1 From Group 13→18, the number of unpaired electrons ↑es from 1 (Group 13) to 3 (Group 15), then ↓es to 0 (Group 18). Hence, **W**, **X**, **Y** and **Z** cannot be main group elements, *i.e.* they are TM.

W must have been $4d^8\,5s^2$ and not $4d^2\,5s^2$ as the number of unpaired electrons ↓es with more electrons added.

$\Rightarrow$ **B**

2 Angle of deflection, $\theta \propto \dfrac{z}{m}$

For a proton, $_1^1H^+$, $\dfrac{z}{m} = \dfrac{+1}{1} = +1$

For particle **X**, $\dfrac{z}{m} = \dfrac{-5°}{+15°}(+1) = -\dfrac{1}{3}$

$A : {}_1^3 A^-$; $B : {}_2^5 B^-$; $C : {}_3^6 C^-$; $D : {}_4^9 D^{3+}$

$\Rightarrow$ **A**

3 **A** ✗: *trans*-isomer is non-polar (C–Cl bond dipole cancels), while *cis*-isomer is polar. Hence *cis*-isomer is more soluble in polar H_2O.

B ✓: C=O is more polar than C–Cl as O is more electronegative. Also, oxygen of C=O can form H-bond with water via its lone pair. ∴ CH_3COCH_3 is more soluble.

C ✗: $CH_3CH_2CH_2CH_2CH(OH)CO_2H$ can form intermolecular H-bond with H_2O, while $CH_3CH_2CH_2CH_2CH(NH_3^+)CO_2^-$ is zwitterionic and forms stronger ion-dipole interaction with H_2O, hence more soluble.

D ✗: 2-nitrophenol can form intramolecular H-bond, while 4-nitrophenol forms intermolecular H-bond with H_2O, hence more soluble.

$\Rightarrow$ **B**

4 **A** ✓: Like graphite, each C is sp^2 hybridised with one unpaired e^- in the remaining p-orbital, which is delocalised, allowing CNT to conduct electricity.

B ✗: Like graphite, the C–C bonds within each molecule is stronger than that in diamond as they result from sp^2-sp^2 overlap. However, between two molecules, there is only weak intermolecular id-id attraction, hence softer than diamond.

C ✗: Like graphite, the high melting point is due to energy required to break the strong intramolecular C–C bond and not to overcome the weak intermolecular id-id attraction.

D ✗: Like graphite, the C–C bonds within each molecule is stronger than that in diamond as they result from sp^2-sp^2 overlap.

$\Rightarrow$ **A**

5 I : H_2SO_4 **oxidises** Br^- to Br_2, itself reduced to SO_2

II : H_2SO_4 **catalyses** the condensation reaction between an acid and an alcohol to give an ester (and water), but making the C=O more electrophilic.

III : Acid-base reaction where H_2SO_4 is the **acid** and NaOH the base, to give salt (Na_2SO_4) and water.

$\Rightarrow$ **D**

6 1 ✗: A more exothermic lattice energy just implies that it takes more energy to vaporise the ionic lattice into gasous ions. No bearing on the decomposition.

2,4 ✓: CO_3^{2-} is more easily polarised as planar CO_3^{2-} has a larger surface area than the near spherical tetrahedral SO_4^{2-} ion. Hence the C–O bond is more readily weakened, causing $CaCO_3$ to decomposing at a lower temperature.

3 ✗: Due to smaller size of the CO_3^{2-} ion compared to SO_4^{2-}, the charge density is higher. However, higher anionic charge density has no bearing on the decomposition.

$\Rightarrow$ **C**

7 Oxidation state of S in SF_6 is +6, SCl_2 is +2 and S_2Br_2 is +1, which correlates with the ability of the halogen to oxidise S.

$\Rightarrow$ **D**

8 Number of ^{13}C atoms $= \dfrac{0.13}{13} \times L = 0.01L$

Each $_6^{13}C$ atom has $13 - 6 = 7$ neutrons

Number of neutrons $= 0.01L \times 7 = 0.07L$

$\Rightarrow$ **B**

9

	P(g)	

ΔH_{atom}(P, white) *less endo* | ΔH_{atom}(P, red)

P(s, white) *more stable*

−17.6 kJ ↓ P(s, red)

ΔH_c(P, white) *more exo* | ΔH_c(P, red)

P_4O_{10}(s)

$\Rightarrow$ **B**

10 $I_2(s) + Cl_2(g) \rightarrow 2ICl(s)$ $\quad \Delta H_1$ --------- (1)
$ICl(s) + Cl_2(g) \rightarrow ICl_3(s)$ $\quad \Delta H_2$ --------- (2)

$\dfrac{1}{2}(1) + (2) : \dfrac{1}{2}I_2(s) + \dfrac{3}{2}Cl_2(g) \rightarrow ICl_3(s)$

$\Delta H_f\left(ICl_3(s)\right) = \dfrac{1}{2}\Delta H_1 + \Delta H_2 = \dfrac{1}{2}(+14) - 88$

$\qquad = -81$ kJ mol^{-1}

$\Rightarrow$ **C**

11 Combustion of fuel (hydrocarbon) is an exothermic process, so ΔH is –ve.

Combustion leads to the production of more gaseous CO_2 and H_2O molecules than $O_2(g)$ consumed. Hence, entropy increases, *i.e.* ΔS is +ve.

$\Delta G = \Delta H - T\Delta S$ is –ve for all T.

$\Rightarrow$ **D**

12 **A** ✓: Since HI, a strong acid is produced, although H^+ is a catalyst, the $[H^+]$ ↑es.

B ✗: The rate constant, $k = Ae^{-\frac{E_a}{RT}}$, is independent of concentration.

C ✗: Given rate $= k[H^+][CH_3COCH_3]$. So rate ↑es by 4 × when concentrations of all reactants are doubled.

D ✗: pH 1 $\Rightarrow [H^+] = 10^{-1} = 0.1$ mol dm^{-3}
pH 2 $\Rightarrow [H^+] = 10^{-2} = 0.01$ mol dm^{-3}
$[H^+]$ ↓es by 10 ×, rate ↓es by 10 ×

$\Rightarrow$ **A**

13 **A** ✗: Adding Ar at constant volume will not cause a spike in the concentration of all three gases.

B ✗: Decrease in temperature of a large body of gas cannot be achieved instantaneously.

C ✓: As conc $= \dfrac{amount}{volume}$, when volume of container is decreased, the total pressure and conc of all three gases will increase suddenly. By LCP, eqm will shift to the side with fewer gaseous particles (right side), in attempt to bring down the pressure, leading to consumption of N_2 and H_2 to form more NH_3 at the new eqm.

D ✗: Removal of NH_3 will not result in a spike in concentration of all 3 gases.

$\Rightarrow$ **C**

14 $pOH = pK_w - pH = -\lg(2.4 \times 10^{-14}) - 7.4$
$\qquad = 6.22$
$[OH^-] = 10^{-6.22} = 6.03 \times 10^{-7}$ mol dm^{-3}

$\Rightarrow$ **B**

15

cis-trans double bond

Since there are two chiral centers and one *cis-trans* double bond,

Number of stereoisomers $= 2^3 = 8$

$\Rightarrow$ **D**

16 There are 8 different types of H on the molecule:

$\Rightarrow$ **C**

17

(Br is more electronegative)

$1°$: less stable $\qquad$ $2°$: more stable

$\Rightarrow$ **C**

18 **A** ✗:

B ✗:

C ✓:

D ✗:

$\Rightarrow$ **C**

19 **1** ✓:

2 ✓: $CH_2{=}CH_2 + H{-}Br \longrightarrow \overset{\oplus}{CH_2}{-}CH_2 + Br^{\ominus}$ (sp2 → sp3)

3 ✗: There is **no intermediate** in S_N2

4 ✓:

⇒ **A**
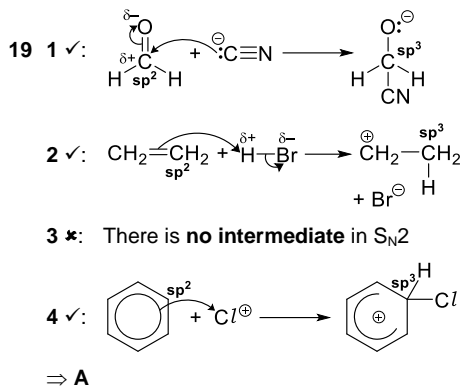
20 From the rate of formation of ppt (solvolysis), **P** is $C_6H_5CH_2Br$, **Q** is $X{-}C_6H_4CH_3$, **R** is $C_6H_5CH_2I$, **S** is $C_6H_5CH_2Cl$

A ✗: **R** should have the longest C–X bond since it is the weakest and most reactive.

B ✗: Free radical substitution does not work with I_2.

C ✓: **Q** can be $BrC_6H_4CH_3$ formed from $C_6H_5CH_3 + Br_2$ in the presence of $AlBr_3$.

