Anglo-Chinese Junior College
JC2 Preliminary Examination
Higher 2

A Methodist Institution
(Founded 1886)

CHEMISTRY **9729/01**
Paper 1 Multiple Choice
17 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 and index number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions in this section. 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 booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **16** printed pages.

1 The most common oxidation state of americium, Am, in aqueous solution is +3.

Recently, Cu^{3+} has been shown to quantitatively oxidise $Am^{3+}(aq)$ in dilute HNO_3, while itself is reduced to Cu^{2+}.

In an experiment, 20.0 cm^3 of 0.0120 mol dm^{-3} $Am^{3+}(aq)$ was found to require 24.00 cm^3 of 0.0300 mol dm^{-3} Cu^{3+} for complete oxidation.

What is the formula of the americium-containing species formed?

A $Am_2O_2^{2+}$
B AmO_2^{2+}
C AmO^{2+}
D AmO^+

n(electrons) = n(Cu^{3+}) = 7.20 X 10^{-4}
change in oxidation state of Am = (7.20 X 10^{-4}) / (20.0 X 0.0120 / 1000) = +3
Initial oxidation state of Am = +3 +3 = +6
Correct option is AmO_2^{2+}

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

The table shows the fifth, sixth, seventh, eighth, ninth and tenth ionisation energies of an element ($Z \leq 20$) in the Periodic Table.

	5th	6th	7th	8th	9th	10th
ionisation energy / kJ mol^{-1}	7975	9590	11343	14944	16964	48610

What can be inferred about the element from the above data?

A It is in the third period of the Periodic Table.
B It is in Group 2 of the Periodic Table.
C It is likely to form an ionic compound when reacted with oxygen.
D Its 6th and 7th electrons are removed from different subshells.

C: There is a large electronegativity difference between the Group 1 element and oxygen (Group 16). Hence, the compound formed will be ionic in nature.

A: There is insufficient data to conclude that the element lies in the third period. Since $Z \leq 20$, this Group 1 element can be in the fourth period.

B: The largest increase in successive ionisation energies (IE) occur between 9th and 10th IE. This implies that the 10th electron is removed from an inner shell. Since $Z \leq 20$, only s and p subshells exists. Hence, each shell can only accommodate up to a maximum of 8 electrons. This would imply that the 2nd to 9th electron also lies in another inner shell. There will be only one electron in the valence shell. This element therefore belongs to Group 1 (either Na or K).

D: As a Group 1 element, the 6th and 7th electrons are removed from the same p-subshell.

BP-71

BP-72

3 Particle **R** has a proton number *n* and forms a stable monoatomic ion of charge –1.

Particle **S** has a proton number of (*n*+2) and it forms a stable monoatomic ion which is isoelectronic with the ion of **R**.

Which statement is correct?

- **A** Ion of **S** has a smaller ionic radius than ion of **R**.
- **B** **R** has a larger atomic radius than **S**.
- **C** Ion of **S** requires less energy than ion of **R** when an electron is removed from each particle.
- **D** Ion of **R** releases more energy than ion of **S** when an electron is added to each particle.

${}_{n}\mathrm{R}$ gains 1 electron to form stable ${}_{n}\mathrm{R}^{-}$, which has (*n*+1) electrons
⇒ **R** is in Group 17.

${}_{n+2}\mathrm{S}$ forms a stable ion which is isoelectronic with ${}_{n}\mathrm{R}^{-}$. Hence ${}_{n+2}\mathrm{S}$ must have **lost** 1 electron, to form ${}_{n+2}\mathrm{S}^{+}$, which has (*n*+2)–1 = (*n*+1) electrons
⇒ **S** is in Group 1 of the *next period.*

A✓ Since ${}_{n}\mathrm{R}^{-}$ and ${}_{n+2}\mathrm{S}^{+}$ are iso-electronic, ${}_{n+2}\mathrm{S}^{+}$ with a higher nuclear charge will have a smaller ionic radius as the effective nuclear charge experienced by the valence e^{-}s is higher.
B× As **S** is an element in the next period, with one additional filled principal quantum shell, **S** has a larger atomic radius despite the higher nuclear charge.
C× ${}_{n+2}\mathrm{S}^{+} - e^{-} \rightarrow {}_{n+2}\mathrm{S}^{2+}$ will be more endothermic than ${}_{n}\mathrm{R}^{-} - e^{-} \rightarrow {}_{n}\mathrm{R}$ since the e^{-} is being removed from positively charged ${}_{n+2}\mathrm{S}^{+}$.
D× ${}_{n}\mathrm{R}^{-} + e^{-} \rightarrow {}_{n}\mathrm{R}^{2-}$ will be endothermic due to repulsion of the incoming e^{-}; ${}_{n+2}\mathrm{S}^{+} + e^{-} \rightarrow {}_{n+2}\mathrm{S}$ will be exothermic due to attraction of the incoming e^{-}.

4 Which statement about the trend in the property of the halogens down the group is correct?

- **A** The electronegativity increases.
- **B** The volatility increases.
- **C** The enthalpy change of reaction with hydrogen becomes less exothermic.
- **D** The reactivity as reducing agents increases.

A: Electronegativity decreases down any Group.

B: IDID gets stronger down Group 17. Volatility should decrease.

C: Halogens react with hydrogen in the gaseous phase to give hydrogen halides. As reactivity/oxidising power of the halogens decreases down the group, the vigour of the reaction also decreases down the group. Hence, the enthalpy change of reaction with hydrogen becomes less exothermic.

D: Halogens are usually oxidising agents, not reducing agents.

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

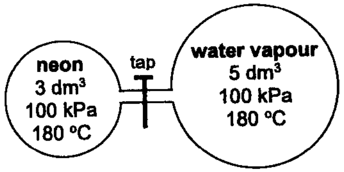
Which sequence is correct in terms of increasing radius?

- **A** $\mathrm{Rb^{+} < Sr^{2+} < As^{3-} < Se^{2-}}$
- **B** $\mathrm{Sr^{2+} < Rb^{+} < Se^{2-} < As^{3-}}$
- **C** $\mathrm{As^{3-} < Se^{2-} < Sr^{2+} < Rb^{+}}$
- **D** $\mathrm{Se^{2-} < Sr^{2+} < Rb^{+} < As^{3-}}$

All ions are isoelectronic, but different number of protons.

	$\mathrm{Sr^{2+}}$	$\mathrm{Rb^{+}}$	$\mathrm{Se^{2-}}$	$\mathrm{As^{3-}}$
Proton / Electron Ratio	38 ÷ 36	37 ÷ 36	34 ÷ 36	33 ÷ 36
Attraction	Strongest			Weakest

6 Two bulbs are connected as shown in the diagram below. The bulbs are connected by a narrow tube of negligible volume.



When the tap is opened, the two gases mix. The connected bulbs were then allowed to cool to room temperature.

What was the final pressure, in kPa, in the connected bulbs?

- **A** 13.9
- **B** 24.3
- **C** 37.5
- **D** 64.7

When the connected bulbs were allowed to cool to room temperature, water vapour condensed to give liquid water, which occupy negligible volume. Hence, we only need to consider the amount of neon gas present in the connected bulbs.

PV = nRT
$100000 \times (3 \times 10^{-3}) = n \times 8.31 \times (180 + 273) \rightarrow n = 0.07969$ mol (amount of neon)

When the tap is opened, and the total volume is 8 dm³,
PV = nRT
$P \times (8 \times 10^{-3}) = 0.07969 \times 8.31 \times 293$
$P = 24254$ Pa
$= 24.3$ kPa

7 $(CH_3)_2S.BCl_3$ is a solid that is commonly used in laboratories as a convenient source of BCl_3. When heated, it reversibly decomposes to $(CH_3)_2S$ and BCl_3.

Which statement is true?

A The dative bond is formed using the 2p orbitals of boron and sulfur.

B $(CH_3)_2S$ and BCl_3 act as the Lewis acid and Lewis base respectively in the formation of $(CH_3)_2S.BCl_3$.

C The dative bond is from boron to sulfur.

D The C-S-C bond angle decreases when the solid decomposes.

A The dative bond is formed using the <u>hybrid sp^3</u> orbitals of boron and sulfur.

B $(CH_3)_2S$ and BCl_3 act as the <u>Lewis base and Lewis acid</u> respectively in the formation of $(CH_3)_2S.BCl_3$.

D The C-S-C bond angle decreases when the solid decomposes.

C The dative bond is from <u>sulfur to boron</u>.

8 The compound $Bi_2Sr_2Ca_2Cu_3O_{10}$ is a superconductor.

In this compound, the oxidation number of bismuth is +3, strontium and calcium is +2 and oxygen is −2.

What are the possible oxidation numbers of the three copper atoms in $Bi_2Sr_2Ca_2Cu_3O_{10}$?

A +1, +1, +2

B +1, +2, +3

C 0, +1, +3

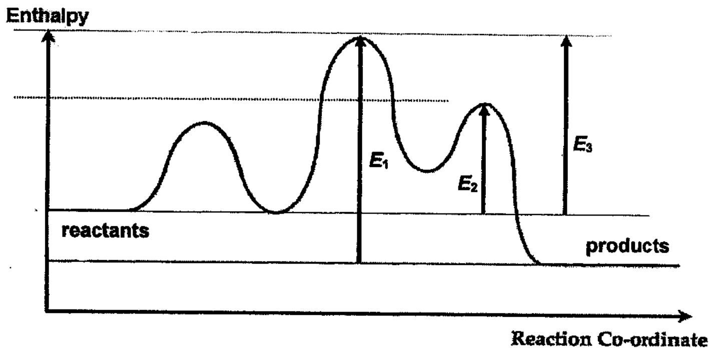
D 0, +2, +3

Transition elements have variable oxidation states.

Let the <u>sum</u> of oxidation numbers of the three Cu atoms be x.

$2(+3) + 2(+2) + 2(+2) + x + 10(-2) = 0$
$x = +6$

9 The energy profile diagram below represents a certain three-step reaction.



Which statements are correct about the above reaction?

1 E_3 is the activation energy of the second step.

2 ΔH can be obtained by subtracting E_2 from E_1.

3 There are equal number of intermediates and transition states.

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

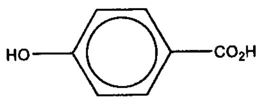
1 E_3 is the activation energy of the second step.

2 ΔH can be obtained by subtracting <u>E_3 from E_1</u>.

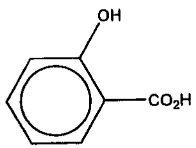
3 There <u>may not be</u> equal number of intermediates and transition states.

BP~74

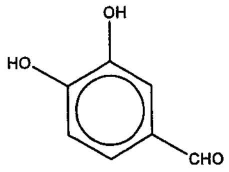
10 4-hydroxybenzoic acid (A), 2-hydroxybenzoic acid (B) and 3,4-dihydroxybenzaldehyde (C) share the same molecular formula.



4-hydroxybenzoic acid



2-hydroxybenzoic acid



3,4-dihydroxybenzaldehyde

All three compounds combust exothermically. Their standard enthalpy changes of formation are tabulated below.

	standard enthalpy change of formation / kJ mol^{-1}
4-hydroxybenzoic acid	−481
2-hydroxybenzoic acid	−493
3,4-dihydroxybenzaldehyde	−392

Which statements are correct?

1 2-hydroxybenzoic acid and 3,4-dihydroxybenzaldehyde are chain isomers.

2 The magnitude of the standard enthalpy change of combustion decreases in the order C > A > B.

3 The thermodynamic stability decreases in the order B > A > C.

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

Statement 1: They are functional group isomers.

To verify statements 2 and 3, it is best to represent both the enthalpy changes of formation and combustion in the same energy level diagram. With this combined energy level diagram, it is clear that statements 2 and 3 are true.

11 A 0.483 g sample of glycine (M_r = 75.0) was placed in a bomb calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.54 °C.

In a separate experiment using the same calorimeter, the combustion of 0.986 g of benzoic acid (M_r = 122.0) gave a temperature rise of 2.14 °C. The enthalpy change of combustion of benzoic acid is −3054 kJ mol^{-1}.

What is the enthalpy change of combustion, in kJ mol^{-1}, of glycine?

A −615 kJ mol^{-1}

B −967 kJ mol^{-1}

C −2423 kJ mol^{-1}

D −3812 kJ mol^{-1}

In the experiment with benzoic acid,
No. of moles of benzoic acid combusted = 0.986 / 122 = 0.008082
q = $-\Delta H_c$ × no. of moles of benzoic acid = 3054 × 0.008082 = 24.68 kJ
Heat capacity of the bomb calorimeter = 24.68 / 2.14 kJ °C^{-1}

In the experiment with glycine,
No. of moles of glycine combusted = 0.483 / 75 = 0.00644
q = (24.68 / 2.14) × 0.54 = 6.228 kJ
Enthalpy change of combustion of glycine = −6.228/ 0.00644 = −967 kJ mol^{-1}

12 Ethyl formate undergoes a slow acid-catalysed hydrolysis in water.

$$HCO_2CH_2CH_3 + H_2O \xrightarrow{H^+} HCO_2H + CH_3CH_2OH$$

The rate law is found to be

$$\text{rate} = k[HCO_2CH_2CH_3][H^+]$$

When 0.1 mol dm^{-3} of HC*l* is reacted with 0.4 mol dm^{-3} of ethyl formate, the half-life was found to be 62 min.

