecule.

Answer: C

A ×: Intermolecular hydrogen bonds for HF is stronger than that of H_2O. This is because F is more electronegative than O, hence H–F bond is more polar than H–O bond, resulting in stronger hydrogen bonding.
B ×: The electron cloud for both are comparable and hence have similar strength of intermolecular instantaneous dipole–induced dipole.
C ✓: Each H_2O can form two hydrogen bonds; HF tends to form with fewer hydrogen bonds per molecule.
D ×: HF has the larger dipole, but dipole–dipole differences don't outweigh water's extensive hydrogen -bond network.

5 For a fixed mass of an ideal gas, which of the following graphs does **not** have the same general shape as the rest?

(ρ = density of the gas; *M* = molar mass of gas)

A $\frac{p}{\rho}$ against T

B pV against $\frac{M}{T}$

C p against ρT

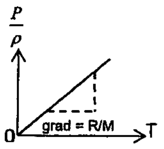
D $\frac{T}{p}$ against V

Answer: B

A: $PV = nRT \Rightarrow PV = \frac{m}{M}RT$

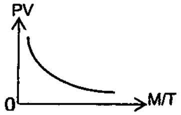
$PM = \frac{m}{V}RT \Rightarrow PM = \rho RT$

$\frac{P}{\rho} = \frac{R}{M}T$



B: $PV = nRT \Rightarrow PV = mR\frac{T}{M}$

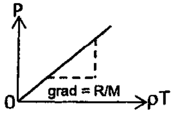
$PV = mR(\frac{1}{M/T})$



C: $PV = nRT \Rightarrow PV = \frac{m}{M}RT$

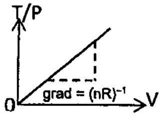
$PM = \frac{m}{V}RT \Rightarrow PM = \rho RT$

$P = \frac{R}{M}\rho T$



D: $PV = nRT$

$\Rightarrow \frac{T}{P} = \frac{1}{nR}V$



6 Which option correctly describes the species in terms of its behaviour as a Lewis base and as an Arrhenius acid?

	species	Lewis base	Arrhenius acid
A	HC*l*	no	yes
B	A*l*H$_3$	yes	no
C	NH$_3$	no	no
D	O^{2-}	yes	yes

Answer: A

A ✓: HC*l* is not a Lewis base and is an Arrhenius acid (produces H^+/H_3O^+ in water)
B ×: A*l*H$_3$ is a Lewis acid (electron-pair acceptor), not a Lewis base; it's also not an Arrhenius acid.
C ×: NH$_3$ is a Lewis base and an Arrhenius base (gives OH$^-$), not an Arrhenius acid.
D ×: O^{2-} is a very strong base (Lewis and Arrhenius base), not an acid.

7 *Use of the Data Booklet is relevant to this question.*

Based on its position in the Periodic Table, which properties will indium, In, be expected to possess?

1 In the vapour state, the chloride dimerises to form In$_2$C*l*$_6$.
2 Its oxide dissolves in both acids and alkalis.
3 Its ionic salts are typically coloured.

A 1 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

Answer: B
Option 1 ✓: Group 13 trichlorides (A*l*, Ga, In) are covalent and dimerise to form a general formula of M$_2$C*l*$_6$.
Option 2 ✓: In$_2$O$_3$ is amphoteric (reacts with both acid and base).
Option 3 ×: In is not a transition metal, hence its salts are usually white.

8 Metal peroxides decompose when heated to form metal oxides and oxygen gas. Which factor contributes to solid BaO_2 being more thermally stable than solid MgO_2?

A The hydration enthalpy of Mg^{2+} ion is more exothermic than that of Ba^{2+} ion.

B The lattice energy of BaO_2 is more negative than that of MgO_2.

C The charge density of Ba^{2+} ion is lower than that of Mg^{2+} ion.

D The O–O bond in O_2^{2-} is weaker than the O=O bond in O_2.

Answer: C
A ×: Hydration enthalpy is more exothermic for Mg^{2+} than Ba^{2+} and however it does not account for the solid-state thermal stability of peroxides.

B ×: Lattice energies of Group-2 peroxides become less negative down the group (|LE|: $MgO_2 > BaO_2$). A more negative BaO_2 lattice energy is not true and wouldn't explain BaO_2's greater stability.

C ✓: Ba^{2+} has lower charge density → lower polarising power → less weakening of the O–O bond in O_2^{2-}, so BaO_2 is more thermally stable (decomposes at a higher temperature) than MgO_2.

D ×: This is a general reason peroxides decompose (forming strong O=O), but it does not explain why BaO_2 is *more stable than* MgO_2.

9 F_2 reacts with BrO_z^- ions in a 2 : 1 molar ratio to form F^- and BrO_4^- ions.

What is the value of ***z***?

A 1 **B** 2 **C** 3 **D** 5

Answer: B

[R]: $2F_2 + 4e^- \rightarrow 4F^-$

Reacting ratio between F_2 and BrO_x^- is 2:1.
⇒ 1 mole of BrO_x^- loses 4 moles of electron to produce BrO_4^-.

Oxidation state of Br in BrO_4^- = +7
⇒ Oxidation state of Br in BrO_x^- = +3

$(+3) + (-2)(x) = -1$
$\therefore x = 2$

10 Diamond is a pure form of carbon. The mass of a diamond can be measured in carats, where one carat is equivalent to 0.200 g of carbon.

How many carats is a diamond made up of 3.01×10^{23} carbon atoms?

A 0.4 **B** 2.5 **C** 30 **D** 60

Answer: C

Amount of diamond = $(3.01 \times 10^{23}) / (6.02 \times 10^{23})$ = ½ mol
Mass = ½ x 12 = 6 g
No. of carats = 6 g / 0.200 g = 30

11 The enthalpy change of formation of potassium bromide, KBr, can be calculated using a Born-Haber cycle.

The enthalpy changes related to potassium and bromine are shown in the table.

	enthalpy change /kJ mol^{-1}
$K(s) \rightarrow K(g)$	+90
$Br_2(g) \rightarrow 2Br(g)$	+193
$K(g) \rightarrow K^+(g) + e^-$	+418
$Br(g) + e^- \rightarrow Br^-(g)$	–325
$K^+(g) + Br^-(g) \rightarrow KBr(s)$	–678

What is the enthalpy change of formation of KBr?

A –302 kJ mol^{-1}

B –399 kJ mol^{-1}

C –958 kJ mol^{-1}

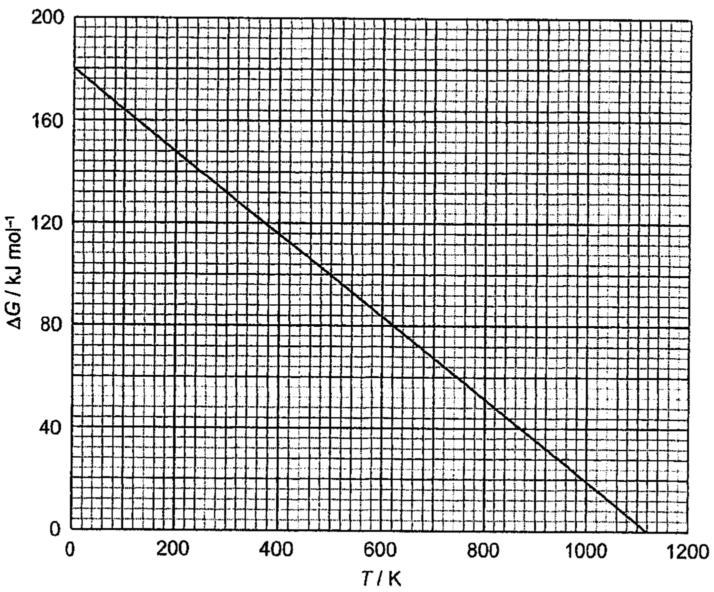
D –1054 kJ mol^{-1}

Answer: B

$\Delta H_f = \Delta H_{atom}$ + I.E. + E.A + L.E.
ΔH_f = +90 + ½ (193) + 418 + (–325) + (–678) = –398.5 kJ mol^{-1} = –399 kJ mol^{-1} (3 s.f.)

12 When heated, magnesium carbonate decomposes to form carbon dioxide and magnesium oxide.

A graphical plot of ΔG versus T, describing the change of the Gibbs free energy of the decomposition of magnesium carbonate with respect to temperature, is shown below.



Using the information from the graph, what is the value of $\Delta S^{\ominus}$ for the decomposition reaction?

A $+6.04 \times 10^2$ J mol^{-1} K^{-1} **B** -6.04×10^2 J mol^{-1} K^{-1}

C $+1.61 \times 10^2$ J mol^{-1} K^{-1} **D** -1.61×10^2 J mol^{-1} K^{-1}

Answer: C

Using: ΔG = ΔH – TΔS,
y = c + mx, where c = ΔH = 180 kJ mol^{-1} and m = –ΔS
Sub in values when ΔG = 0,
ΔH – TΔS = 0
ΔH = TΔS
$180 \times 10^3 = 1120\ (\Delta S)$
$\Delta S = +1.61 \times 10^2$ J mol^{-1} K^{-1}

Alternatively, the gradient of the line may be calculated to obtain the answer.

13 Caesium-137 undergoes radioactive decay to form barium-137. This decay is a first-order reaction with a half-life of 30.2 years.

How long would it take for the molar proportion of caesium to barium to reach a ratio 1:3 from pure caesium-137?

A 30.2 years **B** 60.4 years **C** 90.6 years **D** 120.8 years

Answer: **B**
Amount of caesium: 100% → 50% → 25%
Amount of barium: 0% → 50% → 75%
Hence, Cs: Ba
25 : 75
1 : 3
It takes **two half-lives** to attain a 1:3 ratio of Cs: Ba.
Total time taken = 2 × 30.2 = 60.4 years

14 The reaction of hydrogen peroxide with iodide ions in an acidic solution can be monitored by an initial rates method.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

The rate equation was found to be as follows:

$$\text{rate} = k\,[H_2O_2][I^-]$$

What of the following mechanism correctly describes this reaction?

A $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)
$IO^- + H^+ \rightarrow HIO$ (fast)
$HIO + H^+ + I^- \rightarrow H_2O + I_2$ (fast)

B $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)
$H_2O_2 + IO^- \rightarrow H_2O + IO_2^-$ (fast)
$IO_2^- + I^- + 4H^+ \rightarrow 2H_2O + I_2$ (fast)

C $2H^+ + 2I^- \rightarrow 2HI$ (fast)
$2HI + H_2O_2 \rightarrow 2H_2O + I_2$ (slow)

D $H_2O_2 + I^- + H^+ \rightarrow H_2O + HIO$ (fast)
$HIO + I^- \rightarrow OH^- + I_2$ (slow)
$OH^- + H^+ \rightarrow H_2O$ (fast)

Answer: **A**
A: Mechanism matches overall equation and slow step matches rate equation.
B: Mechanism's slow step matches rate equation but does not match overall equation.
C and D: Mechanism matches overall equation but slow step does not match rate equation.

BP-516

15 When steam is passed over white hot coke, a mixture of combustible gases is obtained.

$$C(s) + H_2O(g) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H_2(g) + CO(g) \qquad \Delta H = +131\ \text{kJ mol}^{-1}$$

When equilibrium has been established, which of the following correctly describes what would happen if a proposed change is made to this system?

	proposed change	value of K_c	forward rate constant, k_f	backward rate constant, k_b
A	add catalyst	no change	increase	increase
B	add more C(s)	no change	increase	no change
C	increase volume	increase	decrease	decrease
D	increase temperature	increase	increase	decrease

Answer: A

In general,

- Value of K_c is only affected by changes in **temperature**.
- Values of k_f and k_b are only affected by changes in **temperature** and **activation energies**.

For **D**, note that:
- Increase in temperature causes equilibrium position to shift to the right to favour the endothermic reaction to absorb excess heat, producing more products. As a result, value of K_c increases.

- Both rate constants, k_f and k_b, increase as the increase in temperature cause more reactants to have energy greater than or equal to activation energy, so rates of both forward and backward reactions increase.

Hence, **D** is incorrect.