**D** ✗: Only **P**, **R** and **S** gives benzoic acid upon vigorous oxidation.

⇒ **C**

21 **A** ✓: hot acidified $K_2Cr_2O_7$ can hydrolyse the ester to release ethanol which can be oxidised into ethanoic acid, reducing orange $K_2Cr_2O_7$ into green Cr^{3+}.
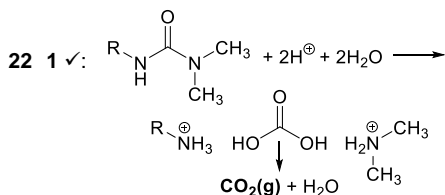
B ✗: $2RCO_2H + Na_2CO_3 \rightarrow 2RCO_2^-Na^+ + CO_2 + H_2O$. 1 mole of benazepril only contains 1 mole of $-CO_2H$.

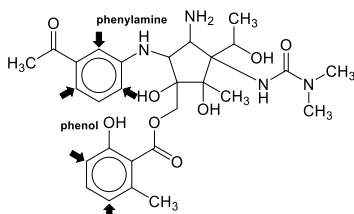**C** ✓: $R_2NH + HCl \rightarrow RNH_3^+Cl^-$. 1 mole of benazepril contains 1 mole of 2° amine.

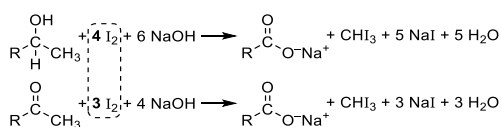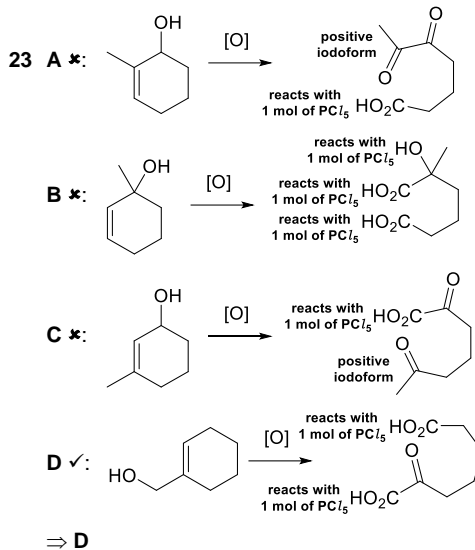**D** ✓: Benazepril hydrolyses in NaOH to give

⇒ **B**

22 **1** ✓:
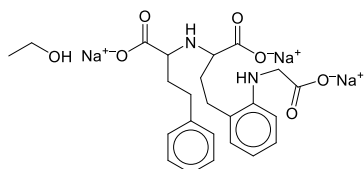
2 ✓: 5 Ar–H relative (2-, 4-, 6-) to phenol or phenylamine can be substituted by Br: $Ar{-}H + Br_2 \rightarrow Ar{-}Br + HBr$
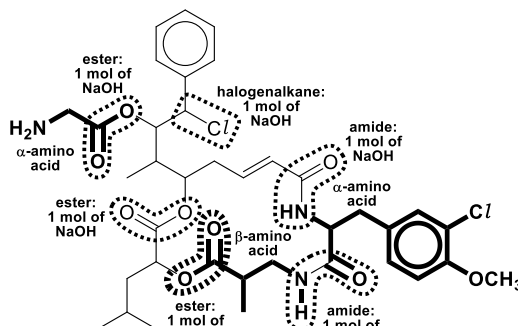

3 ✓: There is one $-CH(OH)CH_3$ and one $-COCH_3$ group in pactamycin.

⇒ **A**

23 **A** ✗:

B ✗:

C ✗:

D ✓:

⇒ **D**

24 The ester, amide and halogenoalkane moieties will be hydrolysed by NaOH(aq), giving 2 α-amino acids and 1 β-amino acid:

⇒ **B**

25 **1** ✓: As HCl is a much stronger acid than H_2O, Cl^- are less basic than OH^-, hence they are better leaving group, making $RC(=O){-}Cl$ better acylating agents than $RC(=O){-}OH$.

2 ✗: Due to the similarity in size of O and C, lone pair of electrons on O in RCO_2H is much more effectively delocalised into the C=O than that on much bigger Cl in $RCOCl$, rendering the C=O carbon in RCO_2H less electrophilic.

3 ✗: While O is more electronegative then Cl, the C=O carbon in RCO_2H is less electrophilic than that in $RCOCl$ as the lone pair of electrons on O is more effectively delocalised into the C=O of RCO_2H.

⇒ **C**

26 In the gas phase, diisopropylamine is the stronger base (more spontaneous protonation, i.e. ΔG is more negative).

In aqueous phase, azepane is the stronger base (smaller pK_b, i.e. larger K_b).

This is primarily due to steric hindrance from the two bulky $-CH(CH_3)_2$ groups which hinders hydration of the $R_2NH_2^+$ ion through H-bonding.

⇒ **D**

27 Extraction is dependent on the oxidation of Au to Au(I) by O_2 in alkaline medium:

[R] $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ $E^{\ominus} = +0.40$ V
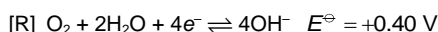
For the oxidation to be feasible

⇒ $E^{\ominus}_{cell} = +0.40 - E^{\ominus}\left(Au(I)|Au\right) > 0$

⇒ $E^{\ominus}\left(Au(I)|Au\right) < +0.40$ V

⇒ **A**

28 The left-hand-side cell is a electrochemical cell, i.e. battery source of +1.52 V:

[O]: $Mn \rightarrow Mn^{2+} + 2e^-$ $E^{\ominus} = -1.18$ V

[R]: $Cu^{2+} + 2e^- \rightarrow Cu$ $E^{\ominus} = +0.34$ V

$E^{\ominus}_{cell} = +0.34 - (-1.18) = +1.52$ V

Electrolysis occurs on the right-hand-side:

Cathode (Reduction):

$E^{\ominus}\left(Ag^+|Ag\right) = +0.80$ V

$E^{\ominus}\left(Na^+|Na\right) = -2.71$ V

$E^{\ominus}\left(H^+|H_2\right) = 0.00$ V

$E^{\ominus}\left(Zn^{2+}|Zn\right) = -0.76$ V

$E^{\ominus}\left(H_2O|H_2\right) = -0.83$ V

Ag is deposited for **A**, while H^+ or H_2O is reduced to $H_2(g)$ for the rest

Anode (Oxidation):

NO_3^- cannot be oxidised

$E^{\ominus}\left(O_2|OH^-\right) = +0.40$ V

$E^{\ominus}\left(S_2O_8^{2-}|SO_4^{2-}\right) = +2.01$ V

$E^{\ominus}\left(O_2|H_2O\right) = +1.23$ V

$E^{\ominus}\left(Cl_2|Cl^-\right) = +1.36$ V

H_2O or OH^- is oxidised to $O_2(g)$ for all cases

⇒ **A**

29 **1** ✓: $[Ti(H_2O)_6]^{2+}$ has a lower charge density, hence the O–H bond is not as polarised as that in $[Ti(H_2O)_6]^{3+}$, thus less likely to hydrolyse.

2 ✗: The titanium in both $[Ti(H_2O)_6]^{3+}$ and $[Ti(H_2O)_5OH]^{2+}$ are +3 oxidation state.

3 ✗: Under acidic conditions, $[H_3O^+]$ is high, hence eqm shifts to the left, supressing the hydrolysis instead.

⇒ **D**

30 Maximum oxidation state of X = number of 4s + **unpaired** 3d electrons = $+(2 + 3) = +5$

A ✗: Oxidation state $= -2 - (-2)\times4 = +6$

B ✓: Oxidation state $= +2 - (-2) = +4$

C ✓: Oxidation state $= -1 - (-2)\times2 = +3$

D ✓: Oxidation state $= - (-2)\times5\div2 = +5$

⇒ **A**

Answer Key

Qn	Ans	Qn	Ans	Qn	Ans
1	B	11	D	21	B
2	A	12	A	22	A
3	B	13	C	23	D
4	A	14	B	24	B
5	D	15	D	25	C
6	C	16	C	26	D
7	D	17	C	27	A
8	B	18	C	28	A
9	B	19	A	29	D
10	C	20	C	30	A

CANDIDATE NAME	

CIVICS GROUP	**1**	**8**	**–**			INDEX NUMBER		

CHEMISTRY **9729/02**

Paper 2 Structured Questions **17 September 2019**
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group, index number 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.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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 Examiner's Use	
Paper 2	
1	**/ 15**
2	**/ 20**
3	**/ 20**
4	**/ 20**
Total	**/ 75**

This document consists of **20** printed pages.

[Turn Over

1 The compounds of magnesium have important applications. Magnesium oxide is often used as a refractory material to line furnaces while magnesium chloride is used to de-ice roads and pavements in winter.

  (a) (i) Explain why magnesium oxide has the formula MgO.

  Each Mg atom has 2 valence electrons. **One Mg atom loses 2 valence electrons** to **one O atom** to achieve stable **octet configuration**.