Another reaction was carried out with 0.3 mol dm^{-3} of HC*l* and 0.4 mol dm^{-3} of ethyl formate.

How long does it take for the concentration of ethyl formate to fall to 0.050 mol dm^{-3}?

A 31 min **B** 62 min **C** 93 min **D** 124 min

When [HCl] = [H$^+$] = 0.1 mol dm^{-3},
t½ = 62 min.
When [HCl] = [H$^+$] = 0.3 mol dm^{-3} (increased by 3 times),
t½ = 62/3 min.
For [ester] to fall to 0.050 mol dm^{-3}, three t½ are required.
Time taken = 3 x (62/3) = 62 min

13 The decomposition of phosphorus pentachloride is reversible.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The rate constants of the forward and backward reactions are given as k_1 and k_{-1} respectively.

What happens to the values of k_1, k_{-1}, K_c and the equilibrium position if an inert gas is introduced into the reaction vessel at constant temperature and pressure?

	k_1	k_{-1}	K_c	equilibrium position
A	unchanged	unchanged	unchanged	unchanged
B	increases	decreases	increases	shifts to right
C	decreases	increases	decreases	shifts to left
D	unchanged	unchanged	unchanged	shifts to right

Addition of an inert gas does not change the value of rate constant.

At a constant pressure, the position of equilibrium shifts towards the direction of the greater amount of gas.

14 Ammonium carbamate, NH_2COONH_4, undergoes thermal decomposition.

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g) \qquad \Delta H > 0$$

A vessel containing only NH_2COONH_4 is heated to 250 °C. The reaction reached equilibrium at time t_1. Subsequently both the temperature and volume of the vessel are decreased, and the reaction established a new equilibrium at time t_2.

Which statements are correct?

1 At t_2, $P_{NH_3} : P_{CO_2}$ is 2 : 1.
2 The rate of the forward reaction at t_1 is the same as that at t_2.
3 The degree of decomposition of NH_2COONH_4 at t_1 is smaller than that at t_2.
4 Decreasing the volume of the vessel at constant temperature has no effect on the equilibrium partial pressures of NH_3 and CO_2.

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

Statement 1	Correct. As there are no addition of any reactant or product to the system, the mole ratio of $NH_3 : CO_2$ should always stay the same at 2 : 1 (following the stoichiometric ratio of the balanced equation). Since p α n, $P_{NH_3} : P_{CO_2}$ is also 2 : 1 at t_2.
Statement 2	Incorrect. Since the temperature at t_1 is higher than that at t_2, the rate of the forward (and backward) reaction at t_1 is greater than that at t_2. (Recall that at higher temperatures, a greater proportion of the reactant molecules have energy greater than or equal to the activation energy for reaction. Hence, the frequency of effective collisions increases resulting in an increase in rate of reaction.)
Statement 3	Incorrect. By Le Chatelier's Principle, a decrease in temperature will favour the backward exothermic reaction and a decrease in volume (or increase in total pressure) will favour the backward reaction which reduces the number of gas particles. Hence at t_2, the degree of decomposition of NH_2COONH_4 is smaller than that at t_1.
Statement 4	Correct. Decreasing the volume of the vessel will cause the total pressure (and partial pressures of NH_3 and CO_2) to increase. By Le Chatelier's Principle, the equilibrium position will shift left to reduce the number of gas particles and the partial pressures of NH_3 and CO_2 will decrease. Since the equilibrium constant (K_p = $(P_{NH_3})^2(P_{CO_2})$) remains unchanged (as temperature is constant) and the $P_{NH_3} : P_{CO_2}$ stays the same at 2 : 1, the equilibrium partial pressures of NH_3 and CO_2 at t_2 will be the same as that at t_1.

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15 Nitrogen dioxide can decompose to form nitrogen monoxide and oxygen.

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

When 2.50 mol of nitrogen dioxide was allowed to undergo decomposition in a 0.8 dm^3 container, 0.528 mol of oxygen was present at equilibrium.

What is the numerical value of the equilibrium constant, K_c, for this reaction?

A 3.54 **B** 2.83 **C** 0.353 **D** 0.282

	$2NO_2(g)$	⇌	$2NO(g)$	+	$O_2(g)$
Initial n / mol	2.50		0		0
Change in n / mol	−1.056		+1.056		+0.528
Eqm n / mol	1.444		1.056		0.528

$$K_c = \frac{\left(\frac{1.056}{0.8}\right)^2\left(\frac{0.528}{0.8}\right)}{\left(\frac{1.444}{0.8}\right)^2}$$

$= 0.35296$

$= 0.353$ mol dm^{-3}

16 The position of equilibrium lies to the right in each of these reactions.

Reaction 1: $N_2H_4 + HOCl \rightleftharpoons N_2H_5^+ + ClO^-$
Reaction 2: $N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$

Which statement can be deduced from the information given above?

A The order of acid strength is $HOCl < N_2H_5^+ < NH_4^+$.

B N_2H_4 is the Bronsted–Lowry acid in Reaction 1.

C $N_2H_5^+$ and NH_3 are a conjugate acid–base pair in Reaction 2.

D N_2H_4 is a weaker base than NH_3

Option A: Incorrect
Since the POE lies to the right for both reactions, $HOCl$ is a stronger acid than $N_2H_5^+$ from Reaction 1 as it prefers to donate a proton. Likewise for Reaction 2 where $N_2H_5^+$ is a stronger acid than NH_4^+.

Option B: Incorrect
They do not differ by just one proton.

Option C: Incorrect
Since the POE lies to the right for both reactions, $HOCl$ is a stronger acid than $N_2H_5^+$ from Reaction 1 as it prefers to donate a proton. Likewise for Reaction 2 where $N_2H_5^+$ is a stronger acid than NH_4^+.

Option D: Correct
N_2H_4 is indeed a weaker base than NH_3 because in Reaction 2, the POE lies to the right.

17 The value of pK_w at 80 °C is 13.94.

What is the pH of an aqueous solution of 0.05 mol dm^{-3} $Ba(OH)_2$ at 80 °C?

A 12.64 **B** 12.94 **C** 13.44 **D** 13.94

pH = pK_w – pOH = 13.94 + log (0.10) = 12.94

18 The table below shows the numerical values of the solubility products (measured at 25 °C) for some salts.

Salt	$CdCO_3$	FeS	$CoCO_3$	CuS
K_{sp}	1.0×10^{-12}	6.0×10^{-19}	1.0×10^{-10}	8.0×10^{-37}

Which statement can be deduced from the information given above?

A CuS is more soluble than FeS.

B $CdCO_3$ is more soluble than $CoCO_3$.

C The solubility of these four salts will be increased at lower pH.

D The K_{sp} value of CuS will decrease as less of it can dissolve when copper(II) nitrate is added to a saturated solution.

C At higher [H^+]

$H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$

$CdCO_3(s) \rightleftharpoons Cd^{2+}(aq) + CO_3^{2-}$

[CO_3^{2-}] decreases, and the position of equilibrium shifts to the right. Hence solubility increases.

This is similar for the other three salts.

$H^+(aq) + S^{2-}(aq) \rightarrow HS^-(aq)$

A Units are different. We need to calculate solubility from K_{sp} values.

CuS is <u>less</u> soluble than Ag_2S.

B Units are the same. Hence we can compare the K_{sp} values.

$CoCO_3$ is <u>more</u> soluble than $CdCO_3$.

D The K_{sp} value remains constant if temperature remains constant.

However, the solubility of CuS will decrease in this case.

19 The solubilities of AgC*l* and AgI are x and y mol dm^{-3} respectively at 298 K.

Which statements are correct about a solution saturated with both AgC*l* and AgI?

1 $[Ag^+] = x + y$
2 $[Ag^+] = [I^-] + [Cl^-]$
3 $[I^-] < y$

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

Given solubility of AgC*l* and AgI are x and y mol dm^{-3} respectively,

$K_{sp}(AgCl) = [Ag^+][Cl^-] = x^2$ mol^2 dm^{-6}
$K_{sp}(AgI) = [Ag^+][I^-] = y^2$ mol^2 dm^{-6}

In a solution saturated with **both** AgC*l* and AgI, let the solubility of AgC*l* and AgI be x' and y' mol dm^{-3} respectively.

$[Ag^+] = x' + y'$, $[Cl^-] = x'$, $[I^-] = y'$

$K_{sp}(AgCl) = [Ag^+][Cl^-] = (x' + y')(x') = x^2$

$K_{sp}(AgI) = [Ag^+][I^-] = (x' + y')(y') = y^2$

$(x' + y')(x') + (x' + y')(y') = x^2 + y^2$

1 ✗ $(x' + y')^2 = x^2 + y^2$

$[Ag^+] = x' + y' = \sqrt{x^2 + y^2} < x + y$

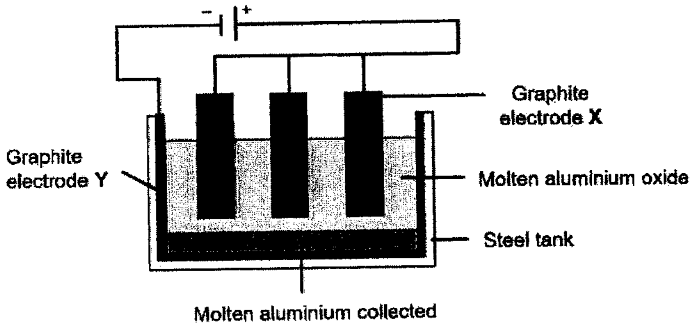
3✓ $[I^-] = y' = \dfrac{y^2}{x' + y'} = \dfrac{y^2}{\sqrt{x^2 + y^2}} < y$

2✓ $[Ag^+] = x' + y' = [Cl^-] + [I^-]$

$\Rightarrow$ **D**

BP-78

20 Aluminium is extracted from its ore by electrolysis.



Which statements are correct?

1 Aluminium ions migrate to electrode X.
2 Oxygen gas is produced.
3 Electrons move from electrode **X** to electrode **Y** via the external circuit.

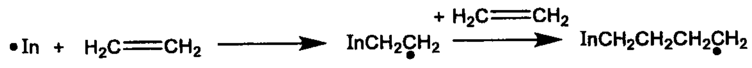
A 2 and 3 **B** 1 only **C** 1 and 3 **D** 1 and 2

Option **2** is correct.
Electrode **X** is the positive electrode i.e. the anode, anions (i.e. O^{2-}) migrate here and oxidation takes place. O^{2-} is oxidised to $O_2(g)$.

Option **3** is correct.
Electrons move from negative terminal of the battery to electrode **Y,** and electrode **X** to the positive terminal of the battery. Thus, electrons move from electrode **X** to electrode **Y**.

Option **1** is incorrect.
Electrode **Y** is the negative electrode i.e. the cathode, cations (i.e. Al^{3+}) migrate here and reduction takes place.

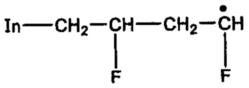
21 Free radical addition is a mechanism used in the synthesis of some addition polymers. Alkene monomers will polymerise in the presence of a radical initiator (In•). For instance, the synthesis of polyethene begins as such.



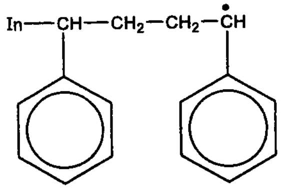
$$\bullet In + H_2C{=}CH_2 \longrightarrow InCH_2\dot{C}H_2 \xrightarrow{+\,H_2C{=}CH_2} InCH_2CH_2CH_2\dot{C}H_2$$

Which chain could **not** have arisen from free radical addition?

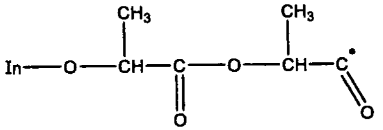
A



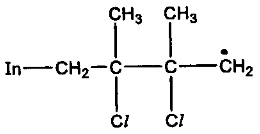
B



C



D



For free radical addition to occur, students must recognise that an alkene is needed as the monomer.