16 Water dissociates into H^+ and OH^- as shown.

$$H_2O \rightleftharpoons H^+ + OH^-$$

The pH of water decreases at higher temperatures.

Which statements are correct?

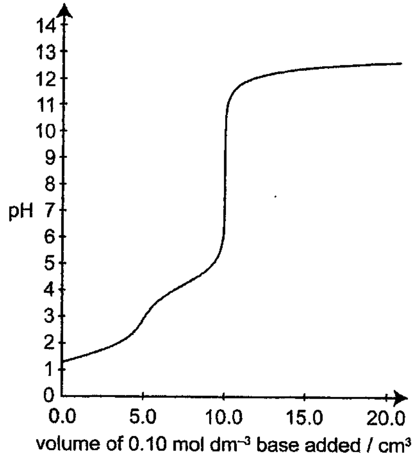
1 Water becomes acidic at higher temperatures.
2 The dissociation of water is endothermic.
3 The pOH decreases at higher temperatures.

A 1 only **B** 3 only **C** 1 and 2 **D** 2 and 3

Answer: D

Option 1 ×: Water remains neutral, since both $[H^+]$ and $[OH^-]$ increases to the same extent at higher temperature, ensuring that $[H^+] = [OH^-]$.
Option 2 ✓: Dissociation of water is endothermic since bond breaking is involved.
Option 3 ✓: Since the dissociation of water is more favourable at higher temperatures, both $[H^+]$ and $[OH^-]$ increase at higher temperature. Hence, both pH and pOH would decrease at higher temperature.

17 The graph shows the changes in pH when excess 0.10 mol dm^{-3} base solution is added gradually to y cm^3 of 0.10 mol dm^{-3} acid solution.



Which combination could have given these results?

	acid	base	y / cm^3
A	H_2SO_4	NH_3	10
B	H_2SO_4	NH_3	5
C	$(COOH)_2$	KOH	10
D	$(COOH)_2$	KOH	5

Answer: D

From the graph, the pH at equivalence point is more than 7. The conjugate base present is relatively strong and about to undergo hydrolysis in water. Hence, it can be inferred that it is a **weak-acid, strong-base** titration. From the options, the acid must be $(COOH)_2$ and the base must be KOH.

From the graph, 10 cm^3 of KOH is required for complete neutralisation. Since the acid and base have the same concentration, 5cm^3 of $(COOH)_2$ (a dibasic acid that gives out 2 H^+ per acid molecule) will be required at the start of the titration. Hence, option **D** is correct.

18 Given the following solubility product, K_{sp}, which of the following statements is correct?

salt	K_{sp}
Ag_2SO_4	1.4×10^{-5}
$PbSO_4$	1.6×10^{-8}
PbI_2	7.1×10^{-9}

A All three K_{sp} values have the same unit.

B $PbSO_4$ has a lower solubility in pure water than PbI_2.

C Solubility product of Ag_2SO_4 decreases when added to sulfuric acid.

D When solid Na_2SO_4 is added to a solution containing 0.01 mol dm^{-3} of Ag^+(aq) and Pb^{2+}(aq), Ag_2SO_4 precipitates before $PbSO_4$.

Answer: B

salt	K_{sp}	Unit of K_{sp}	Solubility / mol dm^{-3}
Ag_2SO_4	1.4×10^{-5}	$mol^3\ dm^{-9}$	1.52×10^{-2}
$PbSO_4$	1.6×10^{-8}	$mol^2\ dm^{-6}$	1.27×10^{-4}
PbI_2	7.1×10^{-9}	$mol^3\ dm^{-9}$	1.21×10^{-3}

Thus, **A** is incorrect while **B** is correct.

C is incorrect. Solubility product does not change when temperature is held constant.

D is incorrect. Assume 0.0100 mol dm^{-3} of aqueous metal ions, it will require

For Ag_2SO_4, $K_{sp} = [Ag^+]^2[SO_4^{2-}]$

$$[SO_4^{2-}] = 1.4 \times 10^{-5} \div (0.01)^2 = 0.140 \text{ mol dm}^{-3}$$

For $PbSO_4$, $K_{sp} = [Pb^{2+}][SO_4^{2-}]^2$

$$[SO_4^{2-}] = [1.6 \times 10^{-8} \div (0.01)]^{0.5} = 0.00126 \text{ mol dm}^{-3}$$

Thus, it will be easier to precipitate $PbSO_4$.

BP-517

19 One molecule of a non-cyclic organic compound contains only carbon atoms, hydrogen atoms and one oxygen atom. The compound is a ketone and contains a chiral carbon atom. One molecule of this compound contains *x* carbon atoms.

What could be the value of *x*?

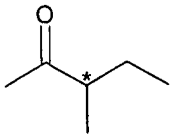
1 $x = 5$
2 $x = 6$
3 $x = 7$

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

Answer: C

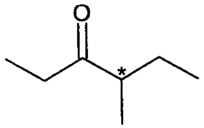
When x = 5, there are no molecules that contain a ketone and a chiral centre.

When x = 6



E.g. 3-methyl-pentan-2-one

When x = 7



E.g. 4-methyl-hexan-3-one

20 Propane undergoes free-radical substitution when mixed with chlorine and exposed to ultra-violet light.
Which compounds are possible products from this reaction?

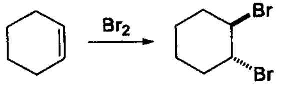
1 $CH_3CH_2CH_2Cl$
2 $CH_2ClCH_2CH_2Cl$
3 $CH_3CH_2CH_2CH_2CH_3$
4 $CH_3CH_2CH_2CH_2CH_2CH_3$

A 1, 2 and 3 **B** 1, 2 and 4 only **C** 1 and 2 only **D** 2 and 3 only

Answer: B

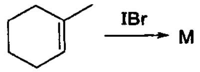
1 ✓: One or more of the H in $CH_3CH_2CH_3$ can be substituted by Cl
2 ✓: One or more of the H in $CH_3CH_2CH_3$ can be substituted by Cl
3 ✗: Requires $CH_3CH_2CH_2\bullet$ to combine with $\bullet CH_2CH_3$ which cannot be obtained from three carbon propane.
4 ✓: Two $CH_3CH_2CH_2\bullet$ radicals combine in the termination step.

21 When cyclohexene reacts with bromine, only racemic *trans*-1,2-dibromocyclohexane is obtained. No *cis*-1,2-dibromocyclohexane is obtained.



cyclohexene *trans*-1,2-dibromocyclohexane

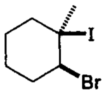
1-methylcyclohexene reacts with iodine monobromide, IBr, via the same mechanism giving the Markovnikov's product, M.



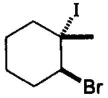
1-methylcyclohexene

Which of the following is likely to be the structure of M?

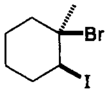
A



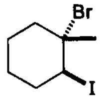
B



C



D



Answer: D

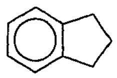
I and Br must add to *opposite* sides of the cyclohexene ring (trans).

Since **X** is the Markovnikov's product, the electron-deficient I of IBr must add to the less substituted C=C carbon to form the more stable carbocation, while Br adds to the more substituted C=C carbon.

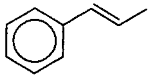
22 Compound **Y**, C_9H_{10}, reacts upon prolonged heating with acidified concentrated $KMnO_4$ to produce $C_8H_6O_4$ as the only organic product.

What is the structural formula of **Y**?

A



B



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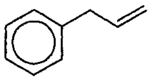
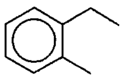
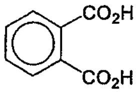


D



Answer: **A**

The product $C_8H_6O_4$ with 4 oxygen atoms would highly suggest the presence of two CO_2H groups, *i.e.*,



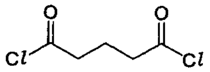
, resulting from the side-chain oxidation of the benzene ring.

Hence, **Y** is expected to have two alkyl "chains" attached to the benzene ring ⇒ **A** or **D**.
D is C_9H_{12}, which does not fit the molecular formula of **Y**.

23 1.00 g of each of the following compounds was heated with NaOH(aq), and then dilute HNO_3(aq) and $AgNO_3$(aq) was added.

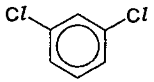
Which compound will produce the largest mass of AgC*l*(s)?

A



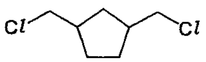
(M_r = 169.0)

B



(M_r = 147.0)

C



(M_r = 167.0)

D CH_3COCl (M_r = 78.5)

Answer: **D**

B will not react with NaOH(aq). No AgC*l* will be produced.
A and **D** will undergo hydrolysis.

- **A** forms 1/169 x 2 x 143.3 = 1.70 g of AgC*l*
- **D** forms 1/78.5 x 143.3 = 1.83 g of AgC*l*

C will undergo nucleophilic substitution. **C** Forms 1/167 x 2 x 143.3 = 1.72 g of AgC*l*

24 Which sets of reagents and conditions can be used to form the organic product $CH_3CH(OH)CH(CH_2NH_2)CO_2H$ from $CH_3COCH(CN)CO_2H$?

1 H_2, nickel catalyst, room temperature
2 $LiAlH_4$, dry ether as solvent, room temperature
3 $NaBH_4$, ethanol as solvent, room temperature

A 1, 2 and 3 **B** 1 and 3 only **C** 2 only **D** 1 only

Answer: D
There are 3 functional groups which can be reduced in the molecule – ketone, nitrile and carboxylic acid. The reducing agent can only reduce the ketone and nitrile functional group to form the desired molecule.
1 ✓ : It is able to reduce ketones and nitriles, but not carboxylic acids.
2 × : It can reduce all 3 functional groups.
3 × : It is able to only reduce ketones.

25 Propanone reacts with HCN at a slower rate compared to propanal.

Which statements are correct?

1 In both reactions, the carbonyl carbon reacts with a cyanide ion in the first step.

2 In propanone, the carbonyl carbon is more nucleophilic which repels the attacking cyanide ion.

3 A trace amount of NaC*l* is needed to catalyse the reaction.

A 1 and 2 **B** 1 only **C** 2 and 3 **D** 3 only

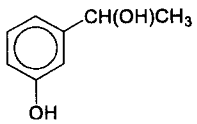
Answer: B

Option 1 ✓: The first step of nucleophilic addition involves nucleophilic attack of CN^- at the electrophilic or electron-deficient carbonyl carbon.
Option 2 ×: The carbonyl carbon in propanone is less electrophilic than that in propanal due to one additional electron-donating alkyl group, hence less susceptible to nucleophilic attack by CN^-
Option 3 ×: The reaction is catalysed by addition of a trace amount of NaCN, which can be formed *in situ* by adding a trace amount of NaOH (NaOH + HCN → NaCN + H_2O)

BP-519

BP~520

26 How many moles of $H_2(g)$ is produced when 1 mole of **Q** reacts with Na(s) and how many moles of $CO_2(g)$ is produced when 1 mole of **Q** reacts with $Na_2CO_3(aq)$?

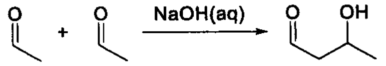


Q

	$H_2(g)$ produced with Na(s)	$CO_2(g)$ produced with $Na_2CO_3(aq)$
A	0	1
B	1	2
C	1	0
D	2	1

Answer: C
In molecule **Q**, there is one phenolic -OH group and one aliphatic -OH group.
Both -OH groups will react with Na(s) to form ½ $H_2(g)$. Hence, the total amount of $H_2(g)$ formed is 1 mole.
The aliphatic -OH group is a weak acid that is not able to undergo acid-base reaction with $Na_2CO_3(aq)$. For the phenolic -OH group, while it reacts with $Na_2CO_3(aq)$, only HCO_3^- is formed as the product and not CO_2. Hence, the total amount of $CO_2(g)$ formed is 0 mole.

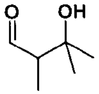
27 Aldol addition products are formed when a small amount of NaOH(aq) is added to carbonyl compounds at room temperature.



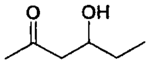
aldol addition product

Which product is **not** formed when a small amount of NaOH(aq) is added to an equimolar mixture of propanone and propanal?