  ....[1]

Comments:
- Many candidates simply wrote "because it is formed from Mg^{2+} and O^{2-}", without explaining why the atoms form those ions in the first place (to achieve stable octet).
- "To form stable ions" is also not accepted as the ions are not stable!

  (ii) State and explain the property that allows magnesium oxide to be used as a refractory material.

  MgO has a **high melting point.** A **large amount of energy** is required to overcome the **strong electrostatic forces of attraction between oppositely charged ions**.

  ....[1]

Comments:
- The term "ionic bonds" are not accepted.
- Some students did not know what a refractory material is.

  (iii) Describe the action of water on magnesium oxide. Write an equation for any reaction that occurs, and suggest the pH of the solution formed.

  MgO does **not** react very **vigorously** and it **dissolves sparingly in water** to form a **weakly alkaline** solution of **pH = 9.**

  $MgO + H_2O \rightleftharpoons Mg(OH)_2$

  ....[2]

Comments:
- This straightforward recall type question was surprisingly not well-answered.

(iv) State and explain whether magnesium or calcium has a higher tendency to form oxides.

Down the group, the **atomic radius increases**. **Weaker electrostatic force of attraction** between the nucleus and valence electrons. Metal atoms **lose their valence electrons** to form M^{2+} cations **more easily**.

Hence, **Ca** has a *greater tendency* to be **oxidised** and form oxide than Mg.

[2]

Comments:
- This straightforward recall type question was surprisingly not well-answered.
- Two common misconceptions involve arguments along the lines of stability of CaO (either involving charge density or lattice energy). However, candidates fail to appreciate that charge density explains why CaO does not undergo thermal decomposition readily, while lattice energy is about forming CaO from its gaseous ions (rather than atoms).

(b) In an experiment, 40.0 cm^3 of aqueous magnesium chloride was titrated with 1.00 mol dm^{-3} sodium hydroxide. The reaction involves the precipitation of magnesium hydroxide.

$$MgCl_2(aq) + 2NaOH(aq) \rightarrow Mg(OH)_2(s) + 2NaCl(aq)$$
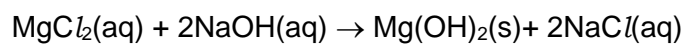
The pH change of the solution is given in Fig. 1.1.
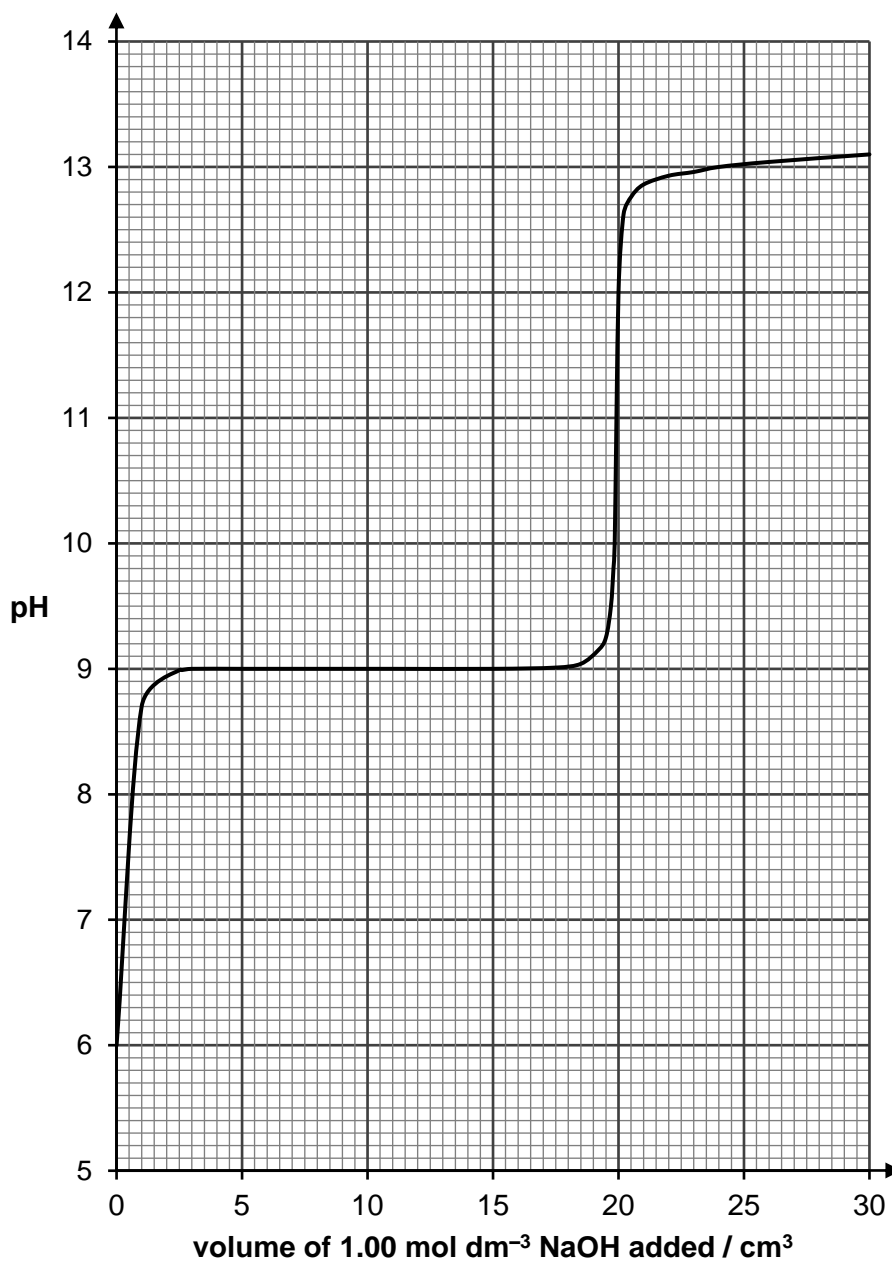
Fig. 1.1

(i) Write an equation to illustrate the hydrolysis of the hydrated magnesium ion, $[Mg(H_2O)_6]^{2+}$.

$[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H^+(aq)$ ....[1]

Comments:
- This straightforward recall type question was surprisingly not well-answered. As the ion undergoes partial hydrolysis, the reversible arrow is required.

(ii) Using your answer to **(b)(i)**, write an expression for the acid dissociation constant, K_a, of the hydrated magnesium ion, $[Mg(H_2O)_6]^{2+}$.

$$K_a = \frac{[H^+]\left[Mg(H_2O)_5(OH)^+\right]}{\left[Mg(H_2O)_6{}^{2+}\right]}$$

[1]

Comments:
- The most common mistake was to put the charge outside of the square bracket, which represents concentration in the K_c expression)

(iii) Using Fig. 1.1, calculate the initial concentration of H^+.

From the graph, initial pH = 6
Initial $[H^+]$ = **1.00×10^{-6} mol dm^{-3}**

[1]

Comments:
- This was generally well-attempted.

(iv) Calculate the concentration, in mol dm^{-3}, of the aqueous $MgCl_2$.

$$n_{MgCl_2} = \frac{1}{2} n_{NaOH}$$

$$[MgCl_2] = \frac{\frac{1}{2} \times \left(1.00 \times \frac{20.0}{1000}\right)}{\frac{40.0}{1000}} = \textbf{0.250 mol dm}^{-3}$$

[1]

Comments:
- Some candidates did not notice the mole ratio.

(v) Using your answer to **(b)(iii)** and **(b)(iv)**, determine the K_a for the hydrated magnesium ion, $[Mg(H_2O)_6]^{2+}$.

$$K_a = \frac{\left[H^+\right]^2}{\left[Mg(H_2O)_6^{2+}\right]_0 - \left[H^+\right]} = \frac{\left(1.00 \times 10^{-6}\right)^2}{0.250 - 1.00 \times 10^{-6}}$$

$$= \underline{\mathbf{4.00 \times 10^{-12}\ mol\ dm^{-3}}}$$

[1]

Comments:
- Some candidates did not know that the concentration of $[Mg(H_2O)_5(OH)]+$ ion is the same as that of H^+.

(vi) When 10 cm^3 of alkali have been added, calculate:

I. the hydroxide ion concentration,

$pOH = 14 - 9 = 5$
$[OH^-] = \underline{\mathbf{1.00 \times 10^{-5}\ mol\ dm^{-3}}}$

II. the hydrated magnesium ion concentration.

$$\left[Mg^{2+}\right] = \frac{\frac{1}{2} \times \left(\frac{40}{1000} \times 0.250\right)}{\frac{50}{1000}} = \underline{\mathbf{0.100\ mol\ dm^{-3}}}$$

[2]

Comments:
- For I, some candidates did not know that they are supposed to make use of the pH to calculate pOH.
- For II, many candidates did not know that they are supposed to make use of the initial amount.