A uses fluoroethene, $H_2C{=}CHF$

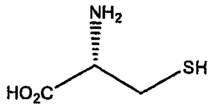
B uses phenylethene, $(C_6H_5)CH{=}CH_2$

D uses 2-chloropropene, $H_2C{=}C(CH_3)Cl$

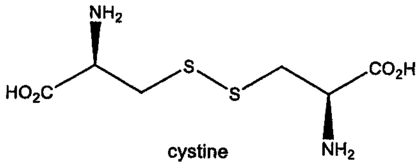
There is no known monomer that can reasonably give rise to the structure in **C**. More accurately, it should be formed as a condensation polymer of lactic acid, 2-hydroxypropanoic acid.

22 Cysteine and cystine are important biochemicals in which the former is biosynthesised from the latter. Cysteine is a naturally occurring α-amino acid, while djenkolic acid is a non-protein amino acid found in the djenkol beans of the Southeast Asian plant.

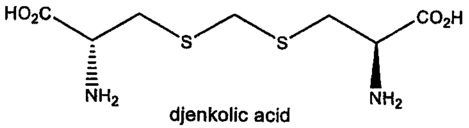
The three pK_a values of cysteine are 1.71, 8.33 (belonging to the thiol, -SH), and 10.78.



cysteine



cystine



djenkolic acid

Which statement about cysteine, cystine and djenkolic acid is true?

A Cystine is a *meso* compound, hence it is non-chiral.

B Cysteine exists solely in its zwitterionic form at pH 5.02.

C Cystine and cysteine share the same empirical formula.

D There are four stereoisomeric forms of djenkolic acid because there are two chiral atoms in djenkolic acid.

A is not true because there is no internal mirror plane in this stereoisomer of cystine.

B – 5.02 is indeed the isoelectric point of cysteine.

C – not true. 2 times cysteine – 2H = cystine.

D – not true. There are only 3 stereoisomers of djenkolic acid, which includes the one in the question. A pair of enantiomers (one of which is in the question) and the *meso* compound.

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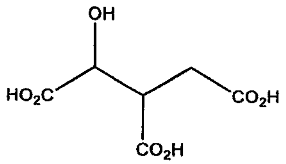
23 Isocitric acid is a naturally occurring compound found in fruit juices, vegetables, and other biological systems. It plays an important role in the citric acid cycle.



Which compound, on reaction with isocitric acid in the presence of concentrated sulfuric acid, will produce an organic product of molecular formula $C_9H_{12}O_8$?

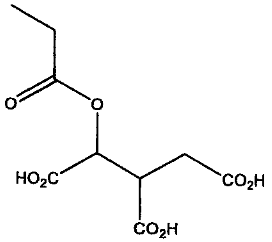
A methanoic acid

B propan-2-ol

C methanol

D propanoic acid

The product is formed via esterification reaction between propanoic acid and the alcohol in isocitric acid.



BP~80

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

A sample of an ester is hydrolysed by heating under reflux with aqueous sodium hydroxide. The two organic products of the hydrolysis are separated, purified and weighed.

Which ester would produce a 3:1 mass ratio of the two products obtained?

A propyl methanoate

B ethyl ethanoate

C butyl methanoate

D methyl propanoate

Methanol (molar mass 32 g mol^{-1}) and sodium propanoate (molar mass 96 g mol^{-1}) are the basic hydrolysis products from methyl propanoate. Indeed the mass ratio of the product is 96 / 32 = 3.

Propanol (molar mass 60 g mol^{-1}) and sodium methanoate (molar mass 68 g mol^{-1}) are the basic hydrolysis products from propyl methanoate. The mass ratio of the product is 68 / 60.

Ethanol (molar mass 46 g mol^{-1}) and sodium ethanoate (molar mass 82 g mol^{-1}) are the basic hydrolysis products from ethyl ethanoate. The mass ratio of the product is 82 / 46.

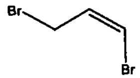
Butanol (molar mass 74 g mol^{-1}) and sodium methanoate (molar mass 68 g mol^{-1}) are the basic hydrolysis products from butyl methanoate. The mass ratio of the product is 74 / 68.

25 0.04 mol of each of the following compounds was heated with KOH(aq), followed by addition of dilute HNO_3 and $AgNO_3(aq)$.

Which compound will produce the highest mass of AgBr(s)?

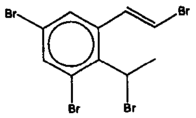
A $BrCOCH_2COBr$

B



C $CH_3CH_2CH_2Br$

D



Per mole of each compound:

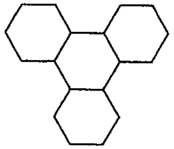
A: two moles of bromide formed.

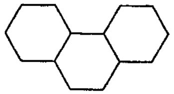
B: one mole of bromide formed.

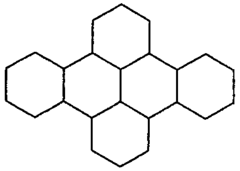
C: one mole of bromide formed.

D: one mole of bromide formed.

26 Which pair of compounds will **not** form when cyclohexane is reacted with excess bromine gas in the presence of ultraviolet light?

1 

2 

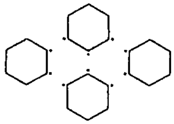
3 

4 

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

1 is formed by three cyclohexyl radicals.

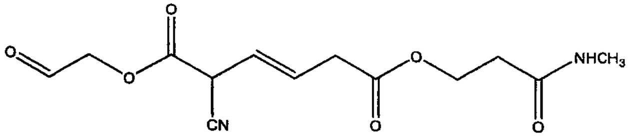
3 is formed by four cyclohexyl radicals.



27 Esters can be reduced by $LiAlH_4$ in dry ether to give two alcohols as shown below.

$$RCOOR' \rightarrow RCH_2OH + R'OH$$

Which product may be formed when the following compound is reacted with excess $LiAlH_4$ in dry ether?



A $H_2NCH_2CH(CH_2OH)CH_2CH_2CH_2OH$

B $NCCH(CO_2H)CH{=}CHCH_2CO_2H$

C $HOCH_2CH_2NHCH_3$

D $HOCH_2CH_2OH$

The products formed are, in order of fragments from the above compound,

- Ethane-1,2-diol (option D)
- $HOCH_2CH(CH_2NH_2)CH{=}CHCH_2CH_2OH$
- $HO(CH_2)_3NHCH_3$

BP-81

28 Chymotrypsin is an enzyme that hydrolyses protein into smaller peptides and amino acids. It specifically hydrolyses the peptide bond on the carboxylic end of Phe.

The structure of tetrapeptide **X** and M_r of selected amino acids are given below.

tetrapeptide **X**: Val–Lys–Phe–Arg

amino acid	M_r
Val	117
Lys	146
Phe	165
Arg	174

What are the M_r of the two fragments obtained when tetrapeptide **X** is hydrolysed by chymotrypsin?

A 174 and 392

B 174 and 428

C 245 and 321

D 263 and 339

Answer: A

By convention, a polypeptide chain is drawn from the amino end (N-terminus) at the left end to the carboxyl end (C-terminus) at the right end.

N⟶C N⟶C N⟶C N⟶C

Tetrapeptide **X**: Val——Lys——Phe——Arg

Since chymotrypsin digested **X** at the carboxylic acid end of Phe, then the two fragments obtained are Val–Lys–Phe and Arg.

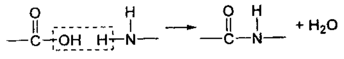
M_r of Val–Lys–Phe

117 + 146 + 165 – 2(18) = **392**

M_r of Arg

174

1 H_2O (M_r = 18) is lost when 2 amino acids form a peptide. 2 H_2O are lost when 2 amino acids form 2 peptide linkages



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

Which statement is true?

A CoF_3 is stable in water because $2Co^{3+} + 2F^- \rightarrow F_2 + 2Co^{2+}$ is a non-spontaneous reaction.

B It is possible to prepare aqueous iron(III) iodide.

C $Cr_2O_7^{2-}$ is the oxidised form of CrO_4^{2-} because it contains more oxygen atoms.

D The oxidation of iron(II) to iron(III) can be prevented at lower pH.

Option A: False

CoF_3 actually undergoes redox with water itself. It reacts with water to make hydrofluoric acid, oxygen, and CoF_2. The E_{cell} = 1.89 – 1.23 = + 0.66 V > 0

Option B: False

Fe^{3+} undergoes redox with iodide in aqueous medium.

E_{cell} = 0.77 – 0.54 = + 0.23 V > 0

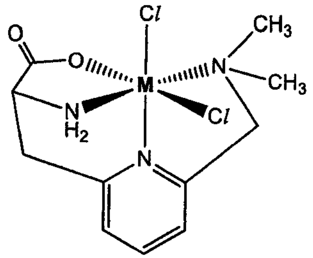
Option C: False

The oxidation states of Cr in both are +6.

Option D: True

The standard reduction potential of Fe^{3+}/Fe^{2+} is positive, while that of $Fe(OH)_3/Fe(OH)_2$ is negative. In alkaline medium, it is easy to oxidise $Fe(OH)_2$ to $Fe(OH)_3$. However in acidic or neutral medium it is not as easy to oxidise Fe^{2+} to Fe^{3+}.

30 Which statement regarding the neutral metal complex below is **false**?



A The oxidation number of **M** in the complex is +2 because the complex is neutral and there are two chloride ligands.

B The coordination number of the complex is 6.

C The complex contains a tetradentate ligand.

D The complex contains a ligand which is an α-amino acid.

Option A: False

The tetradentate ligand is not a neutral ligand, but carries a negative charge on the carboxylate end.

The oxidation number of M should be +3 instead.

Option B: True.

Coordination number is the number of dative bonds around M which is equal to 6 in the complex.

Option C: True.

Option D: True

Anglo-Chinese Junior College
JC2 Preliminary Examinations
Higher 2

A Methodist Institution
(Founded 1886)

CANDIDATE NAME	SUGGESTED SOLUTIONS	FORM CLASS	
TUTORIAL CLASS		INDEX NUMBER	

CHEMISTRY **9729/02**
Paper 2 Structured Questions
27 August 2025
2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number and name in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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

For Examiners' use only	
1	/ 7
2	/ 12
3	/ 10
4	/ 11
5	/ 11
6	/ 16
7	/ 8
Total	/ 75

This document consists of **19** printed pages.

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1 When ammonium dichromate(VI) is added gradually to molten ammonium thiocyanate, Reinecke's salt is formed. It has the formula $NH_4[Cr(SCN)_x(NH_3)_y]$ and the following composition by mass: Cr 15.5 %; S 38.15 %; N 29.2 %.

(a) Calculate the values of x and y in the above formula.

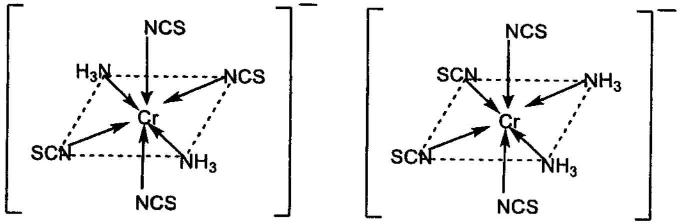
Given Cr is 15.5% of total
Therefore M_r = 100 X 52.0 /15.5 = 335.5
For **S**, 38.15 / 100 x 335.5 = 128
n**S** =128 / 32.1 = 4
x = 4
Therefore $NH_4[Cr(SCN)_4(NH_3)_y]$ = 335.5
Therefore 18 + 52 + 4 x 58.1 + 17y = 335.5
Therefore 17y = 33.5
y = 2

[2]

(b) Suggest a shape for the complex anion.
octahedral

....[1]

(c) Draw two possible structures for the anion and state the type of isomerism it exhibits.



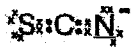
cis-trans isomerism

....[2]

(d) Linkage isomerism is a form of constitutional isomerism in which certain coordination compounds have the same composition but differ in which atom of the ligand is bonded to the metal.

Examples of linkage isomers are violet-colored $[(NH_3)_5Co\text{-}SCN]^{2+}$ (S being the donor atom) and the orange $[(NH_3)_5Co\text{-}NCS]^{2+}$ (N being the donor atom).

Draw the dot-and-cross diagrams of NCS^- and SCN^-. In each diagram, underline the donor atom.



[2]

[Total: 7]

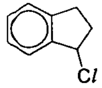
BP - 85

2 (a) **X** can be converted to **Y** via three steps as shown in the reaction scheme below.

(i) There are two isomers possible for **P**. Draw the structure of **P** that will eventually lead on to **Y**.

P

[1]



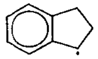
(ii) Explain if your answer in **(a)(i)** is the major product.

....

....

....[2]

Yes

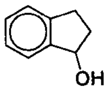


The above radical that leads to P is much more stable as it is benzylic in nature, where the unpaired electron can be delocalised into the benzene ring.
Can answer in terms of stability or probability

(iii) Draw the structure of **Q**. State the reagents and conditions to synthesise **Q** from **P**.