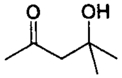
A



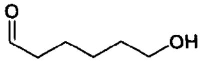
B



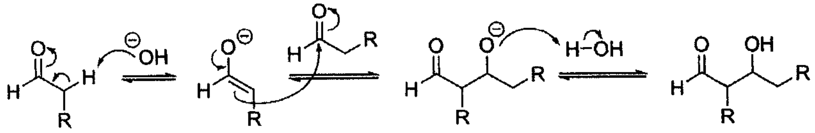
C



D



Answer: D



28 *Use of the Data Booklet is relevant to this question.*

An electrochemical cell is set up using a $Zn^{2+}(aq)|Zn(s)$ half-cell and a $MnO_4^-(aq)|Mn^{2+}(aq)$ half-cell in acidic solution.

Which of the following gives a correct effect on the E_{cell} when each of the changes is made to the corresponding half-cell separately?

	change	half-cell	effect on E_{cell}
A	addition of water	$MnO_4^-(aq)|Mn^{2+}(aq)$	less positive
B	addition of $Mn(NO_3)_2(s)$	$MnO_4^-(aq)|Mn^{2+}(aq)$	no change
C	addition of $Zn(NO_3)_2(s)$	$Zn^{2+}(aq)|Zn(s)$	more positive
D	addition of $Na_2CO_3(s)$	$Zn^{2+}(aq)|Zn(s)$	no change

Answer: A

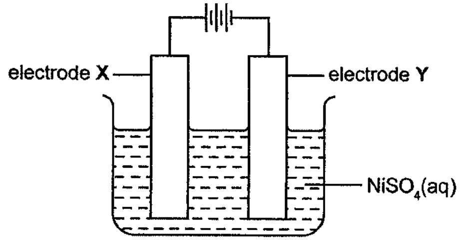
A: Adding water to MnO_4^-/Mn^{2+} half-cell will result in the position of equilibrium to shift to the left as there are more concentration terms and making the E for that half-cell less positive. This makes Ecell less positive.

B: Increasing $[Mn^{2+}]$ will result in the position of equilibrium to shift to the left for MnO_4^-/Mn^{2+} half-cell and making the E for that half-cell less positive. This makes E_{cell} less positive.

C: More Zn^{2+} favours reduction of Zn^{2+}, E of Zn^{2+}/Zn half-cell becomes more positive. E_{cell} becomes less positive.

D: Adding Na_2CO_3 to Zn^{2+}/Zn half-cell will result in the formation of $ZnCO_3(s)$, resulting in the position of equilibrium to shift to the left as it only lowers the $[Zn^{2+}]$ and making the E for that half-cell less positive. This makes E_{cell} more positive.

29 In an experiment, a cell was set up to obtain pure nickel from a nickel-silver alloy.



Which of the following statements is correct?

A Electrode **Y** is the nickel-silver alloy.

B The concentration of the electrolyte must be 1 mol dm^{-3}.

C The electrolyte may be replaced with sodium sulfate solution.

D The mass of the cathode changes by the same mass as the anode.

Answer: C

A Electrode **X** is the nickel-silver alloy as the cathode (electrode **Y**) will be where the pure metal is formed.

B The concentration of the electrolyte may not be 1 mol dm^{-3} since it may not take place at standard conditions

C The purification will not be affected by the change of electrolyte to Na_2SO_4 since both Na^+ and SO_4^{2-} are not likely to undergo redox reaction based on their standard electrode potential.

D The mass of the cathode will not change by the same mass as the anode since the silver at the anode will fall off as sludge.

30 Which of the following about period 4 transition elements is correct?

A The atomic radius decreases across the period.

B First ionisation energy remains relatively constant across the period.

C Period 4 transition elements have lower melting point than s block elements.

D The densities of period 4 transition elements are comparable to those of s block elements.

Answer: B

A: atomic radius remains relatively constant as nuclear charge increases, shielding effect also increase (electrons are added to inner 3d orbitals). The increase in nuclear charge and shielding effect almost cancels each other out. Hence, effective nuclear charge does not increase significantly to result in a significant trend.

C: Higher melting point. In transition elements, the sea of delocalised electrons is contributed by both 3d and 4s electrons, resulting in stronger metallic bonds compared to s block elements.

D: Transition elements are more dense that s block elements.

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2025
General Certificate of Education Advanced Level
Higher 2

Chemistry Paper 2 Suggested Solutions with Marker's comments

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1 Mount Ijen in East Java is famous for its rare blue flames, visible at night. The phenomenon occurs when sulfur vapour, from the volcano's cracks burns, producing bright blue flames and sulfur dioxide. In the cool high-altitude air, some of the vapour condenses into solid sulfur.

(a) A team of environmental chemists were authorised to collect solid sulfur deposits near Mount Ijen's crater to investigate volcanic activity.

The chemists burnt the sulfur sample and measured the temperature change for a fixed amount of water placed in a calorimeter. The data from their experiment is shown in Table 1.1.

Table 1.1

mass of solid sulfur powder burnt /g	0.76
mass of water in beaker /g	150
initial temperature of water /°C	29.8
final temperature of water / °C	39.7

(i) Construct an equation to represent the standard enthalpy change of combustion of solid sulfur, S.

$S (s) + O_2 (g) \rightarrow SO_2 (g)$ .... [1]

(ii) Calculate the enthalpy change of combustion of solid sulfur, S, based on their experiment.

$$q = -mc\Delta T$$
$$= -150 \times 4.18 \times (39.7 - 29.8)$$
$$= -6207.3 \text{ J}$$

$$\Delta H = \frac{q}{n} = \frac{-6207.3}{\frac{0.76}{32.1}}$$
$$= -262176 \text{ J mol}^{-1}$$
$$= -262 \text{ kJ mol}^{-1}$$

[2]

(iii) During volcanic activity, many sulfur-containing gases such as hydrogen sulfide, H_2S, and sulfur dioxide, SO_2, are released. In the atmosphere, H_2S can oxidise to form SO_2, and subsequently sulfur trioxide, SO_3, may be formed.

$$H_2S(g) + 3/2\ O_2(g) \rightarrow SO_2(g) + H_2O(l) \qquad \Delta H_r = -562 \text{ kJ mol}^{-1}$$

Use the data given in Table 1.2 to calculate the enthalpy change of combustion of solid sulfur, S.

Table 1.2

compound	ΔH_f / kJ mol^{-1}
$H_2S(g)$	–20.6
$H_2O(l)$	–285.8

$S(s) + O_2(g) \rightarrow SO_2(g)$ represents $\Delta H_f(SO_2)$ and also represents $\Delta H_c(S)$

$\Delta H_r = [\Delta H_f(SO_2) + (-285.8)] - (-20.6)]$
$-562 = [\Delta H_f(SO_2) + (-285.8)] - (-20.6)]$
$\Delta H_f(SO_2) = -296.8 \text{ kJ mol}^{-1}$

$\Delta H_f(SO_2) = \Delta H_c(SO_2) =$ **−297 kJ mol^{-1}**

[2]

(iv) Comment on the difference in values for the enthapy change of combustion of solid sulfur determined in **(a)(ii)** and **(a)(iii)**.

For (a)(ii), the **heat lost to the surroundings was not accounted** for / the experiment was **not 100% efficient** / the sulfur sample from the volcano was **not pure**. .... [1]

(v) With reference to a relevant chemical equation, explain how the release of sulfur-containing gases during volcanic activity can have a negative impact on the environment.

$SO_3 + H_2O \rightarrow H_2SO_4$

SO_3 dissolves in water to result in the formation of **acid rain** that can lead to **soil degradation/destruction of crops and farmlands / corrision of buildings or structures / water acidification that harms marine life.** .... [2]

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(b) Sulfur in volcanic emissions primarily exists as a mixture of two stable isotopes: ^{32}S and ^{34}S.

The chemists analysed volcanic gas samples to determine the isotopes' relative abundance, which reveals the sulfur's origin.

- If the sample was enriched in ^{32}S, it originated from deep mantle degassing.
- If the sample was enriched in ^{34}S, it originated from hydrothermally recycled sources.

(i) 1.994 g of SO_2 evolved at Mount Ijen allowed the chemists to extract 1.00 g of elemental sulfur containing mixture of isotopes, ^{32}S and ^{34}S, for further analysis.

Calculate the percentage by mass of ^{32}S in the elemental sulfur extracted. You may use the chemical formula S to represent elemental sulfur in your calculations.

Let the mass of ^{32}S to be x g and ^{34}S to be $(1.00 - x)$ g.

amount of $^{32}S = \frac{x}{32}$ mol

amount of $^{34}S = \frac{1.00 - x}{34}$ mol

Molar mass of $^{32}SO_2 = 32 + (16 \times 2)$
$= 64$ g/mol

Molar mass of $^{34}SO_2 = 34 + (16 \times 2)$
$= 66$ g/mol

$S \equiv SO_2$

$$\left(\frac{x}{32}\times 64\right)+\left(\frac{100-x}{34}\times 66\right)=1.994$$
$$2x+1.941-1.941x=1.994$$
$$0.059x=0.053$$
$$x=0.898$$

<u>alternatively</u>

amount of O $= \frac{1.994 - 1.00}{16}$
$= 0.062125$ mol

$S \equiv 2O$

$$\frac{x}{32}+\frac{1.00-x}{34}=\frac{0.062125}{2}$$
$$x=0.898$$

% by mass of $^{32}S = \frac{0.898}{1.00}\times 100\%$
$= 89.8\%$ [3]

(ii) Hence, suggest the likely origin of the sulfur sample.

Deep mantle degassing, since % by mass of ^{32}S is signficantly higher/ the sample is enriched in ^{32}S. [1]

While volcanic emissions affect the isotopic fractions of sulfur, the natural isotopic abundance of sulfur in Earth's environment is generally found to be present as follows.

Table 1.3

isotope	relative isotopic mass	percentage abundance / %
^{32}S	31.972	95.02
^{33}S	32.971	0.75
^{34}S	33.968	4.21
^{36}S	35.967	0.02

(iii) Use the data in Table 1.3 to calculate the relative atomic mass of sulfur, giving your answer to two decimal places.

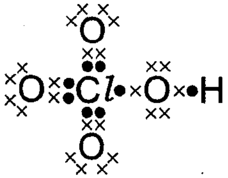
$$A_r \text{ of sulfur} = \frac{95.02\times 31.975+0.75\times 32.971+4.21\times 33.968+0.02\times 35.967}{100}$$
$$=32.06 \text{ (2 d.p.)}$$

[1]

[Total: 13]

2 Group 17 elements form a range of oxoacids with different oxidation states, such as $HClO_4$.

(a) **(i)** $HClO_4$ has two central atoms; one chlorine atom and one oxygen atom. In addition, the H atom is bonded to a O atom. Draw the dot-and-cross diagram of $HClO_4$.



[1]

(ii) Use VSEPR to describe and explain the shape and bond angle about central Cl and O atom in $HClO_4$.

About both O and Cl atoms have 4 electron pairs. **To minimise repulsion, the electrons pairs are directed as far apart as possible,** to corners of tetrahedron.

About O, there are **2 bond pairs and 2 lone pairs** and it is **bent** shape while about Cl there are **4 bond pairs** and it has **tetrahedral** shape.

Extent of repulsion: lone pair-lone pair > lone pair-bond pair > bond pair-bond pair. Hence bond angle about O and Cl is **104.5° and 109.5°** respectively. [3]

(b) With reference to your answer in (a)(i), explain why HFO_4 does not exist?

Fluorine does not have **energetically available and accessible d orbitals for expansion of octet.**

Or F is too small to accommodate 4 oxygen atoms around it

Or F is too electronegative to donate its electron pair for dative bonding..... [1]

(c) The Latimer diagram of some chlorine species in acidic solution is given in Fig. 2.1.

$$\underset{+1}{HOCl} \xrightarrow{+1.64\ V} \underset{0}{Cl_2} \xrightarrow{+1.36\ V} \underset{-1}{Cl^-}$$

Fig 2.1

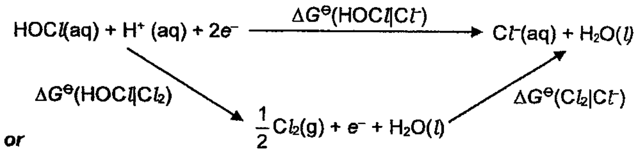
In Latimer diagram, oxidation numbers decrease from left to right and the numerical values of $E^\ominus$ of two adjacent species in volts. For example, the diagram shows that $E^\ominus(HOCl|Cl_2)$ is +1.64 V.