(vii) Hence, calculate a value for the solubility product, K_{sp}, of magnesium hydroxide.

$$K_{sp} = [Mg^{2+}][OH^-]^2$$
$$= 0.100 \times (10^{-5})^2$$
$$= \mathbf{1.00 \times 10^{-11}\ mol^3\ dm^{-9}}$$

[1]

Comments:
- As error carried forward was allowed, this was generally well-attempted.

(viii) Explain the constant pH observed when the volume of NaOH added is in the range of 5.0 cm³ and 15.0 cm³.

The **OH⁻(aq) added is removed as solid Mg(OH)₂.**

$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$. This keeps **[OH⁻] constant** (pH is constant at 9). ....[1]

Comments:
- Majority of the candidates incorrectly assumed that there is a buffer solution without appreciating the type of reaction this is.

[Total: 15]

Comments:
- Average mark for Q2 lies between 10–11 marks. Highest score was 16.
- Refer to detailed comments for the respective parts below.

2 At 1200 K, in the presence of a gold wire, dinitrogen oxide, N_2O, decomposes as follows.

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$
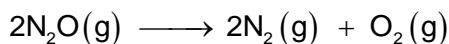
The rate of the reaction can be followed by measuring the total pressure, p, as it changes with time, t. In such an experiment, the total pressure increased as shown in Table 2.1.

Table 2.1

total pressure, p / kPa	25.0	27.5	30.0	32.5	34.0	35.0
time, t / s	0	1030	2360	4230	5870	7420
partial pressure of N_2O / kPa	25.0	20.0	15.0	10.0	7.00	5.00

(a) (i) Calculate the concentration of N_2O at the start of the reaction in mol dm^{-3}.

using $pV = nRT$

$$\frac{n}{V} = \frac{p}{RT} = \frac{25.0 \times 10^3 \text{ Pa}}{8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 1200 \text{ K}}$$

$$= 2.507 \text{ mol m}^{-3}$$

$$= \underline{\mathbf{2.51 \times 10^{-3} \text{ mol dm}^{-3}}}$$

[1]

Comments:
- Majority of the students made use of the correct formula to arrive at the $[N_2O]$ in mol m^{-3}.
- However, many did not know the conversion from **mol m^{-3} to mol dm^{-3}**, thus losing this mark (or they were unaware they need to convert, forgetting the units for V in the equation was in m^3.).

(ii) Show that the partial pressure of N_2O at any time t is equal to $(75.0 - 2p)$ kPa.

Let q kPa be the partial pressure of O_2 at time t.

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$

	$2N_2O(g)$	$2N_2(g)$	$O_2(g)$
initial partial pressure / kPa	25.0	0	0
Δ in partial pressure / kPa	$-2q$	$+2q$	$+q$
partial pressure at time t / kPa	$25.0 - 2q$	$2q$	q

total pressure at time $t = 25.0 - 2q + 2q + q$

$$p = 25.0 + q$$
$$q = p - 25.0$$

partial pressure of N_2O at time $t = 25.0 - 2q$ kPa

$$= 25.0 - 2(p - 25.0) \text{ kPa}$$
$$= 25.0 - 2p + 50.0 \text{ kPa}$$
$$= 75.0 - 2p \text{ kPa } (\textbf{shown})$$

[2]

Comments:
- It was surprising that a considerable no. of students were not able to prove/show this expression for partial pressure of N_2O.
- Most students were able to come out with the relevant ICE table but stopped short of arriving at the final expression.
- A number of students merely substitute the value of total pressure, p (for a particular time) into the expression and then obtain the value of partial pressure of N_2O to be the same as the table and concluding expression was thus correct.

(iii) Hence, complete Table 2.1 for the partial pressures of N_2O after 1030 s, 2360 s, 4230 s, 5870 s and 7420 s. [1]

Comments:
- Large majority of students were able to complete this part.
- Despite the expression given in the previous part, some students obtained incorrect values (common values seen were 5.00 and 0.00 respectively) for the last 2 columns (for p=34.0 and 35.0 [they thought reaction completed at this time.]). It seemed that these students had independently did this part of the table first right from the beginning of the qns without referring to the context given in (a)(ii).

(iv) Plot on the grid in Fig. 2.1, a graph of the partial pressure of N_2O against time, t, and hence determine the order of the reaction with respect to N_2O.

– correct plot and line-of-best-fit
– determination of $t_{1/2}$ (~3200 s)
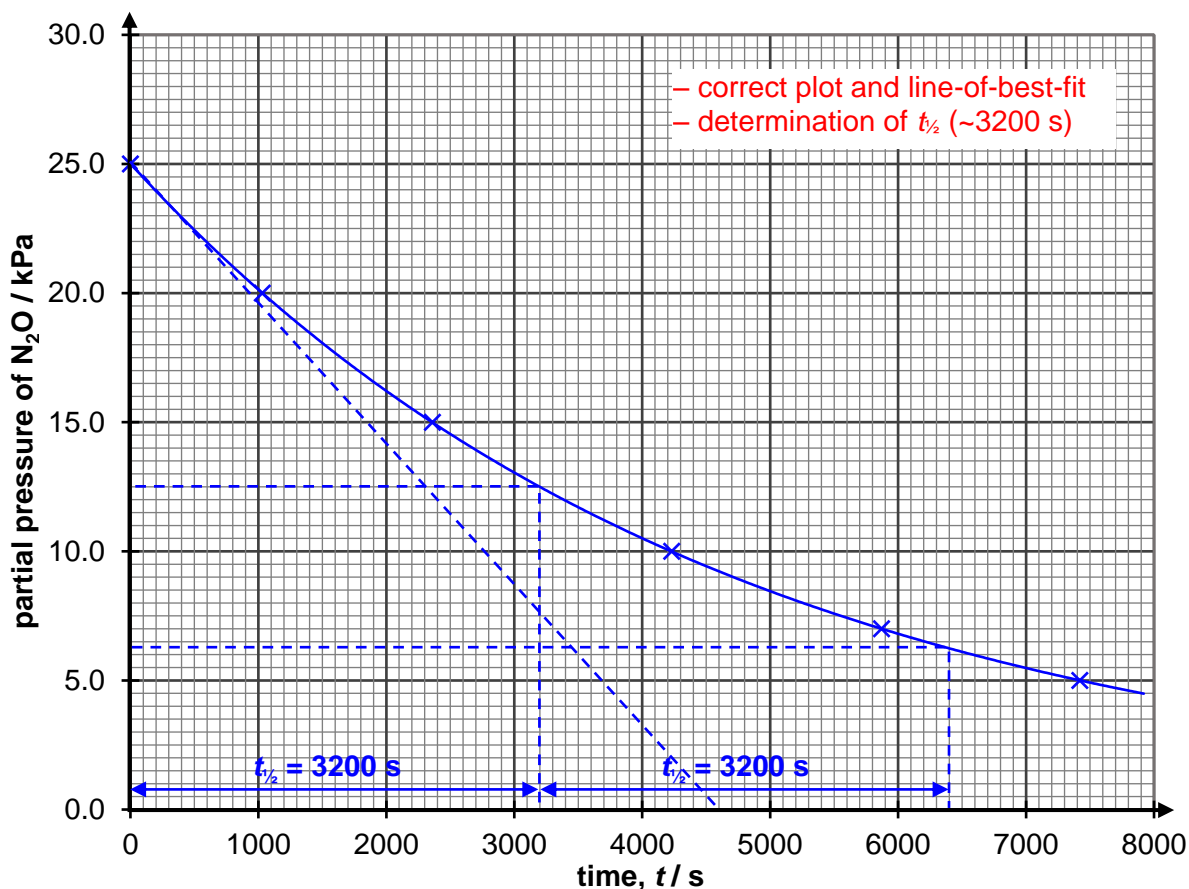
$t_{1/2}$ = 3200 s $t_{1/2}$ = 3200 s

Fig. 2.1

Since the graph of partial pressure of N_2O against t has a **constant half-life of 3200 s** (must be shown on graph),
the order of the reaction with respect to N_2O is **1**.

[3]

Comments:
- Most students were able to obtain the best-fit curve with curve passing through all points.
- They were largely thus able to obtain constant or approx. constant half-lives (around 3200 s). **At least 2 half-lives should be shown (3 half-lives for practical).** For approx. constant half-lives to be concluded, the values should be within 200 s of each other.
- Some students misplotted the (1030, 20.0) and (5870, 7.00), thus affecting the quality of their half-live values. These students will still receive credit for showing their half-lives working clearly on the graph. However, they will be penalised 2m – the 1st mark for plotting and best-fit curve and the 3rd mark for concluding on half-lives and thereby the order. Often these students' half-lives values fall out of the 200s range to be considered approx. constant.