Q

reagents & conditions ....[2]



NaOH(aq) and heat

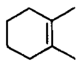
(b) (i) **G** has the molecular formula, C_8H_{14}. Treating **G** with hydrogen in the presence of Ni, yields **H**, with the molecular formula, C_8H_{16}. Upon mild oxidation, **G** gives a tertiary diol, **J**. Upon vigorous oxidation **G** gives a diketone, **K**, which reacts with aqueous alkaline iodine to produce hexanedioic acid upon acidification.

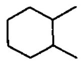
Draw the structures of **G**, **H**, **J** and **K**.

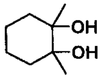
G **H**

J **K**

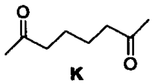
[4]


G


H



J



K

(ii) **L** is an isomer of **G**. Treating **L** with hydrogen in the presence of Ni, yields **W**, with the molecular formula, C_8H_{18}. It undergoes vigorous oxidation to give propanone as the only organic product in addition to CO_2.

Deduce the structure of **L** with reasoning.

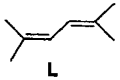
L

....

....

....

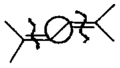
....[3]



L

L, C_8H_{14} with hydrogen in the presence of Ni → reduction. Hence, 2C=C present in **L**.

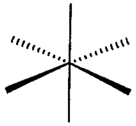
L undergoes vigorous oxidation to give propanone and CO_2 → L has 2  structures.

CO₂ formed from 

[Total: 12]

3 **(a)** At the time of its discovery by Scottish chemist Sir William Ramsay, the noble gas xenon was considered to be inert. It has since been discovered that xenon will react with strong oxidants. For example, xenon reacts with fluorine gas, forming a series of fluorides, XeF_2, XeF_4 and XeF_6.

(i) The structure of xenon tetrafluoride has six electron pairs on xenon and therefore the structure is based on an octahedral configuration as shown below.



On Fig. 3.1, draw the two possible three-dimensional arrangements of the electron pairs on xenon in xenon tetrafluoride and tick the one observed, that gives the molecule its shape, explaining your choice with appropriate reasoning based on the principles of the VSEPR theory.

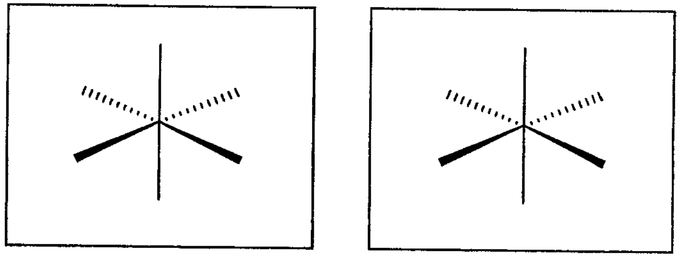


Fig. 3.1

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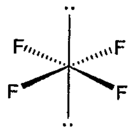
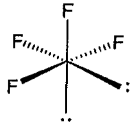
....[2]

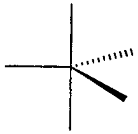


Adopted Arrangement



The **square planar arrangement** is adopted to maximise the separation between the **two lone pairs** by placing them on opposite sides of **plane with the maximum angular separation of 180°** so as to minimise the repulsion due to them resulting in a more stable arrangement.

(ii) The structure of xenon difluoride has five electron pairs on xenon and therefore the structure is based on a trigonal bipyramidal configuration as shown below.



On Fig. 3.2, draw the three possible three-dimensional arrangements of the five electron pairs on xenon in xenon difluoride and tick the one observed, that gives the molecule its shape, explaining your choice with appropriate reasoning based on the principles of the VSEPR theory.

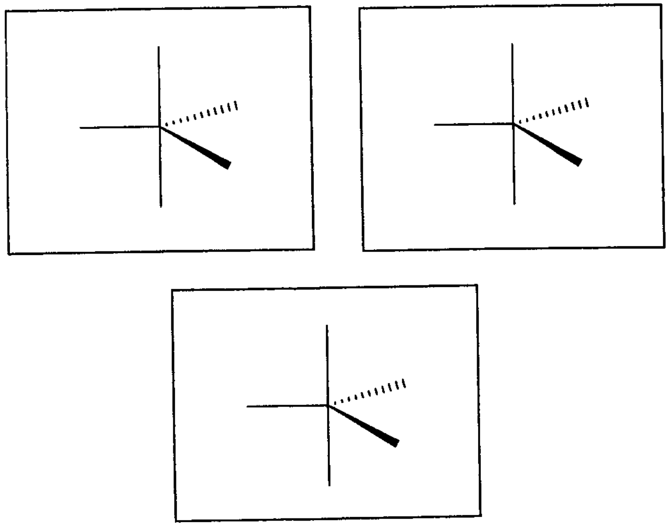


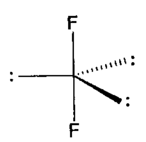
Fig. 3.2

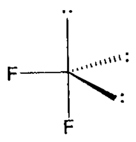
....

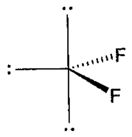
....

....

....[3]







Adopted Arrangement

The **linear arrangement** is adopted to maximise the separation between the three lone pairs by placing them in the **equatorial plane with the maximum angular separation of 120°** so as to minimise the repulsion due to them resulting in a more stable arrangement.

(b) The kinetics of the formation of xenon difluoride from xenon and fluorine has been studied under various conditions. At 120 °C, the rate equation for the formation of XeF_2 is found to be first order with respect to Xe and zero order with respect to F_2.

(i) Write the rate equation for the formation of XeF_2 and suggest the units for the rate constant.

Rate = k [Xe] or Rate = k P(Xe)
$k = t^{-1}$ or s^{-1} or min^{-1}

[2]

(ii) The Arrhenius equation describes the relationship between the rate constant and temperature.

$$k = Ae^{-\frac{E_a}{RT}}$$

The uncatalysed reaction between xenon and fluorine to form XeF_2 at a temperature T has a rate constant k, with collision frequency factor A and activation energy, E_a.

When a nickel difluoride catalyst is added to the reaction mixture, the rate constant changes to k_{cat}, with a different collision frequency A_{cat} and a different activation energy, E_{cat}. It is found that the catalysed reaction is 13 times faster at 120 °C and 23 times faster at 100 °C. The change in activation energy, $\Delta E = E_a - E_{cat}$.

Assuming that the collision frequency factors do not depend on temperature, write an expression for the ratio k_{cat}/k in terms of T, ΔE and any constants.

$$\frac{k_{cat}}{k} = \frac{A_{cat}\, e^{-\frac{E_{cat}}{RT}}}{Ae^{-\frac{E_a}{RT}}}$$

$$\frac{k_{cat}}{k} = \frac{A_{cat}}{A} e^{\frac{\Delta E}{RT}}$$

[1]

(iii) Hence, using the ratio in **(b)(ii)** and the information given below, calculate the change in activation energy, ΔE, in kJ mol^{-1}, when the temperature increased from 373 K to 393 K. Given that $\frac{k_{cat}(393\ K)}{k(393\ K)} = 13$ and $\frac{k_{cat}(373\ K)}{k(373\ K)} = 23$.

$$ln\frac{k_{cat}}{k} = \frac{\Delta E}{RT} + ln\frac{A_{cat}}{A}$$

$$\ln 13 = \frac{\Delta E}{393R} + ln\frac{A_{cat}}{A} \quad ...(1)$$

$$\ln 23 = \frac{\Delta E}{373R} + ln\frac{A_{cat}}{A} \quad ...(2)$$

(1) – (2)

$$\ln 13 - \ln 23 = \frac{\Delta E}{393R} - \frac{\Delta E}{373R}$$

$\ln\frac{13}{23} = \frac{\Delta E}{R}(\frac{1}{393} - \frac{1}{373})$

$\Delta E = +34.7 \text{ kJ mol}^{-1}$

[2]

[Total: 10]

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4 (a) Ethanol is dissolved in blood and distributed to organs in the body. As a volatile compound, ethanol can be vaporised quite easily. In the lungs, ethanol can change its phase from liquid to gaseous and it can be exhaled with air. Since the concentration of alcohol vapor in lungs is directly related to its concentration in blood, blood alcohol concentration can be measured using a device called a breathalyser.

In one of the older versions of breathalyser, a suspect breathes into the device and exhaled air is allowed to pass through a solution of potassium dichromate which oxidises ethanol to acetic acid. This oxidation is accompanied by a colour change from orange to green and a detector records the change in colour intensity, which is used to calculate the percentage of alcohol in breath. When the oxidation of alcohol by potassium dichromate is carried out in an electrochemical cell, either the electrical current generated by this reaction or the change in the electromotive force can be measured and used for the estimation of alcohol content of blood.

(i) Write a balanced ionic equation for the oxidation of ethanol by the dichromate ion in acidic solution.

$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e$

$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$ from Data Booklet

$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$

[2]

(ii) If the standard potential for the reduction of $Cr_2O_7^{2-}$ to Cr^{3+} is 1.330 V and that for the reduction of ethanoic acid to ethanol is 0.058 V, calculate the standard electromotive force, $E^\ominus$, for the overall reaction.

EMF = 1.330 – 0.058 = +1.272 V or +1.27 V

[1]

(iii) When a suspect breathes into a breathalyser which is designed as an electrochemical cell, the oxidation of the ethanol generates a current of 0.10 A for 60 s. Calculate the mass of alcohol in the exhaled breath.

Q = It = 0.1 x 60 = 6.0 C

n(e) transferred from 3 moles of ethanol to 2 moles of $Cr_2O_7^{2-}$ = 12

Hence, $3CH_3CH_2OH \equiv 12F$; $CH_3CH_2OH \equiv 4F$

$n(CH_3CH_2OH) = 6 / [4(96500)] = 1.55 \times 10^{-5}$ mol

$m(CH_3CH_2OH) = 1.55 \times 10^{-5} \times 46 = 7.15 \times 10^{-4}$ g

[3]

(iv) In calculating the alcohol content in blood from the mass of alcohol in a breath, the "2100:1 partition ratio" needs to be considered. The ratio states that each milliliter of blood has 2100 times the mass of ethanol as each milliliter of expired air.

If the volume of expired air described in **(a)(iii)** is 60.0 cm^3, calculate the mass of alcohol per cm^3 of blood.

Hence, 7.15×10^{-4} g of ethanol from 60 cm^3 of expired air means 1.19×10^{-5} g per cm^3 of expired air.

Thus, mass of alcohol per cm^3 of blood = $2100 \times 1.19 \times 10^{-5} = 0.0250$ g

[1]

BP-90

(b) The value of the solubility product is related to the Gibbs free energy change, ΔG°, in J mol^{-1}, by the mathematical expression given below.

$$K_{sp} = 10^{-\left(\frac{\Delta G^\circ}{2.3RT}\right)}$$

Using the expression above and the cycle in Fig. 4.1 that involves the standard reduction potentials in Table 4.1, calculate the numerical value of the solubility product, K_{sp}, of AgCN at 25 °C.

Table 4.1

	E° / V
$AgCN(s) + e \rightleftharpoons Ag(s) + CN^-(aq)$	–0.01
$Ag^+(aq) + e \rightleftharpoons Ag(s)$	+0.80

$$\begin{tikzcd}
AgCN(s) \arrow[rr, "\rightleftharpoons", phantom] \arrow[dr, "+e"'] & & Ag^+(aq) + CN^-(aq) \arrow[dl, "+e"] \\
& Ag(s) + CN^-(aq) &
\end{tikzcd}$$

Fig. 4.1

$AgCN(s) + e \rightleftharpoons Ag(s) + CN^-(aq)$ $\Delta G^\circ = -[1 \times 96500 \times (-0.01)] = +0.965\ kJ\ mol^{-1}$
$Ag^+(aq) + e \rightleftharpoons Ag(s)$ $\Delta G^\circ = -[1 \times 96500 \times (0.80)] = -77.2\ kJ\ mol^{-1}$

Hence,
$AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$ $\Delta G^\circ = +0.965 - (-77.2) = +78.2\ kJ\ mol^{-1}$

Thus,
$K_{sp} = 10^{-\frac{78200}{2.3 \times 8.31 \times 298}}$
$= 1.86 \times 10^{-14}$

[4]

[Total: 11]

5 The Haber process is used to make ammonia, the main use of which is in fertilisers that are often sprayed on crops. Around 1% of the entire global energy supply is used in the Haber process and so research groups are looking to find more sustainable methods of producing ammonia.

One recently published approach to making ammonia uses the following three-step method.

Step 1 Electrolysis of molten lithium hydroxide at 750 K to form lithium metal.

$$4LiOH \longrightarrow 4Li + 2H_2O + O_2$$

Step 2 Reaction of lithium metal with nitrogen to form lithium nitride.
Step 3 Reaction of lithium nitride with water to re-form lithium hydroxide and ammonia.

Thus, the lithium hydroxide formed in Step 3 can be re-used in Step 1 and the process can be repeated.

The relevant thermochemical data are provided in Table 5.1.