(i) Write a half-equation for the conversion of one mole of HOCl to one mole of Cl^- in acidic solution at 298 K.

$HOCl(aq) + H^+(aq) + 2e^- \rightarrow Cl^-(aq) + H_2O(l)$ .....[1]lp

(ii) Hess' Law is applicable to $\Delta G^\ominus$ in the same manner as $\Delta H^\ominus$.

With reference to the *Data Booklet* and Fig. 2.1, calculate $\Delta G^\ominus$ for the conversion of one mole HOCl to one mole of Cl^- in acidic solution.



or

$HOCl(aq) + H^+(aq) + e^- \rightarrow \frac{1}{2}Cl_2(aq) + H_2O(l)$ $\Delta G^\ominus(HOCl|Cl_2)$

$\frac{1}{2}Cl_2(g) + H_2O(l) + e^- \rightarrow Cl^-(aq) + H_2O(l)$ $\Delta G^\ominus(Cl_2|Cl^-)$

$HOCl(aq) + H^+(aq) + 2e^- \rightarrow Cl^-(aq) + H_2O(l)$ $\Delta G^\ominus(HOCl|Cl^-)$

$HOCl(aq) + H^+(aq) + e^- \rightarrow \frac{1}{2}Cl_2(aq) + H_2O(l)$ $E^\ominus = +1.64$ V

$\Delta G^\ominus(HOCl|Cl_2) = -nFE^\ominus = -1 \times F \times (+1.64) = -1.64F$ J mol^{-1}

$\frac{1}{2}Cl_2(g) + H_2O(l) + e^- \rightarrow Cl^-(aq) + H_2O(l)$ $E^\ominus = +1.36$ V

$\Delta G^\ominus(Cl_2|Cl^-) = -nFE^\ominus = -1 \times F \times (+1.36) = -1.36F$ J mol^{-1}

$$\begin{aligned}\Delta G^\ominus(HOCl|Cl^-)) &= \Delta G^\ominus(HOCl|Cl_2) + \Delta G^\ominus(Cl_2|Cl^-)\\ &= -1.64F - 1.36F = -3.00F\\ &= -289500\\ &= -290\ \text{kJ mol}^{-1}\end{aligned}$$

[3]

(iii) Hence, calculate the standard electrode potential for the $HOCl|Cl^-$ half-cell.

$$E^\ominus(HOCl|Cl^-) = \frac{\Delta G^\ominus(HOCl|Cl^-)}{-nF} = \frac{-3.00F}{-2F} = \mathbf{+1.50\ V}$$

[1]

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(d) A sample of group 2 metal ethanedioate, MC_2O_4, is analysed to determine the identity of the metal.

A 4.13 g sample of the metal ethanedioate is reacted with excess acidified potassium manganate(VII), $KMnO_4$.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

A 25 cm³ portion from the remaining solution is reacted with periodate ions, IO_4^-, to produce IO_3^- and MnO_4^-. 22.2 cm³ of 0.2 mol dm⁻³ of IO_4^- was required to react with the manganese(II) ions.

$$2Mn^{2+} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5IO_3^- + 6H^+$$

Deduce the identity of the metal in the metal ethanedioate.

amt of IO_4^- = 0.2 × 0.0222 = 0.00444 mol

$2Mn^{2+} \equiv 5IO_4^-$
amt of Mn^{2+} in 25 cm³ = 2/5 × 0.00444 = 0.001776 mol

total amt of Mn^{2+} in 100 cm³ = 0.001776 × 100/25 = 0.007104 mol

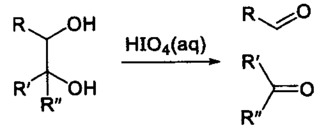
$2Mn^{2+} \equiv 5C_2O_4^{2-}$
Hence, amt of $C_2O_4^{2-}$ = 5/2 × 0.007104 = 0.01776 mol

molar mass of MC_2O_4 = 4.13 / 0.01776 ≈ 232.5 g/mol
A_r of M = 232.5 – [(2 × 12.0) + (4 × 16.0)] = 144.5

The group 2 metal is **barium**.

[3]

(e) Periodic acid, HIO_4, is used as a selective oxidant in organic chemistry to split alcohols with two adjacent hydroxy groups into two carbonyl compounds.
An example is shown in Fig. 2.2.



R, R′, R″ = H or alkyl

Fig. 2.2

Periodic acid also oxidises hydroxycarbonyl and dicarbonyl compounds by a hydration equilibrium, in which the carbonyl group is first converted into a diol.

$R_2C{=}O + H_2O \rightleftharpoons R_2C(OH)_2$ R = H or alkyl

For example:

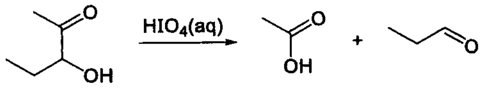


Fig. 2.3

Predict the organic products of the reactions shown in Fig. 2.4.

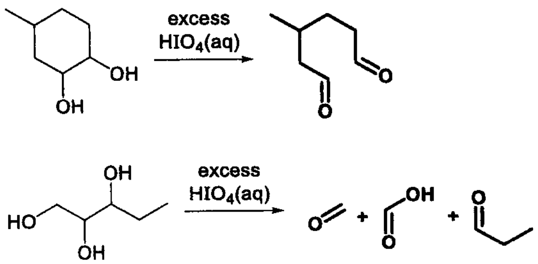


Fig. 2.4

[3]

[Total: 16]

3 **(a)** State whether trichloroethanoic acid or ethanoic acid, is the stronger acid. Explain your answer.

Trichloroethanoic acid is the stronger acid. The more stable the conjugate base, the stronger the acid. Trichloroethanoic acid has **3 C*l* substituents** which are **electron-withdrawing**, which helps to **disperse the negative charge** on the carboxylate group, **stabilising the conjugate base**. Ethanoic acid has an **electron-donating alkyl substituent**, which **intensifies the negative charge** on the carboxylate group, **destabilising the conjugate base**. [2]

(b) Phenyl ethanoate is often used as a solvent and as the building block for the synthesis of other chemicals.

(i) One method of its production involves phenol with an appropriate acid chloride via a **two**-step process. Identify the reactant required for each step.

step 1: **NaOH(aq)**, room temperature

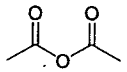
step 2: **ethanoyl chloride, CH_3COCl**, room temperature

[2]

(ii) Give two reasons why phenol does **not** react with carboxylic acids to form esters.

The **lone pair of electrons on the oxygen** of phenol is **delocalised into the benzene ring, rendering phenol to be a weak nucleophile**. The **lone pair of electrons on oxygen** in carboxylic acid **delocalised into the C=O bond, rendering the acid to be a weak electrophile**, hence there is no reaction. [2]

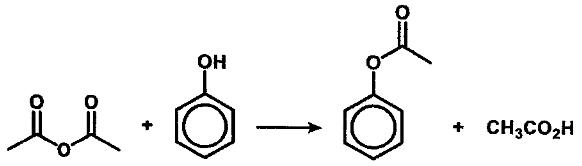
Another method of production involves phenols reacting with a class of compounds known as acid anhydrides. Ethanoic anhydride, $(CH_3CO)_2O$, is an example of a common commercially available acid anhydride.



ethanoic anhydride

Acid anhydrides undergo similar reactions to acid chlorides, and are easier and safer to handle in organic synthesis.

(c) (i) Write a balanced chemical equation for the formation of phenyl ethanoate using phenol and ethanoic anhydride.



[1]

(ii) Suggest why acid anhydrides are generally less reactive than acid chlorides towards nucleophiles.

The **lone pair of electrons** on the C–O–C **oxygen** of acid anhydrides is **more effectively delocalised** into the C=O **than that on the C*l*** of acid chlorides as it is held in a **2p orbital** while the lone pair in Cl is held in a **3p orbital**. Hence, the acyl carbon is **less electrophilic/reactive**. [1]

(d) **R** is formed when an acid anhydride **S**, $C_{14}H_{10}O_3$, reacts with CH_3NH_2.

R is a neutral compound and has the molecular formula C_8H_9NO. **R** reacts with hot $H_2SO_4(aq)$ to produce **P** and CH_3NH_2.

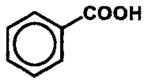
P is not very soluble in water, but dissolves after reacting with an excess of $Na_2CO_3(aq)$.

(i) Name the type of reaction occurring when **R** reacts with hot aqueous sulfuric acid.

Hydrolysis or nucleophilic (acyl) substitution. [1]

(ii) **P** has the molecular formula $C_7H_6O_2$. **P** can be formed when methylbenzene reacts with acidified potassium manganate(VII).

Draw the structure of **P**.



[1]

(iii) Write the equation for the reaction of **P** with an excess of $Na_2CO_3(aq)$.

$2C_6H_5COOH + Na_2CO_3 \rightarrow 2C_6H_5COONa + CO_2 + H_2O$ [1]

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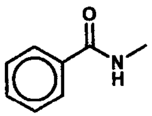
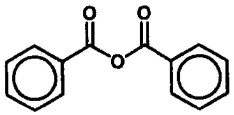
(iv) Suggest the structures of **R** and **S**.



R



S

[2]

(v) Use of the *Data Booklet* is relevant to this question.
Infra-red absorptions are useful in identifying functional groups present in molecules.

Suggest an absorption frequency range which can be used to distinguish between molecule **R** and **P**.

3300-3500 (N–H bond) or 1210–1440 (C–O in COOH) cm^{-1} .... [1]

[Total:14]

4 Industrial wastewater is wastewater produced by industrial facilities during manufacturing or other processes. It differs from domestic wastewater due to the presence of a wider range of pollutants and the potential for higher concentrations of contaminants.

(a) An industrial facility discharges wastewater containing Al^{3+}, Zn^{2+}, and Cu^{2+} ions. To meet environmental standards, the facility designs a treatment process by controlled precipitation to remove these ions from the wastewater.

(i) Table 4.1 shows the K_{sp} values for the hydroxides of the metal ions.
Given that the wastewater initially contains 0.010 mol dm^{-3} of each metal ion, calculate the minimum pH at which copper(II) hydroxide begin to precipitate.

Table 4.1

metal hydroxide	K_{sp}	minimum pH for precipitation
$Al(OH)_3$	1.3×10^{-33}	3.70
$Cu(OH)_2$	2.2×10^{-20}	–
$Zn(OH)_2$	3.0×10^{-17}	6.74

Let the concentration of OH^- be x mol dm^{-3}

$$\begin{aligned} K_{sp} &= (Cu^{2+})(OH^-)^2 \\ 2.2\times10^{-20} &= 0.01x^2 \\ x &= 1.483\times10^{-9} \\ pH &= 14 - pOH \\ &= 14-(-\lg(1.483\times10^{-9})) \\ &= 5.17 \end{aligned}$$

[2]

(ii) Based on your calculations in **(a)(i)**, explain how Al^{3+}, Cu^{2+} and Zn^{2+} ions in the wastewater can be separated in the treatment process.

As each metal hydroxide precipitates at different pH, by **gradually increasing the pH of the solution**, sequential and **selective precipitation** of Al^{3+}, Cu^{2+}, and Zn^{2+} ions can occur. .... [1]

(b) Industrial wastewater containing Cu^{2+} ions must be treated before it can be safe for discharge to a sanitary sewer for further treatment. The allowable limit of Cu^{2+} in the discharge is 1 mg per litre.

(i) Calculate the concentration of Cu^{2+} ions in the wastewater when zinc(II) hydroxide starts to precipitate.

When $Zn(OH)_2$ starts to precipitate,
pH = 6.74, $[OH^-] = 5.495 \times 10^{-8}$ mol dm^{-3}

Let the concentration of Cu^{2+} be y mol dm^{-3}
$(y)(5.495 \times 10^{-8})^2 = 2.2 \times 10^{-20}$
$y = 7.29 \times 10^{-6}$ mol dm^{-3}

[2]

(ii) The industrial wastewater is treated at pH 6.74. Using your answer in **(b)(i)**, deduce if the wastewater is safe for discharge to sanitary sewage for further treatment?