Comments (cont'd):

- For those students who incorrectly determine the last 2 partial pressure values for p=34.0 and p=35.0 (refer to 2nd bulleted point of comments given in **(a)(iii)**), they drew a best-fit straight line instead. They were penalised for the 1st mark for the best-fit curve and the 3rd mark for quality of t$_{1/2}$ and order of reaction (since they will conclude is zero order). They would still receive credit for showing relevant half-lives if they did (most often they did not since they obtained a constant gradient).
- **Students are to be reminded** that they need to show or indicate their half-lives working (construction lines to indicate where they used to determine their respective half-lives e.g. from 25 to 12.5 to 6.25 or 20 to 10 to 5 and their respective t values) and half-live values on the graph as reflected in the answers above. If the 2 half-lives values were different, they should evaluate the average half-live value and conclude on the order. They should not just draw construction lines, show some values like 3,200 and 6,400 on the graph (without indicating the 2 t$_{1/2}$ values) and then conclude since half-lives were constant, order=1. Markers will not interpret this for you since this qns is assessing your understanding of half-live concept.

(v) Calculate the rate constant for the reaction, including its units.

using $k = \dfrac{\ln 2}{t_{\frac{1}{2}}}$

$k = \dfrac{\ln 2}{3200}$ s^{-1}

$= 2.166 \times 10^{-4}$ s^{-1}

$= \underline{\mathbf{2.17 \times 10^{-4}\ s^{-1}}}$

or

initial rate of reaction $= \dfrac{2.51 \times 10^{-3}\ \text{mol dm}^{-3}}{4600\ \text{s}}$

$= 5.45 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

substituting into the rate equation,

$\text{rate} = k[\text{N}_2\text{O}]$

$5.45 \times 10^{-7} = k(2.51 \times 10^{-3})$

$k = \underline{\mathbf{2.17 \times 10^{-4}\ s^{-1}}}$

[1]

Comments:

- Both methods should obtain the same value and units.
- Most students used the 1st method to determine the rate constant. However, some thought there were no units for k (they wrote "no units") or gave incorrect units for k, failing to relate back to the 1st order wrt to N$_2$O which they earlier obtained.
- Students who used the 2nd initial rates method often failed to recognise the y-axis of their graph was in kPa and not in mol dm^{-3} s^{-1}. They then went on to make use of the rate equation dividing by [N$_2$O] (which was in mol dm^{-3}) to obtain their k and still giving the units as s^{-1}. They failed to recognise the units of rate is in kPa and [N$_2$O] is in mol dm^{-3}.
- Students who incorrectly determine the order from **(a)(iv)** was given credit for this part should they do the correct manipulations (with the correct units) based on error carried forward principle.

(vi) When platinum is used instead of gold as the catalyst, the rate equation for the same reaction becomes

$$\text{rate} = \frac{k_2[N_2O]}{1 + b[O_2]}$$

where k_2 is the new rate constant and b is a constant.

Describe and explain how the rate of decomposition will change as the reaction proceeds.

As the reaction progresses, **concentration of the N_2O reactant decreases** as it is being **consumed**, hence the **rate would decrease**.

In addition, the **concentration of the O_2 product increases** as it is **formed**, hence the rate would **further decrease**.

....[2]

Comments:
- Majority of the students were able to explain this part well, identifying both $[O_2]$ and $[N_2O]$.
- Some students focused only on $[O_2]$ or $[N_2O]$ in their explanation.

(b) N_2O is a linear molecule.

(i) Draw the dot-and-cross diagram of a N_2O molecule.

[1]

Comments:
- This part was poorly done. Many students placed the O as the central atom, forgetting a key principle in drawing dot-cross diagrams that the **central atom is usually the less electronegative atom** (though O has only 1 atom in this case).
- All structures with O as the central atom were penalised, even if they satisfy the octet and linear shape conditions.

(ii) The standard enthalpy change of formation of N_2O is $+82$ kJ mol^{-1}.

Using data from the *Data Booklet*, determine a value for the bond dissociation energy of the nitrogen–oxygen bond in N_2O.

$$N\equiv N + \tfrac{1}{2}\, O=O \rightarrow N\equiv N\rightarrow O$$

$$+82 = \sum B.E.(\text{bonds broken}) - \sum B.E.(\text{bonds formed})$$

$$+82 = B.E.(N\equiv N) + \frac{1}{2}B.E.(O=O) - B.E.(N\equiv N) - B.E.(N-O)$$

$$= \frac{1}{2}(+496) - B.E.(N-O)$$

$$B.E.(N-O) = \underline{\textbf{+166 kJ mol}^{-1}}$$

[2]

Comments:
- This part was also poorly done. This was due to either using the incorrect formula (of bonds formed – bonds broken) or failing to express their equation for the formation of N_2O to be in terms of 1 mol of N_2O. Many made use of $2\,N_2 + O_2$ to give $2\,N_2O$ equation and still took this enthalpy change to be +82.
- Students who obtained the incorrect structure for **(b)(i)** was given full credit should they show the correct manipulations based on error carried forward principle.
- Students are reminded that bond energy value has a "+" sign associated with the value. Those who omitted it were not penalised this time.

(iii) The activation energy of the uncatalysed (decomposition) reaction is 90 kJ mol^{-1} and of the catalysed reaction 40 kJ mol^{-1}. The energy profile diagram of the uncatalysed reaction is shown in Fig. 2.2.

On the same axes in Fig. 2.2, draw the energy profile diagram for the catalysed reaction and label all relevant enthalpy changes.
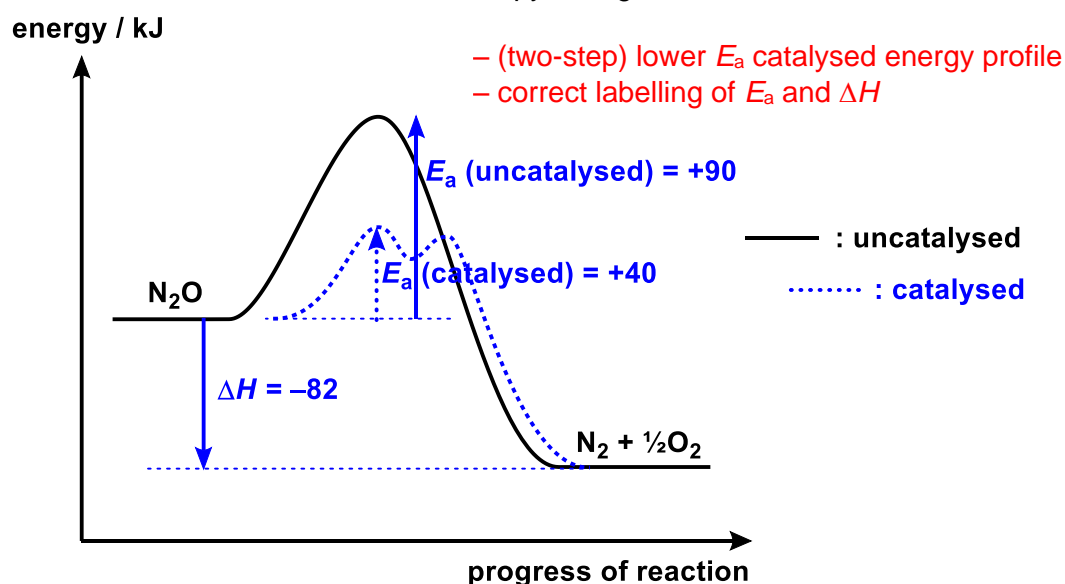

– (two-step) lower E_a catalysed energy profile
– correct labelling of E_a and ΔH

E_a (uncatalysed) = +90
E_a (catalysed) = +40
$\Delta H = -82$
N_2O
$N_2 + \tfrac{1}{2}O_2$

——— : uncatalysed
········ : catalysed

energy / kJ

progress of reaction

Fig. 2.2

[2]

(iv) Hence, explain why it is thermodynamically and kinetically not possible to make N_2O from its elements, even if a gold catalyst is present.

The formation of N_2O is **non-spontaneous** ($\Delta G > 0$) **at all temperature** as the

reaction is endothermic ($\Delta H > 0$) and leads to a decrease in entropy ($\Delta S <$

0) since there is a net consumption of gaseous molecules.

In addition, the **activation energy for the formation of N_2O** from N_2 and O_2 is

much higher than the activation energy for the exothermic decomposition

of N_2O, even in the presence of gold catalyst. Thus, any N_2O even if it is slowly

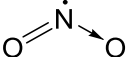formed, would **rapidly decompose** to give back N_2 and O_2.

....[2]

(c) Nitric acid production represents the largest source of N_2O in the chemical industry. Nitrogen monoxide, NO, an intermediate in the production of nitric acid, readily decomposes to N_2O and nitrogen dioxide, NO_2, at high pressures.

$$3NO(g) \longrightarrow N_2O(g) + NO_2(g)$$
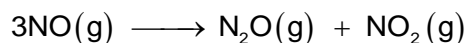
NO_2 is in fact a radical with the following structure:

(i) Given that $\Delta H_f^{\ominus}(NO) = +90$ kJ mol^{-1} and $\Delta H_f^{\ominus}(NO_2) = +33$ kJ mol^{-1}. Together with the data given in **(b)(ii)**, calculate the standard enthalpy change for the decomposition of NO into N_2O and NO_2.

$$\Delta H_r^{\ominus} = \sum \Delta H_f^{\ominus}(\text{products}) - \sum \Delta H_f^{\ominus}(\text{reactants})$$
$$= \Delta H_f^{\ominus}(N_2O) + \Delta H_f^{\ominus}(NO_2) - 3\Delta H_f^{\ominus}(NO)$$
$$= +82 + 33 - (3 \times +90)$$
$$= \textbf{\underline{--155 kJ mol}}^{\textbf{--1}}$$

[1]

Comments:
- This part was generally well done.
- Students who got this wrong were usually due to either due to the incorrect formula they used (reactants – products instead) or forgetting the coefficient "3" for enthalpy change of formation of NO.
- Some students who did the above correct manipulation went on to divide by 3 to their value. They did so thinking Standard enthalpy change of decomposition of NO referred to only 1 mol of NO in the given equation. They are reminded that they should calculate any general enthalpy change of reaction (not within the scope of the definitions which they have learnt) based on the stoichiometric ratio as given by the equation.