Table 5.1

At 750 K	LiOH	Li	H_2O	O_2
ΔH_f / kJ mol^{-1}	–446.0	+15.0	–268.0	+15.8
ΔS_r for step 1 at 750 K is +427 J K^{-1} mol^{-1}				

(a) Explain why the enthalpy changes of formation of the elements Li and O_2 are not zero at 750 K.

The enthalpy of formation of an element in its standard state is zero because no energy is required to form it from itself.
OR
Enthalpy is a thermodynamic property that depends on temperature. As the temperature increases, because the element's energy content has changed due to the temperature change and hence the enthalpy of a substance (including elements) also increases.

....

....

....[1]

(b) Calculate ΔH_r and hence ΔG_r for Step 1 at 750 K.

$\Delta H_r = [4(+15) + 2(-268) + (+15.8)] - 4(-446) = +1320\ kJ\ mol^{-1}$
$\Delta G_r = 1320 - 750(427 \times 10^{-3}) = +1004\ kJ\ mol^{-1} \approx +1000\ kJ\ mol^{-1}$

[2]

(c) Given that the electrolysis will only proceed at an appreciable rate when the applied potential exceeds the electrochemical cell potential by 0.60 V, calculate the minimum potential that should be applied in Step 1.

$E_{cell} = -\Delta G_r/nF = -[1004 \times 10^3 / (4 \times 96500) = -2.60\ V$
Hence, $E_{applied} = |E_{cell}| + 0.60 = 2.60 + 0.60 = +3.20V$

[1]

(d) Write the chemical equations for Step 2 and Step 3. Hence calculate the stoichiometric ratio between the lithium produced in Step 1 and the ammonia produced in Step 3.

$6Li + N_2 \rightarrow 2Li_3N$
$Li_3N + 3H_2O \rightarrow NH_3 + 3LiOH$

Hence, Li : NH_3 is 3 : 1

[2]

(e) In a small-scale experiment, the researchers applied a current of 0.200 A for 1000 seconds. The yield of lithium production in this process was 88.5% in Step 1. The yield of Steps 2 and 3 can be assumed to be 100%.

Calculate the mass of lithium generated in Step 1.

Q = 0.2 × 1000 = 200 C
Amount of e = 200 / 9.65 × 10^4 = 0.00207 mol
Amount of Li = 88.5% × 0.00207 = 0.00183 mol
Mass of Li = 0.00183 × 6.9 = 0.0126 g

[2]

(f) Calculate the volume of ammonia produced, in cm^3, at room temperature and pressure.

Amount of NH_3 = amount of Li × 1/3 = 0.00183 × 1/3 = 6.11 × 10^{-4} mol
Volume of NH_3 = 6.11 × 10^{-4} × 24000 = 14.7 cm^3

[1]

(g) A potential application of this approach is to use renewable energy sources as the source of electricity for the electrolysis and to produce ammonia at a farm where it can be used straight away. The average size of a UK farm is 130 acres, and a farm requires 0.0770 tonnes of ammonia per acre annually.

If the lithium hydroxide was not recycled at the end of the process, calculate the total mass of lithium, in tonnes, that would have to be produced to generate the required mass of ammonia for a year. [1 tonne = 1000kg]

Mass of NH_3 required = 130 × 0.077 = 10.01 tonnes
Amount of NH_3 = 10.01 × 10^6 / 17.0 = 5.888 × 10^5 mol
Amount of Li = 5.888 × 10^5 × 3 = 1.766 × 10^6 mol
Mass of Li = 1.766 × 10^6 × 6.9 = 1.22 × 10^7 g = 12.2 tonnes

[2]

[Total: 11]

6 **(a)** Propanone can exist in ***keto*** and ***enol*** forms.

keto form of propanone

enol form of propanone

The enol form is derived from the keto form by transferring a hydrogen atom to the oxygen atom.

At room temperature and pressure, the keto form is the predominant form at equilibrium suggesting that the keto form is the more stable form.

Using bond energy data from the *Data Booklet*, calculate the enthalpy change for the above interconversion, and hence explain why the equilibrium lies heavily towards the keto form.

Bonds broken = 740 + 410 +350 = +1500 kJ mol^{-1}

Bonds formed = 460 + 610 + 360 = +1430 kJ mol^{-1}

ΔHr = 1500 – 1430 = +70 kJ mol^{-1}

Assuming $\Delta S \approx 0$, hence $\Delta G \approx \Delta H$

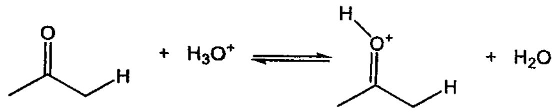
Since ΔG is positive, $K < 1$, hence equilibrium lies to the left.

[2]

(b) The conversion of keto form to the enol form of propanone can be catalysed by an acid.

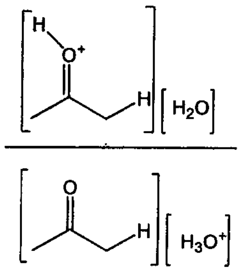
The first equilibrium step of the mechanism involves protonation of oxygen atom of the C=O bond as given below.

equlibrium 6.1



The K_c expression for equilibrium 6.1 is given as follows.

K_c =



(i) Write the K_a expressions for the acid dissociation of H_3O^+ and $(CH_3)_2C{=}OH^+$ using their respective equilibrium equations given below.

$H_3O^+ \rightleftharpoons H_2O + H^+$

$(CH_3)_2C{=}OH^+ \rightleftharpoons (CH_3)_2C{=}O + H^+$

K_a (H_3O^+) = $[H^+]$ $[H_2O]$ / $[H_3O^+]$
K_a $((CH_3)_2C{=}OH^+)$ = $[H^+]$ $[(CH_3)_2C{=}O]$ / $[(CH_3)_2C{=}OH^+]$

[2]

BP-91

BP-92

(ii) Hence, express K_c for equilibrium 6.1 in terms of the two K_a expressions in **(b)(i)**.

$K_c = K_a(H_3O^+) / K_a((CH_3)_2C{=}OH^+)$

[1]

(iii) Given that the pK_a of H_3O^+ is –1.7 and the pK_a of $(CH_3)_2C{=}OH^+$ is –7.2, calculate a value of K_c for equilibrium 6.1.

$K_c = (10^{1.7} / 10^{7.2}) = 10^{-5.5} = 3.16 \times 10^{-6}$

[1]

(iv) Given that $\Delta G^\circ = -RT \ln K$, calculate the Gibbs Free energy change, in kJ mol^{-1}, for equilibrium 6.1.

$\Delta G^\circ = -8.31 \times 298 \times \ln(10^{-5.5}) = +31361\ \text{J mol}^{-1} = +31.4\ \text{kJ mol}^{-1}$

[2]

(v) Based on your answers to the values of K_c and ΔG°, comment on the relative stability of the keto form versus the enol form.

....

....

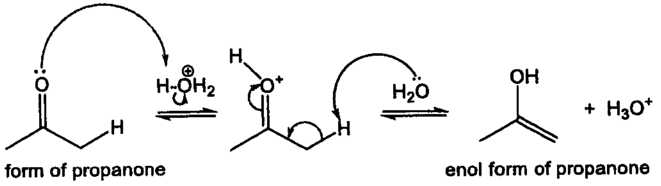
....

....[2]

K_c value is very small indicating that the keto form is predominant in the overall equilibrium.
Also ΔG° is very positive indicating that the enol form is not energetically favourable.

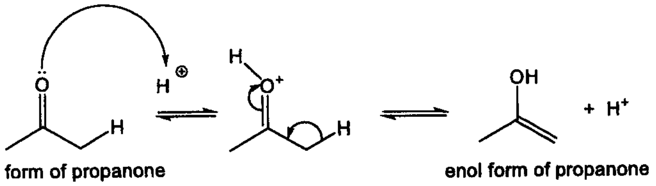
(vi) Tautomerisation is a type of isomerisation where two molecules with the same molecular formula but different connectivity (constitutional isomers) rapidly interconvert in a solution or equilibrium. The most well-known example is the interconversion between a keto (containing a carbonyl group) and an enol (containing an alcohol and a double bond) form of a molecule.

Outline the mechanism for the tautomerisation of propanone to its enol form catalysed by acid, showing all curly arrows, lone pairs and charges.

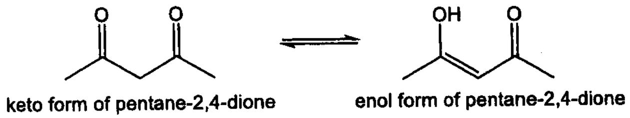


[3]

OR



(c) The enol form of pentane-2,4-dione is unusually stable and hence the equilibrium lies more towards the enol form.



It is also observed that the percentage of the enol form increases as the solvent used is changed from a polar solvent to a non-polar solvent.

(i) By comparing the structures of the enol form with the keto form, suggest a reason for the increased stability of the enol form in pentane-2,4-dione.

....

....[1]

Enol form is stabilised by intra-molecular hydrogen bonding OR

Conjugation of the C=O bond with the C=C bond also contributes to the stability.

(ii) Explain why the keto form is favoured with polar solvents.

....

....

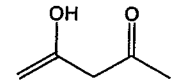
....

....[1]

Keto form participates in dipole-dipole interaction or hydrogen bond formation with polar solvents which suppresses intra-molecular hydrogen bonding.

In a non-polar solvent, the enol form becomes more stable through intramolecular hydrogen bonding.

(iii) Another enol form of pentane-2,4-dione, as shown below can also be drawn.



another enol form of pentane-2,4-dione

Explain if this enol form is likely to be formed as well.

....

....[1]

No / less likely

No conjugation between the C=O bond with the C=C bond.

[Total: 16]

7 **(a)** Solid magnesium hydroxide decomposes when heated to form two products. One of the products formed is steam.

(i) Construct a balanced equation, with state symbols, for the above reaction.

....[1]

$Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g)$

(ii) The variation in thermal stability of Group 2 hydroxides is similar to that of Group 2 carbonates.

Explain whether magnesium hydroxide is more or less thermally stable than barium hydroxide.

....

....

....

....

....

....

....[3]

Magnesium hydroxide is less thermally stable than barium hydroxide.

- ionic radius: $Mg^{2+} < Ba^{2+}$
- charge density: $Mg^{2+} > Ba^{2+}$
- polarising power: $Mg^{2+} > Ba^{2+}$
- extent of polarisation/distortion of OH^- electron cloud: $Mg(OH)_2 > Ba(OH)_2$
- extent of weakening of covalent bond (O-H) within the OH^- anion: $Mg(OH)_2 > Ba(OH)_2$

∴ thermal stability: $Mg(OH)_2 < Ba(OH)_2$

(b) **(i)** Using relevant data from the ***Data Booklet***, comment on the thermal stability of hydrogen bromide and hydrogen iodide.

....

....

....[1]

Bond energy of H-Br (366 kJ mol^{-1}) is more than bond energy of H-I (299 kJ mol^{-1}).

HI has a lower thermal stability as less energy is required to overcome the weaker covalent bond in H-I.

(ii) Identify a transition metal cation that can be used to differentiate the oxidising strengths of Br_2 and I_2. Explain your answer with appropriate workings.

The transition metal cation is Fe^{2+}.

From Data Booklet	$E^\ominus$ / V
$Br_2 + 2e \rightleftharpoons 2Br^-$	+1.07
$I_2 + 2e \rightleftharpoons 2I^-$	+0.54
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.77

$Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$ $\quad E^\ominus_{cell} = +0.30 \text{ V} > 0$

Br_2 can oxidise Fe^{2+} to Fe^{3+} since the reaction is spontaneous.

$I_2 + 2Fe^{2+} \rightarrow 2I^- + 2Fe^{3+}$ $\quad E^\ominus_{cell} = -0.23 \text{ V} < 0$

I_2 cannot oxidise Fe^{2+} to Fe^{3+} since the reaction is non-spontaneous.

[3]

[Total: 8]

Anglo-Chinese Junior College

JC2 Preliminary Examination
Higher 2

A Methodist Institution
(Founded 1886)

CANDIDATE NAME	Solutions	FORM CLASS	
TUTORIAL CLASS		INDEX NUMBER	

CHEMISTRY **9729/03**
Paper 3 Free Response
1 September 2025
2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.
Circle the number of the question you have attempted.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiners' use only	
Section A	
1	/ 15
2	/ 24
3	/ 21
Section B	
4 / 5	/ 20
Presentation	
Total	/ 80

This document consists of **28** printed pages.

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

1 The Mars Curiosity rover's landing in August 2012 was achieved using hydrazine fuelled rocket thrusters. The rapid decomposition of hydrazine, N_2H_4, over a suitable catalyst to produce hot gaseous elements as products provides the thrust. Ammonia can be formed as an intermediate during the decomposition.