Allowable limit of Cu^{2+} = 1mg / L = 1×10^{-3} g dm^{-3}
= 1.575×10^{-5} mol dm^{-3}

Yes, it is safe as the allowable limit is larger than $[Cu^{2+}]$ present in the discharge at pH 6.74.

[1]

(c) There may be difficulty in removing Al^{3+} ion from the wastewater when excess sodium hydroxide solution is added.

Explain, with the aid of suitable equation(s), why this is so.

$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$

NaOH is added to precipitate Al^{3+} ions in the form of $Al(OH)_3$.

$Al(OH)_3 + OH^-$ □ $[Al(OH)_4]^-$ ————————(1) **[1]** accept irreversible reaction

However, when excess NaOH is added, concentration of OH^- increases, thus

position of equilibrium (1) shifts to the right to form the **soluble complex ion**

[1] in the wastewater and **cannot be precipitated.**

[2]

(d) A sample of the industrial wastewater was found to be pale blue in colour due to contamination by Cu^{2+} ions.

(i) Explain why the solution contaminated with Cu^{2+} is blue in colour.

Cu^{2+} has a **partially-filled 3d subshell**. In the **presence of H_2O ligand**, the **3d orbitals of Cu^{2+} splits into two different energy levels**. A **3d electron in the lower energy d orbital absorb light energy corresponding to the wavelengths** for orange light, and is **promoted to a higher energy d orbital**. The **remaining wavelengths are transmitted** and the **complementary** blue colour is **observed**. [3]

(ii) A student took a sample of the solution and added excess concentrated hydrochloric acid. State the type of reaction and describe any observations. Construct a balanced equation for the reaction.

The blue copper(II) solution will turn **green**.

Ligand exchange reaction has occurred due to high concentration of Cl^- ligand which displaces the water ligand in the hexaaquacopper(II) complex.

$[Cu(H_2O)_6]^{2+} + 4Cl^-$ □ $[CuCl_4]^{2-} + 6H_2O$ [3]

[total: 14]

BP-529

BP-530

5 Energy is crucial for life and bodily functions, stored in the form of adenosine triphosphate, ATP. Renown as “energy currency”, ATP consists of a base, adenine, attached to ribose, to which is attached to a triphosphate group, as shown in Fig. 5.1.

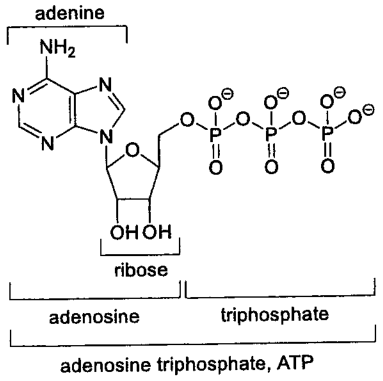


Fig. 5.1

(a) Adenine is made up of a six-membered pyrimidine ring fused with a five-membered imidazole ring, both of which are aromatic and planar.

The imidazole ring specifically contains six π electrons and can exist as an imidazole molecule. Two representations of imidazole molecule are shown in Fig. 5.2.

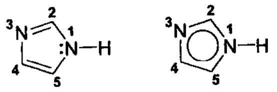


Fig. 5.2

Nitrogen atoms undergo the same type of hybridisation as carbon atoms.

(i) By reference to orbital overlap and the hybridisation of the nitrogen and carbon atoms, suggest how the σ and π bonds are formed in an imidazole molecule.

The **one C–C σ bonds and four C–N σ bonds of the 5-membered ring are formed from head-on overlap of singly filled sp^2 hybrid orbitals on the C and N atoms**. The **three C–H bonds and one N–H σ bond on the 5-membered ring are formed from head-on overlap of singly filled s orbital of H with sp^2 hybrid orbitals on the C and N**, respectively.

The **π bonds are formed from side-on overlap** of the five contiguous **p-orbitals, four singly filled on each of the C and N3 and one filled on N1**, in a cyclic manner within the 5-membered ring.

[3]

(ii) An imidazole molecule is amphoteric as it can function both as an acid and a base.
By considering your answer in **(a)(i)** and its structure or otherwise, suggest and explain:

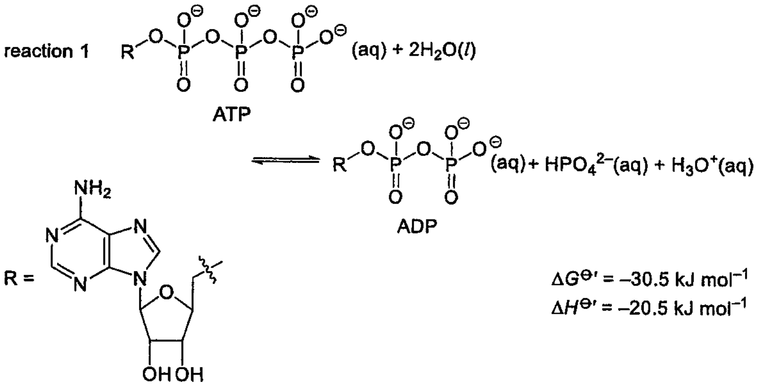
- The acidic proton is the H atom bonded to N1, not H atoms bonded to carbon atoms.
- N3 acts as the base.

The **H bonded to N1 is partially positively charged** as it is bonded to the more electronegative N atom, hence **more likely to be released as H⁺**.
C–H bonds are non-polar and less likely to release acidic protons.
OR N–H bond is weaker than C–H bond (bond energy based on Data Booklet)
OR negative charge of N, not C, can be delocalised into the resonance stabilised anion since lone pair of electrons of C is perpendicular to delocalised π electron cloud
OR consider relative stability of conjugate base whereby negative charge is more likely to reside on N rather than C since N is more electronegative.

The **lone pair of electrons of N3 is available** for protonation as it is **perpendicular to the delocalised π electron cloud**, thus it can act as a base.

[2]

ATP hydrolysis breaks a high-energy P–O bond, releasing energy and forming ADP and HPO_4^{2-}, and is reversible under suitable conditions in reaction 1. The biochemical standard condition (as annotated by the superscript of ⊖') applies here where concentrations of all species are defined to be at 1 mol dm^{-3} at pH 7.0, at 37 °C.



$\Delta G^{\ominus\prime} = -30.5$ kJ mol^{-1}
$\Delta H^{\ominus\prime} = -20.5$ kJ mol^{-1}

(b) The mechanism of the hydrolysis of ATP proceeds via the following stages:

1. Similar to nucleophilic addition, a nucleophilic attack of water on a phosphorus atom of the terminal phosphate unit while breaking the P=O π bond, forming intermediate 1.
2. The negative charge of the oxygen atom in intermediate 1 is then conferred to reforming of the π-bond in the P=O while another P–O bond involving the phosphorus atom of the terminal phosphate unit is cleaved to form intermediate 2 and ADP.
3. Another water molecule abstracts a proton from intermediate 2.

(i) Suggest why a water molecule is a nucleophile.

The presence of **two lone pairs of electrons on the oxygen atom of the water molecule.** enables it **to attack electron-deficient regions to form new covalent bonds.** [1]

(ii) Complete Fig. 5.3 to suggest the mechanism for this reaction for stages 1 and 2 only. Show the displayed structure of intermediate 2, relevant dipoles, relevant lone pairs of electrons and the movement of electrons by using curly arrows. [3]

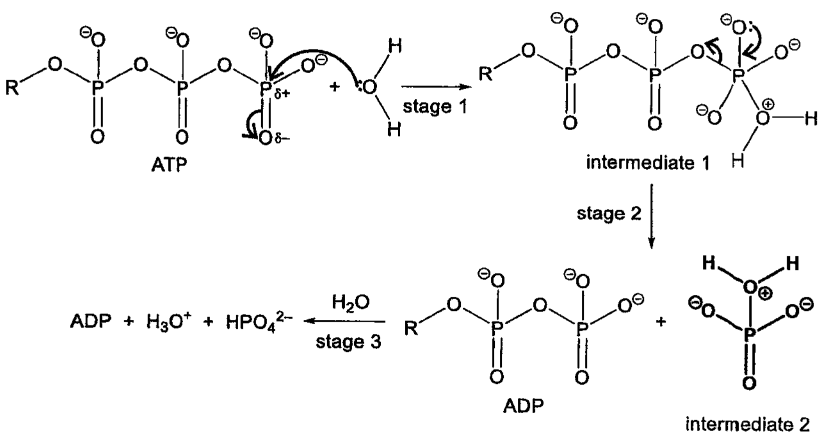


Fig. 5.3

(c) Calculate the entropy change of reaction, $\Delta S^{\ominus\prime}$, at 37 °C and comment on the sign of $\Delta S^{\ominus\prime}$ obtained.

$\Delta G^{\ominus\prime} = \Delta H^{\ominus\prime} - T\Delta S^{\ominus\prime}$
$\Delta S^{\ominus\prime} = (-20.5 - (-30.5)) \div (37+273) = \underline{\mathbf{+0.0322\ kJ\ mol^{-1}}}$

There is **increase in amount of aqueous particles which allows more ways for particles and their energies to distribute amongst themselves**, resulting in increase in entropy [2]

BP-531

(d) Physiological conditions vary depending on the organism, the specific tissue or cell compartment, and the current energy needs for metabolic and other reactions. Table 5.1 shows the concentrations of ATP, ADP and HPO_4^{2-} for various physiological conditions of organism.

Table 5.1

physiological condition of organism	ATP concentration / mol dm^{-3}	ADP concentration / mol dm^{-3}	HPO_4^{2-} concentration / mol dm^{-3}
standard condition	1	1	1
human – resting muscle	8×10^{-3}	9×10^{-6}	4×10^{-3}
human – muscle recovery from severe exercise	8×10^{-3}	7×10^{-6}	1×10^{-3}

(i) Other than concentration to be 1 mol dm^{-3}, state another condition specified by the symbol $^{\ominus}$ when the enthalpy change, entropy change and Gibbs free energy for a reaction are described at 298 K.

The partial pressure of all gaseous species must be at **1 bar**. .... [1]

(ii) By considering Table 5.1 or otherwise, suggest why the standard condition is not applicable to most physiological conditions.

The standard condition defines that **for reactions** (such as reaction 1) **involving H$^+$ ions, the resultant pH would be 0.** This is **not appropriate for living systems where most cells have a physiological pH close to the neutral pH** of 7.

OR The **standard condition is not applicable in cells where the concentrations of ATP, ADP, P$_i$ are the magnitude of mM, much lower than the standard concentration of 1 mol dm^{-3}**. ....

....

.... [1]

(iii) Equation 1 can be used to compute the actual Gibbs free energy change, ΔG due to ATP hydrolysis under physiological condition.

Equation 1 $\Delta G = \Delta G^{\ominus\prime} + RT\ln Q_c$

where Q_c refers to the reaction quotient which has the same expression as K_c.

Using equation 1, Table 5.1 and the *Data Booklet*, calculate the Gibbs free energy change, ΔG due to ATP hydrolysis in reaction 1 for human muscle of athletes recovering from severe physical exertion at 37 °C at pH = 7.4.

$$\begin{aligned}\Delta G &= \Delta G^{\ominus\prime} + RT\ln Q_c \\ &= \Delta G^{\ominus\prime} + RT\ln\frac{[ADP][HPO_4^{2-}][H_3O^+]}{[ATP]} \\ &= -30500 + 8.31\times(37+273)\times\ln\frac{(7\times10^{-6})(1\times10^{-3})(10^{-7.4})}{8\times10^{-3}} \\ &= -110329\ \text{J mol}^{-1} \\ &= -110\ \text{kJ mol}^{-1}\end{aligned}$$

[2]

In the presence of magnesium ions, the Gibbs free energy change of reaction 1 changes. This is shown in Fig. 5.4.