(ii) Comment on the extent of deviation of the two gases, NO_2 and N_2O, from ideal gas behaviour under the following pressure conditions.

High pressure : Both gases **deviate similarly** from ideal gas behaviour. Under high pressure condition, deviation from ideal gas behaviour is due to the **volume occupied by the molecules being not negligible compared to the volume of the container**. Since NO_2 and N_2O are **similar in size**, the two gases will deviate similarly. ....[1]

Low pressure : At low pressure, deviation from ideal gas behaviour is due to the **intermolecular attraction** between molecules. NO_2 has a **larger dipole moment** compared to N_2O. Hence, the **permanent dipole-permanent dipole attraction** between the NO_2 molecules are **stronger** than that between N_2O molecules, causing **NO_2 to deviate more from ideal gas behaviour**. ....[1]

Comments:
- This part was poorly done. Most compared both gases with reference to ideal gas rather than comparing the extent of deviation of NO_2 versus N_2O from ideal gas behaviour.
- For **High pressure**, students need to be reminded that the dominant factor or assumption they should be discussing should be regarding the assumption that volume of gas molecules being negligible as compared to the volume of gas/container being no longer valid since at high pressure, the **pV value for non-ideal gases in general is larger than that of ideal gas**. Students who gave the latter assumption about intermolecular forces of attraction being no longer negligible and concluding that NO_2 having stronger permanent dipole-permanent dipole (pd-pd) interactions than that of N_2O still receive full credit (though they should recognise that when molecules have significant intermolecular forces of attraction, this will result in the impact on the container i.e. pressure being lower. Thus, pV values will be lower than that of ideal gas and thus contradict experimental data).
- Students who did compare the size of NO_2 and N_2O did not realise the difference whether in terms of no of electrons (23 vs 22) or Mr (46 vs 44) was very small and as such their sizes were similar and thus should exhibit similar deviation from ideal gas.
- For **Low pressure**, since the volume of gas molecules being negligible as compared to the volume of gas/container, the key point/assumption to be mentioned is the difference in intermolecular forces of attraction between NO_2 and N_2O, resulting in the **pV values for non-ideal gases to be lower than that of ideal gas**. Students who incorrectly determine in **(b)(i)** the N_2O structure with O as the central atom (so 2 N=O bonds) and thus conclude that N_2O had intermolecular instantaneous dipole-induced dipole interactions (since it is non-polar) and weaker than the stronger intermolecular pd-pd interactions for NO_2 was given credit. It was annotated in their scripts that N_2O is actually polar but error carried forward due to their structure in **(b)(i)**.

[Total: 20]

3 Tris, or tris(hydroxymethyl)aminomethane, is a white crystalline organic compound with the formula $(HOCH_2)_3CNH_2$. It is extensively used in biochemistry and molecular biology as a component of buffer solutions.

(a) State and explain whether Tris will be a stronger or weaker base compared to methylamine, CH_3NH_2.

<u>**Weaker base**</u>. (with correct reason) ....

The <u>**three OH groups**</u> are <u>**electron-withdrawing**</u> due to the <u>**highly electronegative**</u>

<u>**oxygen**</u> atoms, hence rendering the <u>**lone pair of electrons on the nitrogen less**</u> ...

<u>**available for donation to an acid**</u> ....[2]

Comments:
- This part is poorly attempted. Many concluded wrongly that Tris is a stronger base because N atom in Tris is bonded to three larger electron donating alkyl groups and that increased the availability of the lone pair of electrons on N. The presence of the electron withdrawing OH group was overlooked.
- Some who have concluded that Tris is a weaker base but gave the wrong or contradicting reasons and were not awarded any mark.
- Those who have correctly concluded Tris is a weaker base but had some inaccuracy in the reason was awarded 1 mark. Some of the inaccuracy are as follows.
  - Presence of electron withdrawing groups intensify the negative charge on N (wrong! There is no negative charge on N)
  - Presence of electron withdrawing groups increase the lone pair on N (wrong! The no. of lone pair of electrons on N atom will not increase!)
- Many indicated that $(HOCH_2)$ group is electron withdrawing. Mark was not deducted for this, but it is more accurately to state the electron withdrawing group as the OH group.

When one mole of Tris is treated with one mole of ethanoyl chloride, a mixture of products is obtained, involving ethanoylation at both the nitrogen and oxygen atoms of Tris:
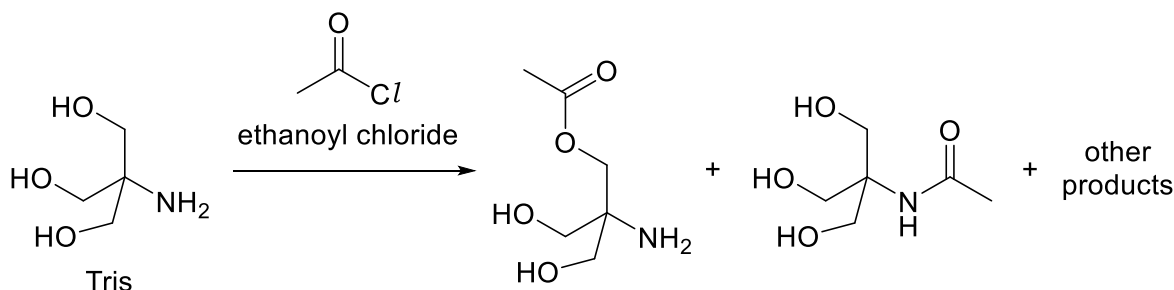
However, when one mole of Tris is treated with one mole of $CH_3CO_2CO_2CH_2CH_3$ (a mixed anhydride), *N*-ethanoyl-Tris is obtained cleanly in high yield:

Tris → mixed anhydride → *N*-ethanoyl-Tris
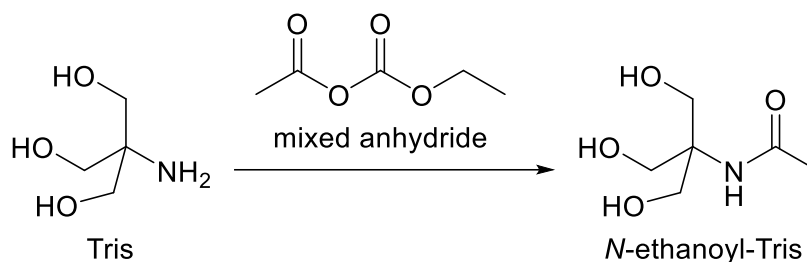
(b) Suggest a likely explanation for the differences in selectivity observed using the two ethanoylating reagents.

As the C=O carbon in ethanoyl chloride is **more electrophilic / electron-deficient** than that in the mixed anhydride, it is **less selective** towards the **more nucleophilic amine nitrogen atom** compared to the alcohol oxygen atom.
or
As the C=O carbon in the mixed anhydride is **less electrophilic / electron-deficient** than that in ethanoyl chloride, it is **more selective** towards the **more nucleophilic amine nitrogen atom** compared to the alcohol oxygen atom. [2]

Comments:
- It can be seen that many candidates do not understand the question and end up describing the difference in selectivity instead of explaining why.
- Many only went as far as stating ethanoyl chloride is more reactive than the mixed anhydride without stating that the C=O carbon is more electron deficient than that in the mixed anhydride. Some incorrectly state that ethanoyl chloride is a better nucleophile!
- Many also failed to identify that the amine nitrogen atom is more nucleophilic than the alcohol oxygen atom. They simply state ethanoyl chloride is a better electrophile and hence can react with both the N and O atom in Tris. The full two marks cannot be given for this.

A Tris–HCl buffer can be prepared by dissolving solid Tris in a suitable volume of hydrochloric acid.

Tris has a pK_b of 5.93 at 25 ºC.

(c) (i) Explain whether Tris or hydrochloric acid should be used in excess.

Tris should be used in excess.

This is because a buffer is composed of a **weak base and its conjugate acid,**

thus there must be excess Tris, the weak base. [1]

Comments:
- While many correctly identified that Tris should be in excess, few were able to explain the need for both a weak base and its conjugate acid to be present to act as a buffer.
- Many answers incorrectly focused on why an excess of HCl would not give a buffer, rather than explain how a buffer is obtained.