(a) Write a balanced equation for hydrazine decomposing to ammonia and nitrogen gas. [1]

$3N_2H_4 \rightarrow 4NH_3 + N_2$

(b) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide as shown in equation 1.

equation 1 $2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l)$ $\Delta H_r^\circ = -241.0$ kJ mol^{-1}

Table 1.1 shows the standard enthalpy change of formation, ΔH_f°, for some compounds in equation 1.

Table 1.1

compound	ΔH_f° / kJ mol^{-1}
NH_3	−46.1
H_2O_2	−187.8
H_2O	−285.8

Calculate the standard enthalpy change for the decomposition of hydrazine to its elements. [2]

$\Delta H_r^\circ = -(2 \times -46.1) - (-187.8) + \Delta H_f^\circ(N_2H_4) + (2 \times -285.8) = -241.0$

$\Delta H_f^\circ(N_2H_4) = +50.6$ kJ mol^{-1}

$\Delta H_{decomp}^\circ(N_2H_4) = -50.6$ kJ mol^{-1}

(c) The first ever rocket-powered fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol fuel mixture, known as 'C-Stoff', and hydrogen peroxide, known as 'T-Stoff'.

(i) Hydrazine reacts with hydrogen peroxide as shown in equation 2.

equation 2 $N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$

State the oxidation number of nitrogen and oxygen in the reactants and products. [1]

(ii) Methanol reacts with hydrogen peroxide to form carbon dioxide and water.

Write a balanced equation for this reaction. [1]

(iii) The fighter plane would hold 225 dm³ of hydrazine and 862 dm³ of methanol.

Table 1.2 shows the standard enthalpy change of combustion, ΔH_c°, and densities of hydrazine and methanol.

Table 1.2

compound	ΔH_c° / kJ mol^{-1}	density / g cm^{-3}
N_2H_4	−622.2	1.021
CH_3OH	−726.0	0.7918

Use data in Table 1.2 to calculate the heat energy evolved during the combustion of this quantity of rocket fuel at standard conditions. Assume that hydrazine and methanol are fully combusted. [2]

(i) N: −2 in N_2H_4 and 0 in N_2; O: −1 in H_2O_2 and −2 in H_2O

(ii) $CH_3OH + 3H_2O_2 \rightarrow CO_2 + 5H_2O$

(iii) Amount of hydrazine = (225000 × 1.021) / 32.0 = 7179 mol

Amount of methanol = (862000 × 0.7918) / 32.0 = 21329 mol

Heat energy evolved from hydrazine = 7179 × 622.2 = 4.467 x 10⁶ kJ

Heat energy evolved from methanol = 21329 × 726.0 = 15.485 x 10⁶ kJ

Total heat energy evolved from oxidation of rocket fuel = 19.9 x 10⁶ kJ

(d) Hydrazine is also commonly combined with dinitrogen tetroxide, N_2O_4, in rocket fuels.

(i) Reactions used in rocketry produce chemically stable gaseous products.

Suggest the products that are formed in the reaction between N_2H_4 and N_2O_4. [1]

(ii) Pure N_2O_4, when warmed, does not immediately decompose into its elements, but instead forms a brown gas.

Suggest the identity of this brown gas. [1]

(iii) N_2H_4 does not exhibit ideal gas behaviour.

State and explain two reasons for its deviation from ideal gas behaviour. [2]

(i) N_2 and H_2O

(ii) NO_2

(iii) There are significant intermolecular forces of attraction / hydrogen bonding between molecules and is not negligible.

The particles of N_2H_4 take up space relative to the volume of the gas and are not negligible.

Collisions are inelastic. 2 of 3

e) A derivative of hydrazine with formula $C_2H_8N_2$ was used as rocket fuel in the Apollo missions. Draw two isomers of $C_2H_8N_2$ containing an N–N bond. [1]

$(CH_3)_2N{-}NH_2$, $(CH_3)NH{-}NH(CH_3)$, or $CH_3CH_2NH{-}NH_2$. 2 of 3

(f) Phosphorus is one element below nitrogen in the Periodic Table.

Describe the reactions of the oxide and chloride of phosphorus with water. Write equations where appropriate and suggest the pH of the solutions formed. [3]

P_4O_6 / P_4O_{10} is readily <u>soluble</u> in water to form an acidic solution. [√]

$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$ [√]

OR $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$ [√]

pH 2 or 3 [√]

PCl_3 / PCl_5 undergoes <u>complete hydrolysis</u> with water to give an acidic solution. [√]

$PCl_3(s) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$ [√]

OR $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$ [√]

pH 1 or 2 [√]

[Total: 15]

2 Cocoa trees have been used as a source of food for more than 5,000 years. In modern times, they are used to make chocolates.

(a) Palmitic acid and stearic acid are saturated fatty acids, while oleic acid and linoleic acid are unsaturated fatty acids commonly found in chocolates.

An example of an unsaturated fatty acid is shown below in Fig. 2.1.

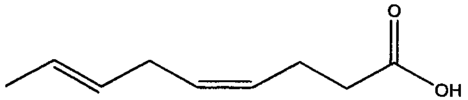


Fig. 2.1

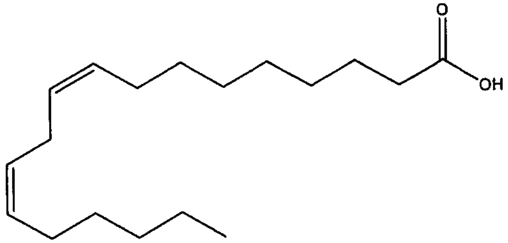
The systematic name of the unsaturated fatty acid in Fig. 2.1 is ***cis,trans***-4,7-nonadienoic acid. The numbers indicate the positions of the alkene functional groups, and "dien" indicates that there are two alkenes in the chain.

Table 2.2 shows the percentage composition of fatty acids found in three different cocoa butter samples.

Table 2.2

fatty acid	% of fatty acids in cocoa butter samples		
	A	B	C
palmitic acid	28	25	35
stearic acid	35	40	40
oleic acid	31	28	21
linoleic acid	6	12	4

(i) The structure of linoleic acid is shown below.



Given that 'octadeca' refers to an 18-carbon chain, write the systematic name for linoleic acid. [1]

(ii) Using given information about the arrangement of atoms about the C=C bond of unsaturated fatty acids and data in Table 2.2, state and explain which cocoa butter sample is expected to have the highest melting point. [2]

(i) *cis*,*cis*-9,12-octadecadienoic acid (AOB)

(ii) Unsaturated fatty acids contain kinks / bends in the chain caused by the C=C double bonds which prevents them from packing as well as saturated fatty acids which generally have more linear structures allowing them to pack closer together. Saturated fatty acids have stronger intermolecular forces of attraction, leading to higher melting points as they are able to pack more closely together compared to unsaturated fatty acids. [1]

Hence, sample C is expected to have the highest melting point due to the highest percentage of saturated fatty acids, i.e. palmitic + stearic acids. [1]
(AOA+AOB)

(b) A chocolatier investigated the quality of two varieties of cocoa beans from the same producer. Table 2.3 shows the results of the chemical analysis.

Table 2.3

chemicals	variety of cocoa beans	
	D	E
theobromine (mg / g)	12.5	15.2
epicatechin (mg / g)	4.8	6.1
ash content (% mass)	3.0	3.5
reducing sugars (% mass)	2.5	3.0

(i) The ash content of cocoa beans is determined by burning the sample until all organic matters are combusted, leaving behind the inorganic residue, which is reported as the percentage mass of the original sample.

Suggest one use for determining the ash content. [1]

(ii) Chocolate is poisonous to dogs as they metabolise theobromine much more slowly compared to humans. The median lethal dose of theobromine for dogs is 120 mg per kg of body weight.

A 60 g of a dark chocolate bar contains 85% cocoa content of variety E.

Calculate the percentage of a chocolate bar, to 1 decimal place, that would be the median lethal dose for a small dog weighing 5.4 kg. [2]

(iii) Theobromine is metabolised more slowly than caffeine in the human body. Following a first-order kinetics, the half-life of theobromine is 8 hours.

The integrated rate law for a first-order reaction is given.

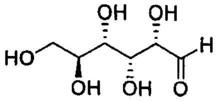
$$\ln [A]_t = -kt + \ln[A]_0$$

where k = rate constant
t = time
$[A]_t$ = concentration of A at time t
$[A]_0$ = initial concentration of A

A social media influencer consumed a large quantity of giant chocolate bars during a broadcast. An immediate blood test revealed a theobromine level of 15.5 mg dm^{-3}.

Calculate the time taken for his theobromine level to fall below 1.5 mg dm^{-3}. [2]

(iv) D-glucose is one of the main reducing sugar molecules found in chocolates. The structure of D-glucose is shown below.



With reference to the changes in the reaction of D-glucose with Fehling's solution, explain why D-glucose is called a reducing sugar. [1]

(i) It gives insights into the total mineral content / quality (such as iron and calcium) of the cocoa beans.
OR
It may help to detect adulteration or impurities if the ash content is different from that of pure cocoa beans.

(ii) Mass of theobromine in a chocolate bar = 60 x 85/100 x 15.2 = 775.2 mg
Median lethal dose for the dog = 5.4 x 120 = 648 mg
Percentage of a chocolate bar = 648 / 775.2 x 100% = **83.6%**

(iii) $k = \ln 2 / t_{1/2} = 0.6931 / 8 = 0.08664\ h^{-1}$
$\ln [A]_t = -kt + \ln[A]_0$
$\ln (1.5) = -0.08664t + \ln (15.5)$
t = 26.95 ≈ **27.0 h** (3 s.f.)

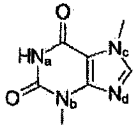
OR

proportion left = 1.5 / 15.5 = 0.09677
let n = no. of half-lives
$0.09677 = (½)^n$
n = log 0.09677 ÷ log ½ = 3.369

t = 8 x 3.369 = 26.95 ≈ **27.0 h** (3 s.f.)

(iv) Glucose reduces the copper(II) complex in Fehling's solution to Cu_2O, while itself is oxidised from aldehyde to carboxylic acid.

(c) Theobromine is the principal alkaloid in cocoa beans. In the structure below, four nitrogen atoms are labelled N_a, N_b, N_c and N_d.



Theobromine has a pK_b value of 4.1.

(i) Theobromine is an aromatic compound. It is known that N_a, N_b and N_c are not basic, while N_d is basic in nature. All the nitrogen atoms are sp^2 hybridised and lie on the same plane.

With reference to the orbitals, explain why N_c is not basic while N_d is basic. [2]

(ii) To study the effects of theobromine on certain biological systems, a buffer solution at a pH of 10.1 is prepared by adding 300 cm^3 of 0.500 mol dm^{-3} of hydrochloric acid to 700 cm^3 of theobromine solution, which is in excess.

Calculate the original concentration of the theobromine solution used to make the buffer solution. [3]

(i) In N_c, the three sp^2 hybrid orbitals are used to form sigma bonds with the neighbouring carbon atoms. As such, the lone pair of electrons occupies the unhybridised p orbital that delocalises into the pi electron cloud and thus is not available for accepting a proton.

In N_d, the unhybridised p orbital is used to form a pi bond with a neighbouring carbon atom. As such, the lone pair of electrons occupies one of the sp^2 hybrid orbital and is not part of the pi electron cloud, making it available for accepting a proton.

(ii) Let c be the original concentration of Tb

$Tb + HCl \longrightarrow TbH^+ + Cl^-$

$n(TbH^+)$ in buffer = n(HC*l*) added = 0.300 x 0.500 = 0.150 mol
n(Tb) in buffer = n(Tb) original – n(HC*l*) added = 0.700c – 0.150 mol

$pOH = pK_b + \lg\frac{[TbH^+]}{[Tb]}$

$14.0 - 10.1 = 4.1 + \lg\frac{[0.15]}{[0.700c - 0.15]}$

$10^{-0.2} = \frac{[0.15]}{[0.700c - 0.15]}$

c = 0.554 mol dm^{-3}

BP~100

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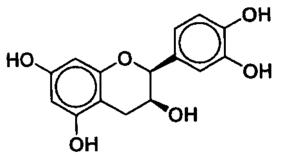
(d) Compared to other types of chocolate, dark chocolate is richer in epicatechin, which is an antioxidant.



epicatechin

Fig 2.4 shows a possible synthetic pathway of epicatechin in the laboratory.

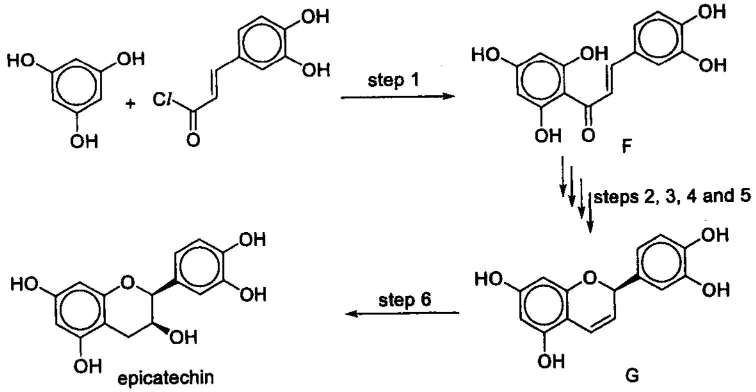
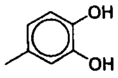


Fig. 2.4

(i) In step 1, electrophilic substitution occurs to form F in the presence of $AlCl_3$.