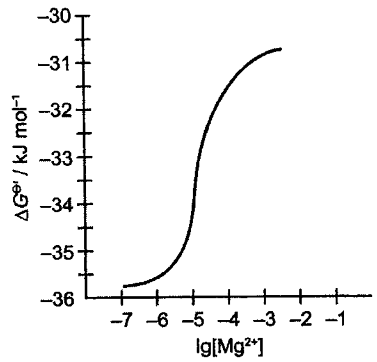


Fig. 5.4

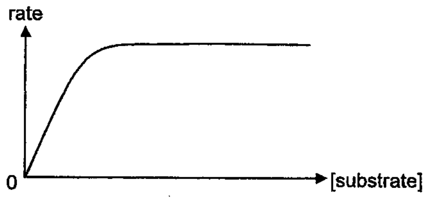
(e) (i) Based on Fig. 5.4, describe how Gibbs free energy change varies with increasing concentration of magnesium ions.

As **concentration of Mg^{2+} increases, the Gibbs free energy change becomes less negative.** .... [1]

(ii) ATP can form several complexes with magnesium ions such as the $[MgATP]^{2-}$ complex. The $[MgATP]^{2-}$ complex serves as the substrate for ATPase, the enzyme that catalyses reaction 1.

The rate of reaction 1 using a fixed amount of ATPase is investigated. Experiments are performed using different concentrations of $[MgATP]^{2-}$ complex (substrate) and the rate of each reaction is measured.

Sketch a graph to describe the relationship between the rate of the reaction and substrate concentration, using a fixed amount of ATPase enzyme, in this reaction. Explain your reasoning.



When **[substrate] is low, additional substrate is able to bind to an active site on the enzyme and react, hence reaction is first order w.r.t. substrate**.

At **high [substrate], active sites are saturated**. No active sites for additional substrate to bind. Hence reaction becomes **zero order w.r.t. substrate**.

[2]

[Total: 18]

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2025
General Certificate of Education Advanced Level
Higher 2

Chemistry Paper 3 Suggested Solutions with Marker's comments

Section A

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

1 Indirect calorimetry is used to estimate energy expenditure in humans by measuring the difference in oxygen concentration between inhaled and exhaled air. During aerobic respiration at 37 °C, glucose, $C_6H_{12}O_6$, is oxidised to carbon dioxide and water while producing energy as shown in reaction 1 below.

reaction 1 $\quad C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H^{\ominus} = -2818\ \text{kJ mol}^{-1}$

(a) **(i)** It is assumed that there are negligible intermolecular forces of attraction between gas particles in an ideal gas.

State **two** other basic assumptions of kinetic theory as applied to an ideal gas. [2]

(ii) Air contains about 21% oxygen, by volume. Exhaled air contains 14% oxygen. At complete rest, a typical adult exchanges approximately 500 cm^3 of air per breath at a rate of 12 times per minute at a temperature of 37 °C at 1 atmospheric pressure.

By assuming oxygen to be an ideal gas, calculate the volume of oxygen gas consumed per minute. Hence, determine amount of oxygen gas used per minute. [3]

(iii) Assuming that the oxygen inhaled is used for respiration directly, use relevant information in reaction 1 and your answer in **(a)(ii)**, calculate the approximate amount of energy released per minute. [1]

(i) The gas particles are in <u>**constant, random motion**</u>,
<u>**the volume of ideal gas particles are zero**</u>, and
there are <u>**perfectly elastic collisions between gas particles**</u>.

(ii) volume of O_2 consumed per minute $= (21 - 14)/100 \times 500\ \text{cm}^3 \times 12$
$= 420\ \text{cm}^3 = 4.20 \times 10^{-4}\ \text{m}^3$

$pV = nRT$

$(101325)(4.20 \times 10^{-4}) = n(8.31)(37 + 273)$

$n = 0.0165\ \text{mol} = \underline{\mathbf{1.65 \times 10^{-2}\ mol}}$

(iii) From equation 1, total of 6 mol of O_2 releases 2818 kJ of energy

Amt of energy released per minute $= (2818 \div 6) \times 0.0165 = 7.7495$ kJ
$= \underline{\mathbf{7.75\ kJ}}$

(b) Glucose, $C_6H_{12}O_6$, is the ubiquitous source of energy for cells in the body.

(i) Define the standard enthalpy change of formation of glucose, $C_6H_{12}O_6(s)$. [1]

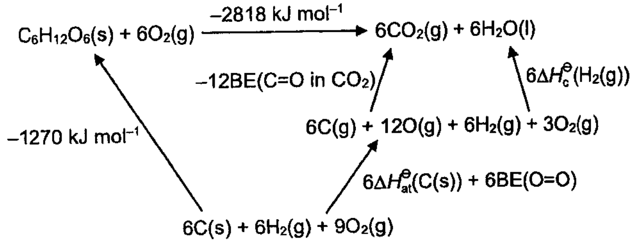
(ii) Use the following data, reaction 1 and appropriate data from the *Data Booklet*, to construct an energy cycle and calculate the standard enthalpy change of atomisation of C(s). Show your working.

enthalpy change of formation of $C_6H_{12}O_6(s)$ = –1270 kJ mol^{-1}
enthalpy change of combustion of $H_2(g)$ = –286 kJ mol^{-1}

[3]

(i) **<u>The energy change when 1 mole of glucose is formed from its constituent elements in their standard states</u>.**

(ii)



$-2818 - 1270 = 6\Delta H_{at}^\ominus(C(s)) + 6BE(O{=}O) - 12BE(C{=}O \text{ in } CO_2) + 6\Delta H_c^\ominus(H_2(g))$

$-2818 - 1270 = 6\Delta H_{at}^\ominus(C(s)) + 6(+496) - 12(+805) + 6(-286)$

$6\Delta H_{at}^\ominus(C(s)) = +4312 \text{ kJ mol}^{-1}$

$\Delta H_{at}^\ominus(C(s)) = +\underline{718.67 \text{ kJ mol}^{-1}} \approx \underline{+719 \text{ kJ mol}^{-1}}$

(c) Glucose exists in two forms, α-glucose and β-glucose as shown in Fig. 1.1. If a solution of α-glucose is left some time, it will come into dynamic equilibrium with β-glucose.

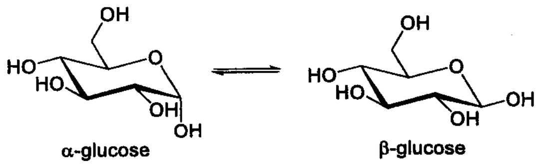


Fig. 1.1

When plane-polarised light is passed through an aqueous solution of glucose, the angle of rotation of the light is dependent upon the structure of the molecule. The angles of rotations of plane-polarised light caused by the two forms of glucose solutions under identical conditions are shown in Table 1.1.

Table 1.1

solution	angle of rotation of plane-polarised light
1.0 mol dm^{-3} of α-glucose	+111°
1.0 mol dm^{-3} of β-glucose	+19°

(i) When 1 dm^3 of a freshly prepared solution of 1.0 mol dm^{-3} α-glucose is left till equilibrium is achieved, the measured rotation is +53°. Assuming that the angle of rotation due to each glucose is directly proportional to its concentration, calculate a value for the equilibrium constant, K_c, for the conversion of α-glucose into β-glucose. [2]

(ii) The conversion of α-glucose into β-glucose is catalysed by acids. State and explain the effect on the final measured rotation if the conversion is now carried out in the presence of dilute sulfuric acid. [2]

(i)

	α-glucose	▯	β-glucose
initial conc / mol dm^{-3}	1		–
change in conc / mol dm^{-3}	$-y$		$+y$
eqm conc / mol dm^{-3}	$1-y$		y

At equilibrium,

optical rotation due to α-glucose + optical rotation due to β-glucose = 53°

$(1-y)(111°) + (y)(19°) = 53°$

$92y = 58$

$y = 58/92 = 0.63$

K_c = [β-glucose] / [α-glucose]
= y / (1–y)
= 0.63 / (1– 0.63)
= **1.71**

(ii) **The dilute sulfuric acid catalyst does not affect on the final measured rotation since a catalyst does not affect the equilibrium position since the rates of both forward and reverse reactions are increased to the same extent.** It only enables the equilibrium (i.e. the final rotation) to be established at an earlier time.

(d) Oxygen used in respiration binds to haemoglobin in red blood cells, which can undergo ligand exchange with water in tissues to regulate oxygen delivery. Both deoxyhaemoglobin and oxyhaemoglobin contain iron atoms in the +2 oxidation state. The oxygen-containing ligand is H_2O in deoxyhaemoglobin, Hb, and O_2 in oxyhaemoglobin, $Hb(O_2)_4$.

One molecule of deoxyhaemoglobin, Hb, can bind with four molecules of oxygen, as shown in equilibrium 1.

equilibrium 1 $Hb(aq) + 4O_2(aq)$ □ $Hb(O_2)_4(aq)$ $\Delta H^\ominus = -630.9 \text{ kJ mol}^{-1}$
$\Delta G^\ominus = -160.7 \text{ kJ mol}^{-1}$

(i) State *Le Chatelier's Principle.* [1]

(ii) During the initial stage of vigorous exercise, rapid muscle contractions generate heat that spreads through the body, raising core temperature.

Using Le Chatelier's Principle, explain how the initial increase in temperature affects equilibrium 1. [1]

(iii) Suggest how the magnitude of K_c for equilibrium 1 is likely to be and explain its significance. [2]

(iv) Carbon monoxide, CO, can bind to haemoglobin at the same binding site as oxygen. Explain why CO is poisonous. [2]

[Total: 20]

(i) Le Chatelier's principle states that if **a system in equilibrium is subjected to a change which disturbs the equilibrium, the system responds in such a way to counteract the effect of the change imposed, in order to re-establish the equilibrium of the system**.

(ii) **The equilibrium position shifts to the left** in order **to favour the endothermic reaction to absorb excess heat**.

(iii) **The magnitude of K_c is likely to be very large**. **Hence, the extent of this reaction is effectively complete or equilibrium position lies mostly on the right since $\Delta G^\ominus$ is highly negative implying that the forward reaction is thermodynamically spontaneous.**

BP-537

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2 (a) The Williamson ether synthesis involves nucleophilic substitution between a halogenoalkane (RX) and alkoxides (RO^-), the conjugate base of an alcohol. The alkoxide serves as the nucleophile in the reaction. An example of the reaction can be seen below:

$$RO^- + R'X \longrightarrow ROR' + X^-$$

A solution containing CH_3ONa, is reacted separately with 1-bromopropane and 2-bromo-2-methylpropane.

(i) Predict the predominant mechanism for:

I) the reaction of 1-bromopropane with CH_3ONa

II) the reaction of 2-bromo-2-methylpropane with CH_3ONa

Explain your reasoning. [3]

(ii) For each mechanism, state and explain the stereochemical outcome of the nucleophilic substitution reaction. [2]

(i) **I)** 1-bromopropane is a primary halogenoalkane. If it were to undergo substitution **via S_N1, the intermediate produced is a highly unstable primary carbocation**. **Rear-side attack by the nucleophile is relatively unhindered**. Hence, 1-bromopropane will react **via S_N2 mechanism**.

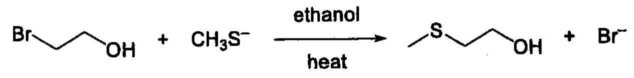
II) 2-bromo-2-methylpropane is a tertiary halogenoalkane. **Steric hinderance for the rear-side attack via S_N2 is severe due to the presence of three bulky alkyl groups**. However, the **formation of tertiary carbocation, stabilised by three electron-donating alkyl groups will be favourable**. Hence, 2-**bromo-2-methylpropane will react via S_N1 mechanism**.

(ii) **S_N1 mechanism will result in a racemic mixture** since the alpha-carbon become a positively charged carbocation carbon which is **trigonal planar**. **Attack of the nucleophile occurs with equal probability from both sides of the plane, leading to an equimolar mixture of two enantiomerically pure product**.

S_N2 mechanism will result in a single enantiomer since attack takes place from **opposite side of the C-X bond, forming a new C-Nu bond and cleaving the C-X bond resulting in an inversion of stereochemistry**.

(b) Thiolates such as methyl thiolate, CH_3S^-, act similarly to alkoxides in the nucleophilic substitution of halogenoalkanes, forming a sulfide.