(ii) Explain how the Tris–HC*l* buffer works.

The mixture consists of a **large reservoir** of the **base** (Tris) and its **conjugate acid** (TrisH$^+$), and hence is able to remove **small amounts of acid and base added, respectively,** hence **maintaining the pH relatively constant**.

....[2]

Comments:
- Many students did not realise that the question was simply asking them to define how a buffer works.
- Many answers failed to mention the need for a large reservoir of the base and its conjugate acid. A large number thought that HC*l* was the acid component of the buffer, failing to realise that the buffer must be made of a weak base and its conjugate acid (or vice versa), rather than a strong acid of HC*l*.
- A number of answers omitted to mention that the buffer was only able to remove small amounts of acid and base.
- Weaker answers repeated the terms given in the question, for example, by saying that the buffer buffers against pH changes, or completely omitted to explain that the removal of small amounts of acid and base added maintained a relatively constant pH.

(iii) Explain whether the hydrochloric acid can be replaced by ethanoic acid.

Yes. So long as there are **sufficient amounts** of the weak base and its conjugate acid (*or* weak acid and conjugate base) to remove the small amount of acid or base added. ....[1]

Comments:
- This was poorly done.
- Majority thought that ethanoic acid being a weak acid would only partially dissociate, hence not be able to provide H$^+$ required to react with Tris to form sufficient conjugate acid. It should be noted that when H$^+$ from ethanoic acid has been reacted, more ethanoic acid would dissociate to form more H$^+$.
- Some thought that adding small amounts of ethanoic acid would convert the basic buffer to an acidic buffer, without realising that ethanoic acid would need to be in large excess of Tris for it to happen. (Since the acidic buffer would need to consist of the weak acid and its conjugate base)

(iv) By means of an equation, show how the Tris–HCl buffer functions when a small amount of dilute sodium hydroxide is added.

$(HOCH_2)_3CNH_3^+ + OH^- \rightarrow (HOCH_2)_3CNH_2 + H_2O$ ....[1]

Comments:
- This was generally well done.
- Some thought that HCl which was added to the buffer would be able to react with NaOH, not realising that it would have already reacted with the basic Tris to form the conjugate acid (which would react with NaOH added).

(v) State the effective pH range of Tris buffer.

pK_a of conjugate acid = 14 − 5.93 = 8.07.   Effective pH range is pK_a ± 1, so will

be **7.07 to 9.07**. ....[1]

Comments:
- While many realised that the range was ± 1, many wrongly thought that they could use pK_b instead of pK_a.

(vi) Based on your answer to **(c)(v)**, suggest a reason why Tris is used extensively in biochemistry and molecular biology as a buffer.

The working range of Tris buffer **lies in the physiological pH** typical of most

living organisms. ....[1]

Comments:
- Few students realised that the physiological pH lies within the working range of the buffer. Many related the use of Tris to the blood pH or working pH of enzymes which was not accepted.

(vii) Determine the volume of 1.00 mol dm^{-3} hydrochloric acid that must be used to dissolve 5.00 g of Tris to obtain a buffer solution at pH 8.50.
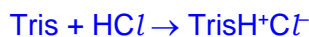[M_r of Tris = 121.0]

$$n_{\text{Tris solid}} = \frac{5.00}{121.0} = 0.04132 \text{ mol}$$

Let the buffer contains x mol of Tris and the volume of 1.00 mol dm^{-3} HCl be V dm^3,

$$K_a\left(\text{TrisH}^+\right) = \frac{\left[\text{H}^+\right]\left[\text{Tris}\right]}{\left[\text{TrisH}^+\right]}$$

$$10^{-(14-5.93)} = \frac{10^{-8.50}\left(\dfrac{x}{V}\right)}{\dfrac{0.04132 - x}{V}}$$

$$x = \frac{0.04132}{1 + 10^{-0.43}} = 0.03013$$

$$\text{Tris} + \text{HC}l \rightarrow \text{TrisH}^+\text{C}l^-$$

$$n_{\text{HC}l} \text{ needed} = n_{\text{TrisH}^+} = 0.04132 - 0.03013 = 0.01119 \text{ mol}$$

$$V = \frac{n_{\text{HC}l}}{\left[\text{HC}l\right]} = \frac{0.01119}{1.00} = \underline{\textbf{0.0112 dm}^3} = \underline{\textbf{11.2 cm}^3}$$

[3]

Comments:
- This was poorly done. Many students failed to realise that they were dealing with a buffer solution and applied equations for weak bases instead. Those who attempted to use the buffer equation often quoted the wrong Henderson Hasselbach (HH) equation, confusing pH with pOH, and pK_a with pK_b. Many did not correctly identify the base/acid species and the corresponding salt in the equation used.
- Many thought that the [acid] was the same as that of [HCl]. Those who were able to identify the correct species for the HH eqn did not realise that the amount of Tris at equilibrium would differ from the starting amount as some would have already reacted with the added HCl.

Tris is manufactured industrially by the exhaustive reaction of nitromethane, CH_3NO_2, with methanal under basic conditions to produce the intermediate $(HOCH_2)_3CNO_2$, which is subsequently reduced to give the final product:

$$CH_3NO_2 + 3HCHO \xrightarrow{\text{NaOH}} (HOCH_2)_3CNO_2 \xrightarrow{\text{[H]}} (HOCH_2)_3CNH_2$$

(d) Nitromethane, CH_3NO_2, has a low pK_a of 10.2, which is comparable to that of phenol ($pK_a = 9.95$) and much more acidic compared to most alcohols ($pK_a \sim 16$).

For Examiner's Use

(i) Explain why phenol is more acidic than most alcohols.

The **negative charge** of the phenoxide conjugate base is **delocalised into the**

benzene ring, **dispersing the charge**, rendering the phenoxide ion **more**

stable than alkoxide ions, hence phenol a stronger acid.

....[1]

Comments:
- This was generally well done.
- Some answers mentioned that benzene was electron withdrawing, hence dispersing the negative charge. It should be noted that it is not sufficient to state as such since benzene can be either electron-donating or electron-withdrawing, depending on what it is attached to. Hence how benzene is electron-withdrawing in this case must be fully explained.
- Many answers omitted to explain how the charge was stabilised, with answers often left as the phenoxide ion being more stable.

(ii) Suggest likely reasons for the low pK_a of nitromethane.

The negative charge on the conjugate base is stabilised by both **delocalisation**

into the NO₂, as well as by the **electron-withdrawing (inductive) effect** of the

highly electronegative N and O.

....[1]

Comments:
- This was poorly done. Few realised that the H on CH_3NO_2 was acidic and could dissociate. Many answers attempted to explain the low basicity of nitromethane instead, or thought that the negative charge was on N.
- Most answers only gave either the mesomeric effect or inductive effect.

The first stage involves the Henry reaction, which is a classic carbon–carbon bond formation reaction between a nitroalkane and a carbonyl compound:
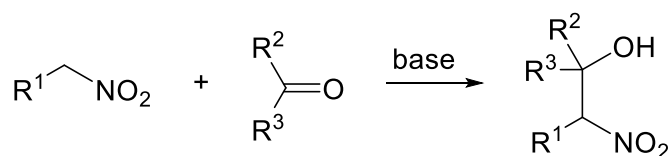
(e) The Henry reaction begins with deprotonation of the acidic nitroalkane on the α-carbon forming a negatively charged carbanion:
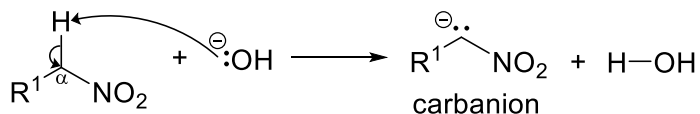
Complete Fig. 3.1 to suggest a mechanism for the subsequent attack of the carbanion onto the carbonyl carbon, and protonation of the intermediate to give the 2-hydroxynitro product. Show the structure of the intermediate, all charges and relevant lone pairs, and show the movement of electron pairs by using curly arrows.
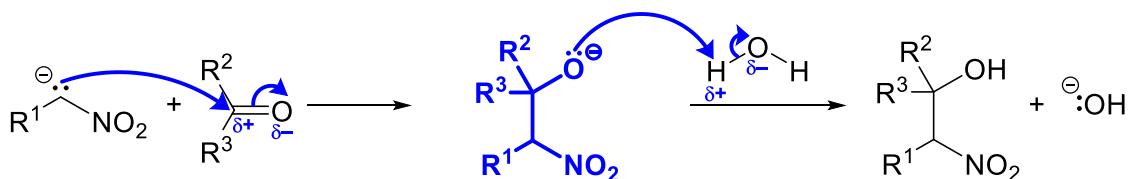
intermediate

Fig. 3.1

[3]

Comments:
- This was generally well done. Common mistakes include omission of partial charges of water and the C=O.

(f) Suggest a reagent for reduction of the intermediate, $(HOCH_2)_3CNO_2$, to give Tris.