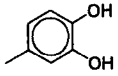
Draw the mechanism for step 1. Show the relevant curly arrows and charges, and all the products formed.

You may represent the non-reacting group  with R. [3]

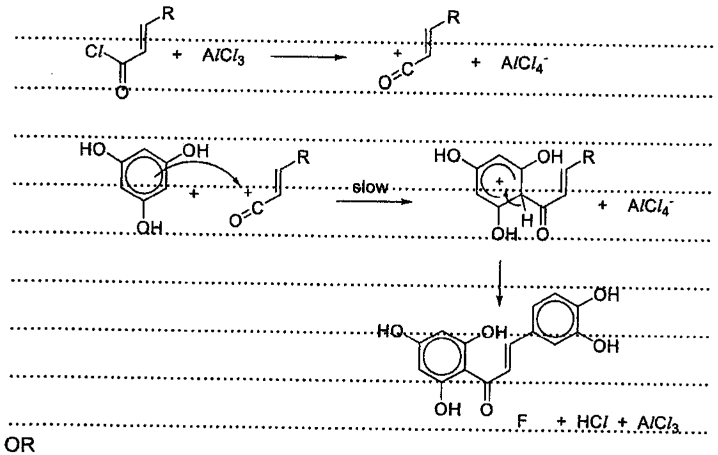
(ii) Intermediate G can be formed from F in four steps. The reactions involved are:

- electrophilic addition,
- acid-base reaction and intramolecular nucleophilic substitution,
- reduction, and
- elimination.

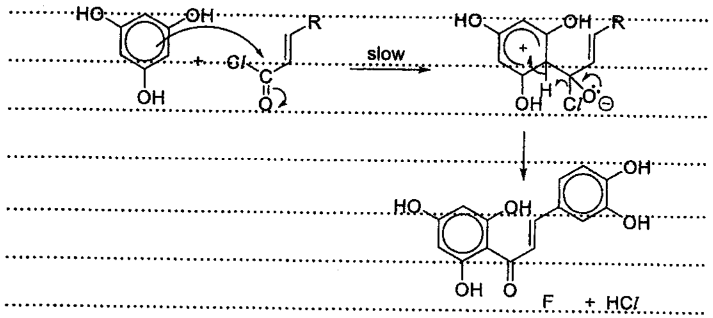
Suggest reagents and conditions for each step. Draw the structure of the intermediate compound formed after each step.

You may represent the non-reacting group  with R. [7]

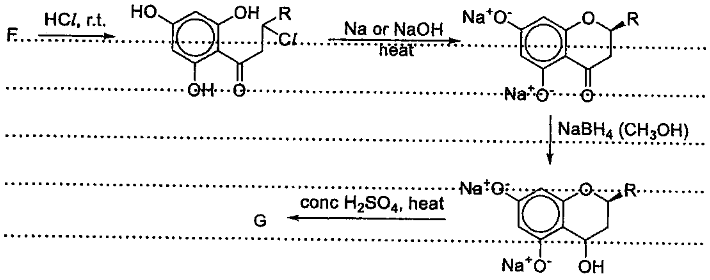
(i)



OR



(ii)



EA HCl, Na or NaOH to NS RCl, reduce ketone, eliminate H_2O [4x1m]
Accept alternative reagents/conditions.
Intermediate [3x1m]

[Total: 24]

3 Iron is the fourth most abundant element in the crust of the Earth, deposited mainly by meteorites in its metallic state.

(a) Depending on the arrangement of the particles in the solid state, iron exists as a few allotropes, one of which is α-iron.

Paramagnetism and ferromagnetism are two types of magnetic behaviour found in materials. In ferromagnetic materials, the magnetic moments due to unpaired electrons in each particle align strongly in the same direction, resulting in them behaving as magnets. In paramagnetic materials, however, the magnetic moments are randomly oriented such that they can only behave as magnets when an external magnetic field is applied.

At room temperature, α-iron is ferromagnetic, but it becomes paramagnetic above 770 °C.

With reference to the electronic configuration of $_{26}$Fe, explain why this is so. [2]

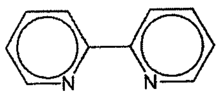
$_{26}$Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

At lower temperatures, due to the 4 unpaired electrons in the 3d subshell aligning in the same direction in each particle, α-iron is ferromagnetic.

However, at higher temperatures, the electrons gain significant (kinetic) energy, resulting in the disruption of the alignment of the magnetic moments / excitation of electrons to be randomly oriented, thus exhibiting paramagnetism instead.

BP~102

(b) Bipyridine, bipy, is a bidentate ligand.



bipy

(i) A molecule with a conjugated system has multiple p orbitals overlapping with each other, resulting in delocalised electrons.

A compound is said to be aromatic when it has a conjugated, planar and cyclic structure with $[4n + 2]$ π electrons (where $n = 0$ or a positive integer 1, 2, 3, etc.).

Given that bipyridine is an aromatic compound, with each ring maintaining its own aromaticity, deduce the total number of π electrons present in the molecule.

Explain your answer. [2]

(ii) Explain what is meant by the term *bidentate ligand*. [1]

(iii) The 3d orbitals in an isolated Fe^{2+} ion are degenerate.

Draw a diagram to show the relative energies of the 3d orbitals' energy levels in an isolated Fe^{2+} ion **and** when Fe^{2+} ion forms an octahedral complex. [2]

(iv) The octahedral complex ion $[Fe(bipy)_3]^{2+}$ exists as two stereoisomers.

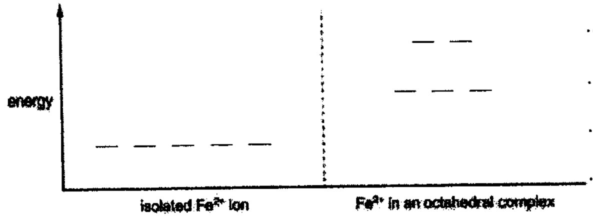
Using  to represent the structure of bipy, draw three-dimensional diagrams to show the two stereoisomers of $[Fe(bipy)_3]^{2+}$. State the type of stereoisomerism shown. [3]

(i) Each of the ten sp^2 hybridised carbon contributes one electron from the unhybridised p orbital, while each of the two sp^2 nitrogen atoms contributes one electron from the unhybridised p orbital into the π system.

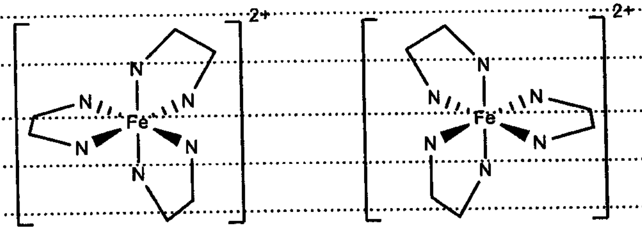
Hence, there are 12 π electrons present, with 6 from each ring.

(ii) It is a neutral or anionic species that donates two lone pairs of electrons to form dative covalent bonds to a metal atom or ion.

(iii)



(iv)



Enantiomerism

(c) The relationship between the energy of a photon of light and its wavelength is shown.

$$E = \frac{hc}{\lambda}$$

E = energy of a photon, in J
h = Planck constant = 6.63×10^{-34} J s
c = speed of light in a vacuum = 3.00×10^8 m s^{-1}
λ = wavelength, in m

Fig. 3.1 shows the visible spectrum with the approximate range of wavelengths for each colour of light.

violet	blue	green	yellow	orange	red

λ / nm 380 450 495 570 590 620 700

Fig. 3.1

(i) Calculate the amount of energy, in J, in 1 photon of light that contains the maximum amount of energy in the visible spectrum. [2]
[1 nm = 1×10^{-9} m]

(ii) Transition metal complexes are often coloured due to the absorption of photons of light at specific wavelengths. The colour observed is complementary to the colour absorbed.

$[Fe(H_2O)_6]^{2+}$ is green in colour, while $[Fe(H_2O)_6]^{3+}$ appears yellow.

With reference to Fig. 3.1 and the electronic configuration of the two complex ions, suggest why they exhibit different colours. [2]

(i) Shortest λ = 380 nm = 3.80×10^{-7} m
$E = hc / \lambda$
$= (6.63 \times 10^{-34})(3.00 \times 10^{8}) / (3.80 \times 10^{-7})$
$=$ **5.23×10^{-19} J**

(ii) Fe^{3+} and Fe^{2+} have different number of electrons (OR electronic configurations), which results in the different extent of interactions with the H_2O ligands that causes the energy gap between the split 3d orbitals in both complexes to differ.

As $[Fe(H_2O)_6]^{3+}$ absorbs photons of light with shorter wavelengths compared to $[Fe(H_2O)_6]^{2+}$, the former appears yellow while the latter appears green.

(d) Prussian Blue is a deep blue solid. The word 'blueprint' was coined from the use of Prussian Blue on sensitised paper to lay out detailed plans for architectural and engineering projects in the 19th century.

(i) Prussian Blue can be precipitated out by adding a solution of $Fe^{3+}(aq)$ to a solution of $[Fe(CN)_6]^{4-}(aq)$.

Write a balanced chemical equation, with state symbols, for the formation of Prussian Blue. [1]

Standard electrode potentials can be used to compare the stability of different complex ions of a given transition element.

Table 3.2 lists electrode potentials for some electrode reactions of Fe^{3+} / Fe^{2+} systems.

Table 3.2

electrode reaction	E° / V
$[Fe(H_2O)_6]^{3+} + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$[Fe(bipy)_3]^{3+} + e^- \rightleftharpoons [Fe(bipy)_3]^{2+}$	+0.96

(ii) State and explain which iron(II) complex is the most stable. [2]

(iii) Given,
$Fe^{3+}(aq) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{3-}(aq)$ $\Delta G^\circ = -250$ kJ mol^{-1}
$Fe^{2+}(aq) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{4-}(aq)$ $\Delta G^\circ = -210$ kJ mol^{-1}

Calculate ΔG° for $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$, and hence construct an energy cycle to calculate the E° for, $[Fe(CN)_6]^{3-}(aq) + e^- \rightleftharpoons [Fe(CN)_6]^{4-}(aq)$. [4]

(i) $4Fe^{3+}(aq) + 3[Fe(CN)_6]^{4-}(aq) \rightarrow Fe_4[Fe(CN)_6]_3(s)$

(ii) The electrode potential of $[Fe(bipy)_3]^{3+}$ / $Fe(bipy)_3]^{2+}$ is the most positive, which means $[Fe(bipy)_3]^{2+}$ has the lowest tendency to be oxidised. Hence, $[Fe(bipy)_3]^{2+}$ is the most stable.

(iii) $\Delta G^\circ_{(Fe3+/Fe2+)} = -(1 \times 96500 \times +0.77) = -74.3$ kJ mol^{-1}

$$\begin{tikzcd}
{[Fe(CN)_6]^{3-}(aq) + e^-} \arrow[r, phantom, "\rightleftharpoons"] & {[Fe(CN)_6]^{4-}(aq)} \\
{Fe^{3+}(aq) + e^-} \arrow[u, "6CN^-(aq)"'] \arrow[r, phantom, "\rightleftharpoons"] & {Fe^{2+}(aq)} \arrow[u, "6CN^-(aq)"']
\end{tikzcd}$$

$\Delta G^\circ = -(-250) + (-74.3) + (-210) = -34.3$ kJ mol^{-1}

$E^\circ = -(-34300) / 96500 =$ **+0.355 V**

BP~103

BP~104

[Total: 21]

Section B

Answer **one** question from this section.

4 (a) Trichloroethanoic acid decarboxylates steadily in aqueous solution at room temperature and pressure.

$$CCl_3CO_2H(aq) \rightarrow CHCl_3(aq) + CO_2(g)$$

In an experiment, 100.0 cm^3 of an aqueous trichloroethanoic acid was allowed to decarboxylate at room temperature and pressure, and the volume of CO_2 collected was tabulated against time. The results are as shown in Table 4.1.