The synthesis of 2-hydroxyethyl methyl sulfide from 2-bromoethanol using CH_3S^- can be seen from the following reaction scheme:



(i) Describe a simple chemical test to distinguish between 2-bromoethanol and 2-hydroxyethyl methyl sulfide. [2]

The kinetics of the reaction was studied with the results given in Table 2.1.

Table 2.1

experiment	$[CH_3S^-]$ / mol dm^{-3}	$[CH_2BrCH_2OH]$ / mol dm^{-3}	relative rate
1	0.100	0.150	1.00
2	0.150	0.150	1.50
3	0.200	0.200	2.67

(ii) Define the term *order of reaction*. [1]

(iii) Use the data to determine the order of reaction with respect to both CH_3S^- and CH_2BrCH_2OH. [2]

(iv) Hence, write a rate equation for the reaction. [1]

(v) Using your answer in **(b)(iv)**, describe the mechanism for the reaction. [3]

(i) **Test**: Add to the reactant and product separately, **$AgNO_3$ in ethanol and heat**. (or the longer 3-step way: NaOH(aq) + heat, HNO_3, $AgNO_3$(aq))

Observation: The reactant **will form a cream precipitate of AgBr** while the product will **not form any precipitate**.

(ii) The order of reaction with respect to a particular reactant is the **power to which the concentration of that reactant is raised in the experimentally determined rate equation.**

(iii) Comparing experiment 1 and 2,

When **$[CH_3S^-]$ increases to 1.5 times**, while keeping $[CH_3BrCH_2OH]$ constant, the **relative rate increases to 1.5 times**.

Order of reaction with respect to CH_3S^- is **one**.

Let rate equation be rate = $k[CH_3S^-][BrCH_2CH_2OH]^b$

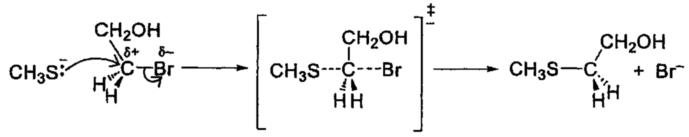
Comparing experiment 1 and 3,

$$\frac{2.67}{1.50} = \frac{k(0.200)^1(0.200)^b}{k(0.150)^1(0.150)^b} \Rightarrow b = 1$$

Order of reaction with respect to $BrCH_2CH_2OH$ is **one**.

(iv) rate = $k[CH_3S^-][BrCH_2CH_2OH]$

(v) **S_N2 Nucleophilic substitution**

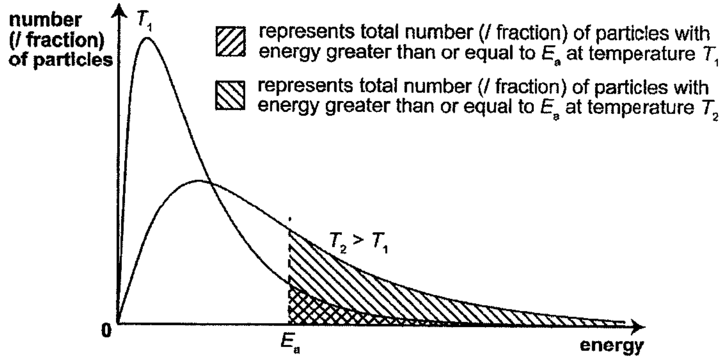


(c) Sodium methoxide, CH_3ONa, can also be used to synthesis 2-hydroxyethyl methyl sulfide from 2-bromoethanol. The rate of reaction was found to be slower than when sodium methanethiol, CH_3SNa, is used.

By considering the strength of the nucleophile, suggest why the rate of reaction is slower when using sodium methoxide. [1]

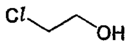
The O atom on the methoxide anion has **a stronger electronegativity** as compared to the S atom on the methyl thiolate. Hence, the **lone pair of electrons is less available, making it a weaker nucleophile**, resulting in a slower rate of reaction.

(d) The rate of reaction for the synthesis increases when the temperature is increased. With the aid of a clearly labelled Maxwell-Boltzmann distribution curve, explain this observation. [3]

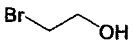


As temperature increases, **average kinetic energy of the particles increases**, and this results in an increase in frequency of collisions. In addition, **the number (/ fraction) of particles with energy equal to or greater than E_a increases**. Both factors result in **frequency of effective collision increases**, and the rate constant increases, hence the rate of reaction increases.

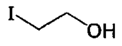
(e) Another series of experiments were done to study the difference in the rates of nucleophilic substitution for the following compounds using methyl thiolate.



2-chloroethanol



2-bromoethanol



2-iodoethanol

Deduce the order of increasing rate of reaction of the following compounds. Explain your answer. [2]

[Total: 20]

2-chloroethanol < 2-bromoethanol < 2-iodoethanol

Down the group, the **C-X bond strength decreases due to the decreasing effective overlap of the halogen orbitals with the C orbitals**. Thus, the bond becomes easier to break.

BP~540

3 Hydroformylation shown in Fig. 3.1 is one of the largest homogeneous catalytic reactions used to manufacture aldehydes industrially. The aldehydes are subsequently hydrogenated to alcohols or oxidised to carboxylic acids.

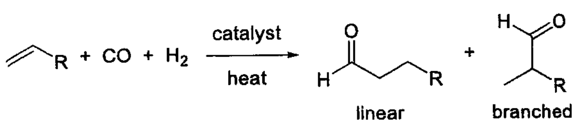


Fig. 3.1

The phosphine-modified cobalt catalyst, $HCo(CO)_3(PR_3)$, was developed to increase the linear : branched aldehyde selectivity. This catalyst also functions as an effective aldehyde hydrogenation catalyst to produce the corresponding alcohol.

The proposed mechanisms for the hydroformylation cycle are shown in Fig. 3.2.

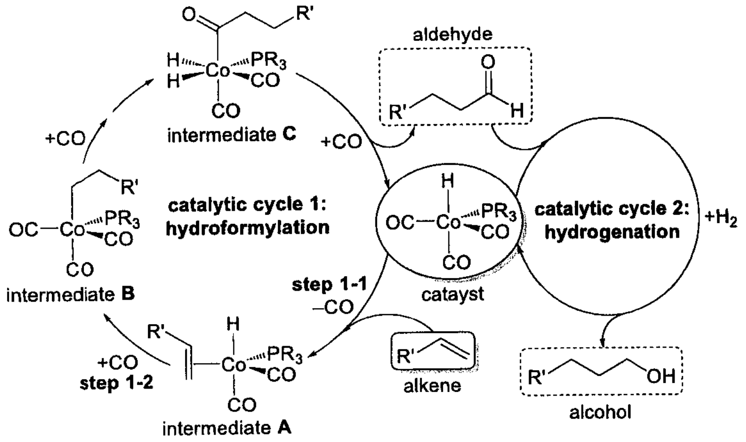


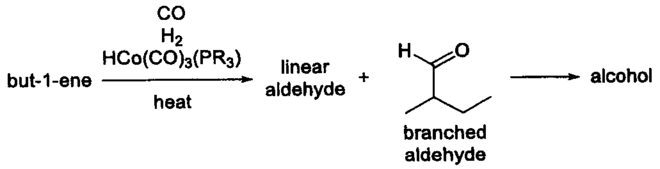
Fig. 3.2

An important step in catalytic cycle 1 is **step 1-2**, which involves addition of a Co–H bond adds across the C=C double bond within intermediate **A**, with binding of a carbon monoxide ligand, to give intermediate **B**.

Intermediate **B** reacts with more carbon monoxide, eventually giving intermediate **C**. Finally, intermediate **C** breaks down to give the aldehyde with regeneration of the catalyst.

The aldehyde formed from catalytic cycle 1 then enters catalytic cycle 2 and is reduced to give the corresponding alcohol.

(a) **But-1-ene was reacted with CO and H_2 using $HCo(CO)_3(PR_3)$ as catalyst.**



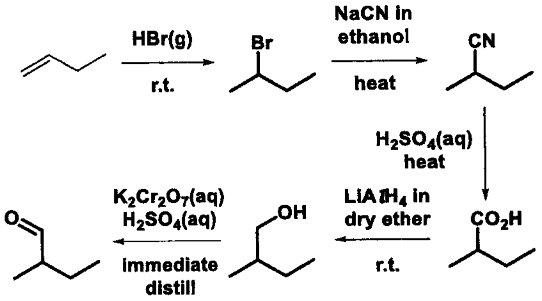
(i) **Draw the skeletal structure of the linear aldehyde.** **[1]**

(ii) **Starting from but-1-ene, suggest an alternative 5-step synthesis to form the branched aldehyde. The synthesis involves a nitrile intermediate.** **[5]**

(iii) **Suggest a simple chemical test to confirm that all the aldehydes have been hydrogenated to the corresponding alcohols.** **[2]**

(i)

(ii)



(iii) Test: Add **2,4-dinitrophenylhydrazine** to the product mixture at room temperature

Observation: **No orange ppt observed;** accept Tollens' and Fehling's

(b) **(i)** State the type of reaction in **step 1-1**. [1]

(ii) State the type of bond between the alkene and Co in intermediate **A** and suggest how it is formed. [2]

(iii) State the shapes of intermediate **B** and intermediate **C** about Co. [1]

(iv) Given that the Co in intermediate **C** is in the +3 oxidation state. State its full electronic configuration. [1]

(i) **ligand exchange reaction**

(ii) **Dative / coordinate** bond formed then alkene **donates its pair of π electrons** to the Co

(iii) intermediate **B** : trigonal bipyramidal

Intermediate **C** : octahedral

(iv) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6$

(c) The linear and branched product arises in **step 1-2** as the addition of Co–H across the C=C double bond can occur in two ways as shown in Fig. 3.3.

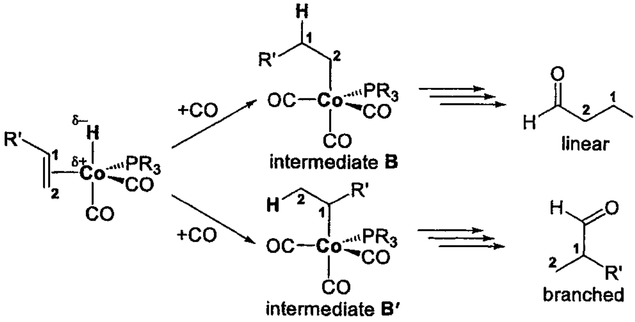


Fig. 3.3

(i) Based on your understanding of the mechanism of electrophilic addition, explain why intermediate **B** is formed preferentially over intermediate **B'**. [2]

(ii) Phosphine ligand, PR_3, with different R groups gives different linear : branched product ratio. State and explain one characteristic of the alkyl group, R, which will further favour formation of intermediate **B**. [2]

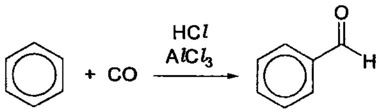
(i) Since the Co–H bond is polarised with Co carrying the partial positive charge and H carrying the partial negative charge, during addition of the Co–H across the C=C, the pair of C=C **π electrons** will preferentially **attack the electrophilic Co atom** leading to a **more stable secondary carbocation at carbon 1 than a primary carbocation at carbon 2** and **H:⁻**, which then combine to give intermediate **B**.

(ii) A **sterically bulky R group** will further favour formation of intermediate **B**.

This is because a bulky PR_3 will render intermediate **B'** **more unstable / less stable** compared to intermediate **B** due to **steric repulsion between PR₃ and R'**. *or*

The bulky PR_3 will render **electrophilic attack** of the $Co(CO)_2(PR_3)$ fragment **faster at carbon 2** compared to carbon 1 due to **steric hindrance by R' at carbon 1**

The Friedel-Crafts formylation of benzene using carbon monoxide can be achieved by the Gatterman-Koch reaction in which CO(g) and HCl(g) are used *in-situ* with a Lewis acid catalyst such as $AlCl_3$.



Assuming that CO(g) and HCl(g) reacts in the presence of $AlCl_3$ as shown.