Table 4.1

vol. of CO_2 (V_t) / cm^3	9.5	17.0	22.5	32.5	35.5	37.5	40.0
time / s	500	1000	1500	3000	4000	5000	∞
$V_\infty - V_t$ / cm^3	30.5	23.0	17.5	7.5	4.5	2.5	0.0

(i) Calculate $V_\infty - V_t$ and fill in the table accordingly. [1]

(ii) Explain the significance of $V_\infty - V_t$. Make reference to V_∞ and V_t. [2]

(ii) V_∞ is the volume of CO_2 produced when **decarboxylation is complete** and hence it is **directly proportional to the initial [CCl_3COOH]$_o$.**

V_t is the volume of **CO_2 produced in the given time** and hence it is directly proportional to the **change in [CCl_3COOH]** based on the amount that reacted.

(V_∞ - V_t) is therefore directly proportional to the **[CCl_3COOH]$_t$ remaining** at time t.

(iii) Plot a suitable graph on Fig. 4.2 on page 19 that will allow you to determine the rate equation for the decarboxylation reaction, ensuring it can be extrapolated to t = 0 s. [3]

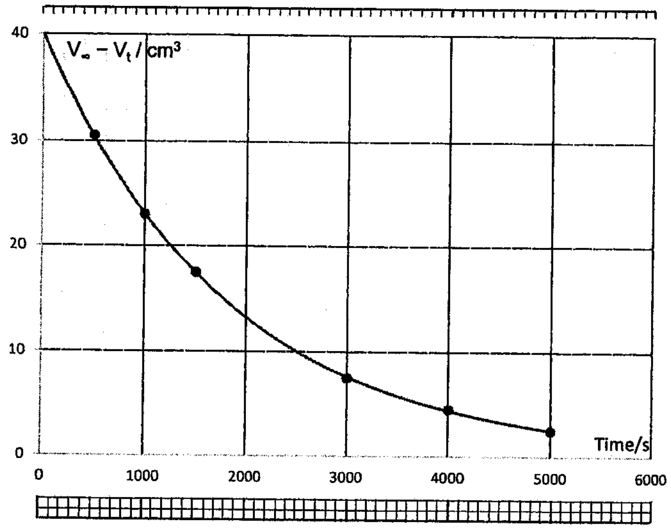


Fig. 4.2

(iv) Calculate the initial concentration of the trichloroethanoic acid used in the experiment. [2]

(v) Use your graph in Fig. 4.2 to deduce the order of reaction with respect to trichloroethanoic acid, calculate the value of the rate constant, and write an expression for the rate equation. Show how you obtained your answer. [3]

(vi) Use the graph to estimate the time taken for the initial concentration of trichloroethanoic acid to fall by 10 %. [1]

(iv) n(CCl_3COOH) = 40.0/24000 = 0.00167 mol

[CCl_3COOH] = 0.00167/0.1 = 0.0167 mol dm^{-3}

(v) Constant $t_{1/2}$ = 1250 s

Hence, 1st order with respect to [CCl_3COOH]

k = ln 2 / $t_{1/2}$ = 5.55 x 10^{-4} s^{-1}

Rate = k [CCl_3COOH]

(vi) 200 s

(b) **(i)** The pK_a of trichloroethanoic acid is 0.52 while that of ethanoic acid is 4.76. Explain why the pK_a of trichloroethanoic acid is smaller. [2]

(ii) With reference to the pK_a value of trichloroethanoic acid, state an assumption about its dissociation and use it to estimate the pH of 0.05 mol dm^{-3} trichloroethanoic acid. [2]

(iii) Suggest if partial neutralisation of trichloroethanoic acid can result in a buffer solution. [1]

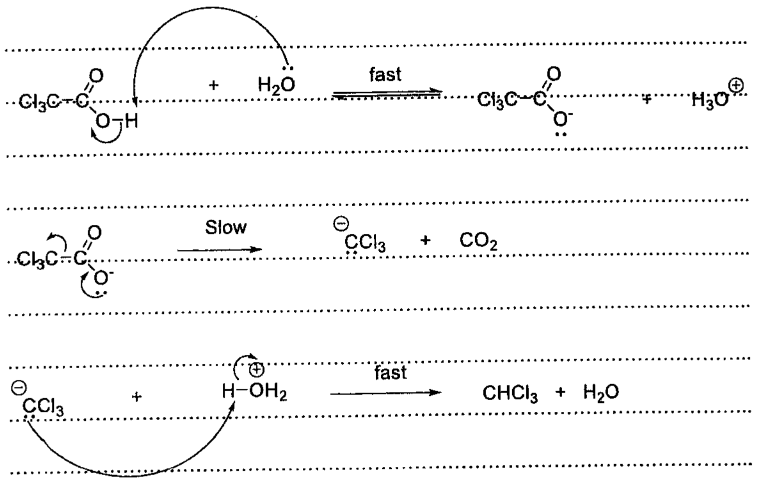
(i) The three chlorine atoms are very strongly electron withdrawing and hence help to disperse the negative charge on the conjugate base thereby stabilising it OR weakens O–H bond more. This leads to a stronger acid and smaller pK_a value.

(ii) [H^+] = 0.05 mol dm^{-3} as K_a is very large and hence can be assumed to be fully dissociated.

pH = –lg0.05 = 1.30

(iii) Since trichloroethanoic acid is a very strong acid which dissociates almost fully, it will not be able to form a buffer upon partial neutralisation.

(c) Draw the mechanism for the decarboxylation of trichloroethanoic acid, showing all curly arrows, lone pairs and charges. The steps are as follows:
Step 1: Water reacts with trichloroethanoic acid as a Brønsted-Lowry base.
Step 2: Loss of CO_2 from the conjugate base from step 1.
Step 3: Formation of $CHCl_3$ from the intermediates formed in steps 1 and 2. [3]



[Total: 20]

5 Iodoform reaction is a chemical reaction in which a methyl ketone or a secondary alcohol with a methyl group in the alpha position is oxidised to a carboxylate by reaction with aqueous OH^- and I_2. Ethanoic acid, esters of ethanoic acid and ethanoyl chloride do not undergo the iodoform reaction even though they possess the methyl keto, $CH_3CO–$, moiety in their structures.

(a) Fig. 5.1 shows the mechanism of the different stages in the iodoform reaction.

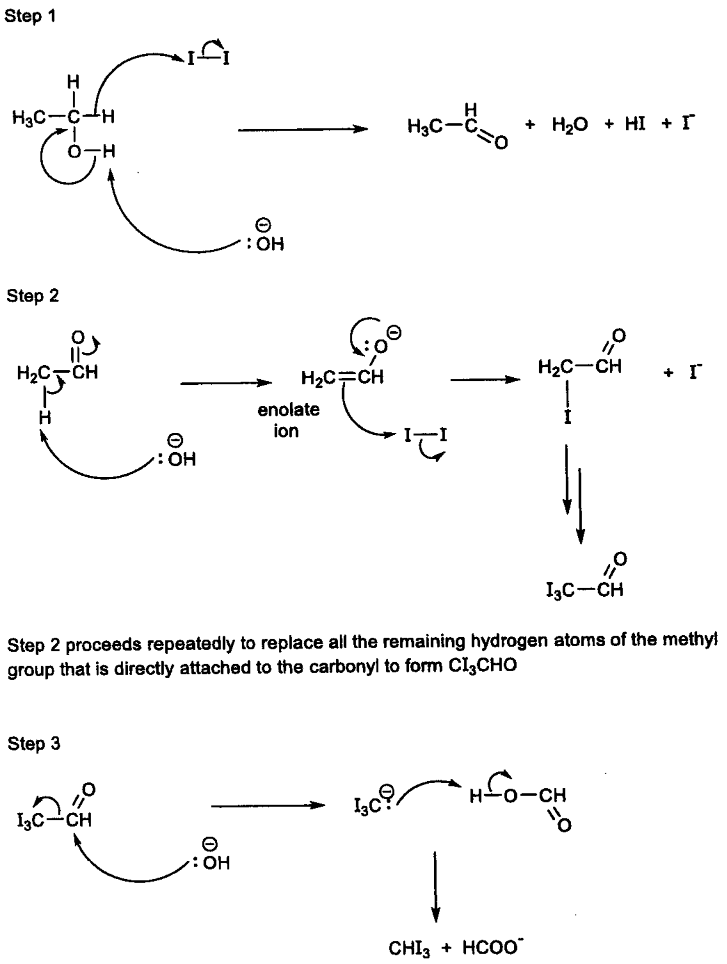


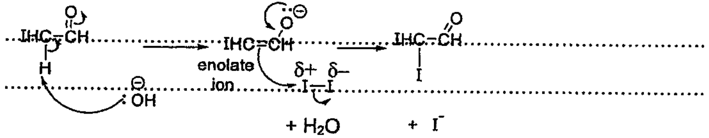
Fig. 5.1

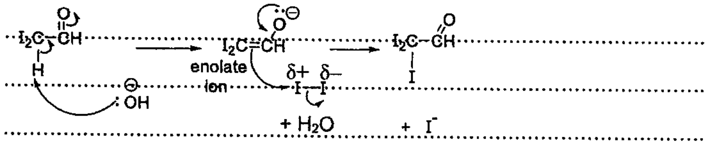
(i) Outline the portion of step 2 in the mechanism for the repeated replacement of the remaining H atoms in CH_2ICHO to form CI_3CHO. Show all lone pairs, dipoles, charges and curly arrows. [4]

(ii) The repeated replacement of the hydrogen atom is made possible by the repeated abstraction of the H^+ by OH^- from the α-methyl group.

State the behaviour of the methyl ketone in this step and explain how it can give up the H^+. [2]

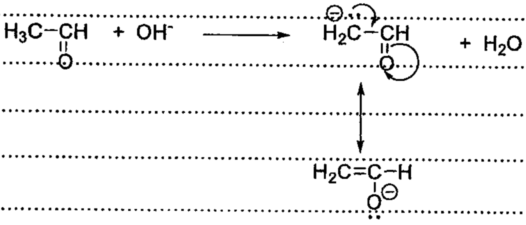
(i)





(ii) Methyl ketone behaves as a proton donor or Brønsted-Lowry acid. The strongly electron withdrawing carbonyl group stabilises the negative charge on the alpha carbon due to delocalisation forming the conjugate enolate ion OR weakens the C–H bond.

For illustration:



(iii) Based on the mechanism, explain why only ketones with the α-methyl group can undergo the iodoform reaction while acids such as ethanoic acid or esters, such as, CH_3COOCH_3, which have the α-methyl group do not undergo a similar reaction. [2]

(iv) In step 3, the triiodoethanal undergoes a substitution reaction instead of the expected addition reaction with the nucleophile, OH^-.

Suggest why this reaction occurs. [2]

(iii) The reaction requires a structure that can form a stable conjugate base / enolate ion under basic conditions and ketones can do that.

Esters will undergo alkaline hydrolysis while carboxylic acids will undergo acid-base reactions respectively instead.

(iv) The $-CI_3$ group alpha to the ketone group is strongly electron withdrawing which weakens the bond between the CI_3-group and the adjacent C=O group and hence results in the bond breaking resulting in substitution. OR makes C more electron deficient and susceptible to nucleophilic attack.

BP~108

(b) Study the reaction scheme in Fig. 5.2. State the reagents and conditions for each step from steps 1 to 7, as well as the identities of U, V and W. [10]

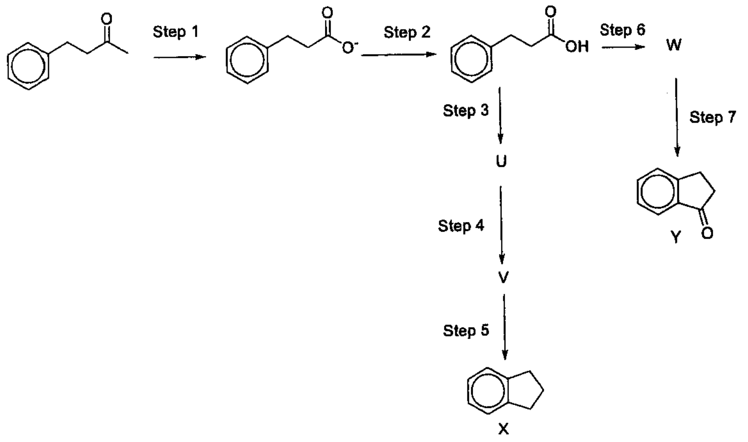


Fig. 5.2

Step 1 – I_2, NaOH(aq) and r.t.p. / warm

Step 2 – aqueous HC*l* or H_2SO_4

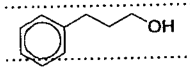
Step 3 – LiA*l*H_4 (dry ether), reflux

Step 4 – PC*l*$_5$ or PC*l*3 or PBr_3 or SOC*l*$_2$ or conc HC*l*

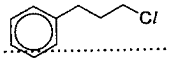
Step 5 – A*l*C*l*$_3$, (heat optional)

Step 6 – PC*l*$_5$ or PC*l*3 or PBr_3 or SOC*l*$_2$ or conc HC*l*

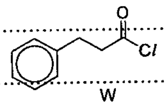
Step 7 - A*l*C*l*$_3$, (heat optional)



U



V



W

[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.