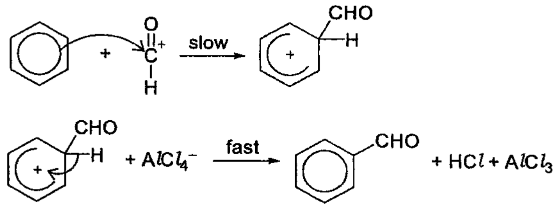
$$CO + HCl + AlCl_3 \;\square\; {}^{+}CHO + AlCl_4^{-}$$

(d) Describe the mechanism for the Friedel-Crafts formylation of benzene to give benzaldehyde. Show the displayed structure of the electrophile, the structure of the intermediate and the movement of electron pairs by using curly arrows.

[3]

[Total: 20]

Electrophilic substitution



Section B

BP-541

BP-542

Answer **one** question from this section.

4 **(a)** Glycolic acid, $CH_2(OH)COOH$, is an α-hydroxy acid used in some skincare products.

Sodium glycolate can be prepared by adding disodium hydrogen phosphate to a solution of glycolic acid in a cosmetic formulation. The reaction establishes the following equilibrium in water:

equilibrium 1 $CH_2(OH)COOH + HPO_4^{2-}$ □ $CH_2(OH)COO^- + H_2PO_4^-$

The K_a values for $CH_2(OH)COOH$ and $H_2PO_4^-$ are given in Table 4.1.

Table 4.1

acid	K_a
$CH_2(OH)COOH$	1.48×10^{-4}
$H_2PO_4^-$	6.20×10^{-8}

(i) Write down the IUPAC name for glycolic acid. [1]

(ii) Identify the two different conjugate acid-base pairs in equilibrium 1. [1]

(iii) Use the K_a values in Table 4.1 to calculate the equilibrium constant, K_c, for equilibrium 1. [2]

(iv) In an experiment, a buffer solution of pH 4.00 is prepared using 50.0 cm³ of 0.0500 mol dm⁻³ glycolic acid and *x* cm³ of 0.100 mol dm⁻³ NaOH.

$$CH_2(OH)COOH + NaOH \rightarrow CH_2(OH)COONa + H_2O$$

Assume that all NaOH reacts with glycolic acid, what is the volume, *x* cm³, of 0.100 mol dm⁻³ NaOH required to make the buffer? [4]

(i) 2-hydroxyethanoic acid

(ii) Acid: **$CH_2OHCOOH$** Conjugate base: **$CH_2(OH)COO^-$**

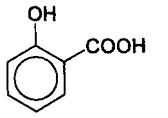
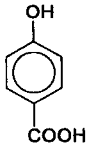
Base: **HPO_4^{2-}** Conjugate acid: **$H_2PO_4^-$**

(iii) $$K_c = \frac{[CH_2(OH)COO^-][H_2PO_4^-]}{[CH_2(OH)COOH][HPO_4^{2-}]}$$

$$= \frac{[CH_2(OH)COO^-]}{[CH_2(OH)COOH]} \times \frac{[H_2PO_4^-]}{[HPO_4^{2-}]}$$

(b) Table 4.2 shows the pK_a values of two isomeric benzoic acids: salicylic acid and 4-hydroxybenzoic acid.

Table 4.2

acid	pK_{a1}	pK_{a2}
 salicylic acid	3.0	13.4
 4-hydroxybenzoic acid	4.1	9.7

Explain the following:

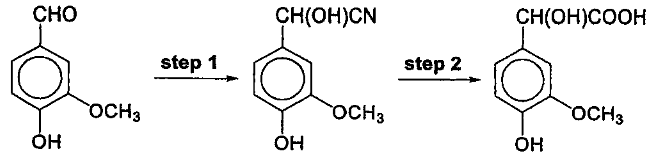
(i) pK_{a2} is larger than pK_{a1} of salicylic acid. [1]

(ii) pK_{a1} of salicylic acid is smaller than pK_{a1} of 4-hydroxybenzoic acid. [1]

(i) **Electrostatically unfavourable** / **more difficult to remove H^+ from a negatively charged anion,** conjugate base less likely to dissociate a secpmd H^+.

(ii) This is because the **conjugate base of salicylic acid is stabilised by intramolecular hydrogen bonding**. In 4-hydroxybenzoic acid, the –OH and –COO⁻ groups are too far away for hydrogen bonding to form.

(c) Vanillin, a common flavor and fragrance ingredient, can be converted into vanillic acid by a two-step laboratory synthesis.



vanillin vanillic acid

(i) State the reagent and conditions used in **step 1**. [1]

(ii) State the type of reaction that occurs in **step 1** and **2**. [2]

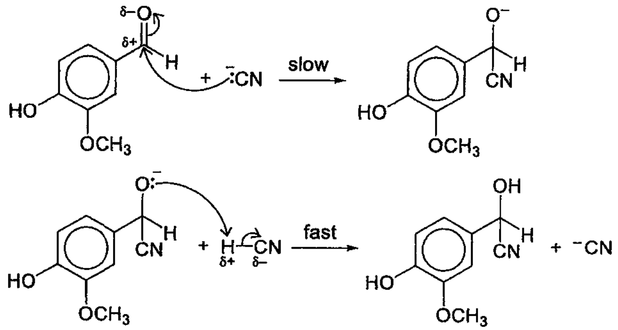
(iii) Draw the mechanism of the reaction in **step 1**. Show clearly all charges and the ntermediate formed and use curly arrows to indicate the movement of electron pairs. [3]

(i) HCN, trace amount of NaCN/NaOH, cold

(ii) Step 1: nucleophilic addition

Step 2: acidic hydrolysis

iii) $NaCN \rightarrow Na^+ + CN^-$



(d) Hexagonal boron nitride, h-BN, consist of planar sheets of alternate boron and nitrogen atoms, similar in arrangement to the carbon atoms in graphite. Its softness and sheen make powdered h-BN widely used in cosmetics.

(i) h-BN is often referred to as 'white-graphite'. With reference to chemical bonding and structure, explain why both h-BN and graphite have a soft and slippery feel. [2]

(ii) Explain, with reference to electronegativity, why h-BN does not conduct electricity readily, whereas graphite does. [2]

[Total: 20]

(i) Both are **giant covalent structure**, with strong covalent bonds found within the **layer/plane**. In both h-BN and graphite, the atoms are in trigonal planar arrangements. Each plane/sheet are held by **weak instantaneous dipole-induced dipole interactions.** Hence the layers can **slide over each other easily**.

(ii) In both compounds, since the C, B and B atoms are sp^2 hybridised each with a unhybridised **p orbital** that can **overlap sideway** to give a **delocalised** π electron cloud. For graphite, **each carbon atom** has **one lone electron that can move freely** through the structure, enabling electrical conduction.
In h-BN, **lone pair of electrons are more localised on more electronegative nitrogen atom**, and so there are no free electrons to carry charge, making it an electrical insulator.

BP-543

BP~544

5 In an effort to address pollution caused by industrial nitroaromatics and agricultural nitrates, researchers have developed a dual-function electrochemical system that converts these nitrogen-containing wastes into useful products. At the cathode, the electrolytic reduction of nitrobenzene to phenylamine is described in Fig. 5.1.

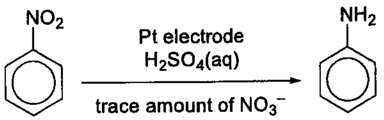


Fig 5.1

(a) State the reagents and conditions for the conversion of nitrobenzene to phenylamine in a laboratory. [1]

Sn, conc HC*l*, heat (followed by NaOH)

(b) (i) Given the nitrogen in nitrobenzene has an oxidation state of +3, describe the change in oxidation state of the nitrogen, in Fig. 5.1. [1]

(ii) Hence or otherwise, write the half-equation for this reaction. [1]

(iii) During a 4-hour electrolysis, a steady current of 2 A was passed. However, only 2.79 g of phenylamine was formed.

Using your answer to **(b)(ii)**, calculate the theoretical amount of electrons required to form 2.79 g of phenylamine. [1]

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

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

Hence, calculate the Faradaic efficiency of the electrolysis in **(b)(iii)**. [3]

(i) The oxidation state of the N decreases from +3 in nitrobenzene to −3 in phenylamine.

(ii) $\mathbf{C_6H_5NO_2 + 6H^+ + 6e^- \rightarrow C_6H_5NH_2 + 2H_2O}$

(iii) $n_{\text{phenylamine}} = \dfrac{2.79}{12.0\times6+1.0\times5+14.0+1.0\times2} = 0.0300 \text{ mol}$

$n_{\text{electrons}}$ required = 0.0300 × 6 = **0.180 mol**

(iv) (theoretical) charge required, $Q = n_eF$ = 0.180 × 96500 = 17370 C

(actual) charge passed = 2 × 4 × 60 × 60 = 28800 C

$\text{Faradaic efficiency} = \dfrac{17370}{28800} \times 100\% =$ **60.3%**

(c) The use of the *Data Booklet* is relevant to this question.

(i) A student suggests that the trace amounts of NO_3^- ions at the cathode could also be reduced to NH_4^+ ions. Discuss how electrode potential and concentration might influence this competition.
(The $E^\ominus$(nitrobenzene | phenylamine) is +0.79 V.) [3]

(ii) Suggest other possible side products at the cathode. [1]

(i) The reduction of NO_3^- has a **more positive $E^\ominus$** (+0.87 V) than that of nitrobenzene (+0.79 V), indicating its reduction is thermodynamically more favourable.

However, since NO_3^- ion is present in trace amount, by LCP, the position of the equilibrium $NO_3^- + 10H^+ + 8e^- \ \square\ NH_4^+ + 3H_2O$ is **shifted to the left, favouring oxidation**, making the electrode potential **less positive**.

Since the electrode potential for both competing reactions are similar, it is possible for the $E(NO_3^-|NH_4^+)$ to be **less positive than *E*(nitrobenzene | phenylamine)**.

(ii) $\mathbf{HNO_2}$ **or** $\mathbf{NO_2}$

(d) Rank the following compounds in order of increasing basicity and explain your reasoning.

phenylamine, methylamine, ethanamide [4]

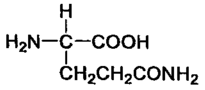
Increasing basicity: $CH_3CONH_2 < C_6H_5NH_2 < CH_3NH_2$

Phenylamine and ethanamide are less basic than CH_3NH_2 as the **p orbitals of N overlap with the π electron cloud of benzene and the C=O groups respectively**.

For ethanamide, the **lone pair of electrons on N atom is delocalized into the π electron cloud of the C=O bond**, thus this lone pair of electrons is **not available for donation** to a proton, hence it is **neutral.**

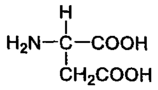
For phenylamine, the **lone pair of electrons on N atom is delocalized into the π electron cloud in the benzene ring**. This **reduces the availability of the lone pair of electrons** on N atom **for donation** to a proton. **CH_3NH_2 has an electron donating alkyl group** so the lone pair on N is **more available** for donation to H⁺. Hence, it is the most basic.

(e) The structures of two amino acids, glutamine and aspartic acid are given below.



$H_2N-\underset{CH_2CH_2CONH_2}{\overset{H}{C}}-COOH$

glutamine



$H_2N-\underset{CH_2COOH}{\overset{H}{C}}-COOH$

aspartic acid

(i) Suggest a simple chemical test to distinguish between glutamine and aspartic acid. [2]

(ii) The three pK_a values associated with aspartic acid are 1.99, 3.90 and 9.90.

Draw the structures of the predominant species of aspartic acid at

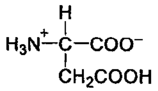
- pH 3
- pH 8
- pH 11

[3]

[Total: 20]

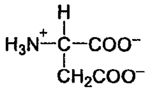
(i) Add **NaOH(aq)** to the separate samples and **heat** them in water bath. **Glutamine will produce ammonia which turns moist red litmus paper blue** but **aspartic acid does not produce a gas that turns moist red litmus paper blue**.

(ii) pH 3 :



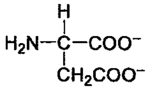
$H_3\overset{+}{N}-\underset{CH_2COOH}{\overset{H}{C}}-COO^-$

pH 8 :



$H_3\overset{+}{N}-\underset{CH_2COO^-}{\overset{H}{C}}-COO^-$

pH 11 :



$H_2N-\underset{CH_2COO^-}{\overset{H}{C}}-COO^-$

BP-545