Sn or Fe, concentrated HC*l* / LiA*l*H$_4$ / H$_2$ with Ni or Pt ....[1]

[Total: 20]

Comments:
- This was generally well done.

4 (a) Caffeine is a stimulant drug that is the world's most widely consumed psychoactive drug. It is found naturally in tea leaves and coffee beans, but can also be synthesised in the laboratory. One method involves converting theobromine into caffeine *via* a two-step route shown in Fig. 4.1.

theobromine → (CH$_3$ONa, step 1) → → (CH$_3$I, step 2) → caffeine
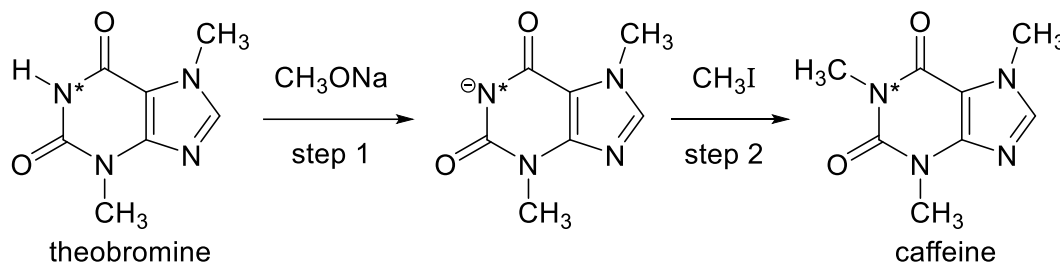
Fig. 4.1

(i) State the type of reaction in step 1.

Acid-base reaction ....[1]

> **Comments:**
> - Generally well done. However, some students gave it as "deprotonation", benefit of doubt was given.
> - Some students gave all sorts of organic reaction mechanism thinking that the question is about Step 2.

(ii) Step 1 is necessary as the lone pair on the N* atom of theobromine is not available for reaction directly with CH$_3$I.

Suggest an explanation for this.

The lone pair on the N* atom **delocalises into the π-electron cloud of the**

adjacent C=O bond. Hence it is unavailable for reaction.

....[1]

> **Comments:**
> - Generally okay. Many students lack the appreciation of the importance of the π-electron cloud of the bond that allows for the delocalisation of the lone pair but credit was still given if idea of delocalisation into the C=O bond is present.
> - Some students gave the reason of the lone pair being unavailable due to the presence of the electron-withdrawing O atom. This is insufficient.
> - Some students gave vague reasoning that the lone pair was able to delocalise into the O atoms which is not possible without the C in the C=O bond.

(iii) Describe the mechanism for the reaction in step 2. You may represent the anionic intermediate as R_2N^-.

Bimolecular Nucleophilic Substitution / S_N2

pentavalent transition state

[3]
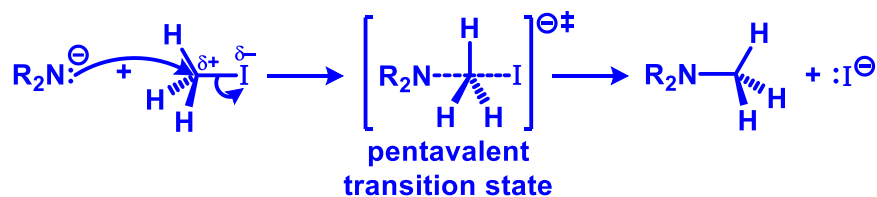
Comments:
- This part was poorly attempted. Many students were unable to see that step 2 is an S_N2 reaction, with the anionic intermediate serving as the nucleophile and CH_3I as the electrophile. Also, many students who wrote S_N2 gave the wrong superscript/subscripts such as SN_2/S_{N2}/etc.
- Many students who gave the correct reaction were unable to completely complete the mechanism. Many omitted the correct arrows, charges, double dagger representing the transition state, the weakening bond in the transition state and all products.
- Students are reminded that 3D configuration should be observed for S_N2 reactions even though it is not a marking point.

(b) Caffeine can be extracted from an aqueous solution using liquid-liquid extraction, where the caffeine solute is partitioned between an aqueous phase (aq) and an organic phase (org). The resulting equilibrium for caffeine extraction may be written as:

$$\text{caffeine(aq)} \rightleftharpoons \text{caffeine(org)}$$
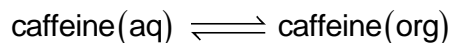
The ratio of the concentrations of caffeine in the two phases can be written as an equilibrium constant called the partition coefficient, K_D.

$$K_D = \frac{[\text{caffeine}]_{org}}{[\text{caffeine}]_{aq}}$$

Caffeine can be extracted using different organic solvents such as trichloromethane and benzene. After extraction, it can be purified further into white crystals.

The K_D of caffeine in benzene and trichloromethane are given in Table 4.1.

Table 4.1

solvent	K_D
benzene	0.450
trichloromethane	8.30

(i) Using Table 4.1, determine which is the better solvent in extracting caffeine from the aqueous phase. Explain your answer with reference to the structure and bonding.

Trichloromethane is the better solvent as it has the **largest K_D value**. Both

caffeine and trichloromethane are **both polar** but benzene is **non-polar**. Hence,

caffeine and trichloromethane are able to interact strongly via **permanent**

dipole–permanent dipole interactions between the molecules. Hence,

trichloromethane is a better solvent than benzene.

....[2]

Comments:
- This was poorly done in general. Many students were unable to comprehend the question correctly.
- Many students simply stated which is a better solvent without using information from the table. Also, many students chose the wrong solvent as they thought that caffeine is to be extracted into the aqueous phase when it should be **from** the aqueous phase.
- The explanation using the structure and bonding for why it is a better solvent was done very poorly. Many students were unable to identify correctly that caffeine is polar. Some students thought that trichloromethane is CCl_4 instead of $CHCl_3$. Therefore, indicating the wrong polarity of the molecule. Also, many students tried to explain that benzene has resonance structure/pi electrons etc. to explain its structure and bonding but this is not necessary. Students should be careful that with reference to structure and bonding in terms of chemical bonding, it is referring to in this case, simple molecules structures of the solvents, their polarity and hence the type of intermolecular forces of attraction that exists.
- Students who correctly identified that type of intermolecular forces of attraction between the solvents only did not answer the question. Ultimately, students must be able to explain why the solvents can interact well with the caffeine molecules and hence why which solvent is a better solvent.

(ii) After the extraction, the solvent is removed to give crude solid caffeine. Suggest how you can purify the crude caffeine and describe how you can ascertain the purity of the caffeine thus obtained.

The caffeine can be purified via a single solvent **recrystallisation** using trichloromethane. To ascertain the purity, take a few crystals of caffeine and **determine its melting point** using a thiele tube/melting point machine. If the crystals melt at a **sharp and accurate** (compared to literature value) **melting point, it is pure**. If the crystals **gradually melt over a temperature range, it is not pure**..[2]

Comments:
- This part was poorly done. Many students were unable to identify the method in purifying organic compounds. Students are reminded to be familiar with laboratory knowledge from practicals.
- For students who attempted to explain how to ascertain purity of the compounds were not specific enough in their answers and hence did not get the credit.

Nowadays, liquid CO_2 is the preferred solvent used to extract caffeine even though it is non-polar.

(iii) Explain why caffeine is able to dissolve in liquid CO_2.

Although CO_2 is not polar, it has **polar C=O bonds**. Hence, the polar bonds is able to interact with the **polar bonds within caffeine via permanent dipole–permanent dipole interactions**, making caffeine soluble in liquid CO_2.

....[1]

Comments:
- This part was poorly done. Even though the question stated that liquid CO_2 is non-polar, many students repeated this in their answer or even gave that CO_2 is polar.
- Many students were unable to appreciate that caffeine is a polar molecule and should be interacting with liquid CO_2 via permanent dipole-permanent dipole interaction due to the polar bonds present.
- Many students also reasoned that caffeine was able to undergo hydrogen bonding with liquid CO_2, which is not possible as the H atoms of caffeine are directly bonded to C, which is not electronegative enough to generate a $H^{\delta+}$ capable of hydrogen bonding.

(iv) Compared to trichloromethane and benzene, suggest why liquid CO_2 is the preferred solvent in extracting caffeine.

Liquid CO_2 is **non-toxic/very volatile and easy to remove**......................

....[1]

Comments:
- This part was poorly attempted with many vague answers such as easier to obtain or less costly. To get the credit for easier to obtain, students must be able to explain that it is accessible from the atmosphere. Liquid CO_2 in reality is not easy to generate as it requires a very high pressure/low temperature which will result in a costly procedure.

(c) To determine the amount of caffeine in the organic extract described in **(b)**, the organic extract can be analysed spectrophotometrically, a method that measures the absorption of a specific wavelength of light in the ultraviolet–visible light region by the analyte, in this case, caffeine.

Prior to the determination of the caffeine content, a calibration plot using known concentrations of caffeine using trichloromethane as a solvent was prepared and analysed using a UV-Vis spectrophotometer. Fig. 4.2 shows the calibration plot from the analysis.
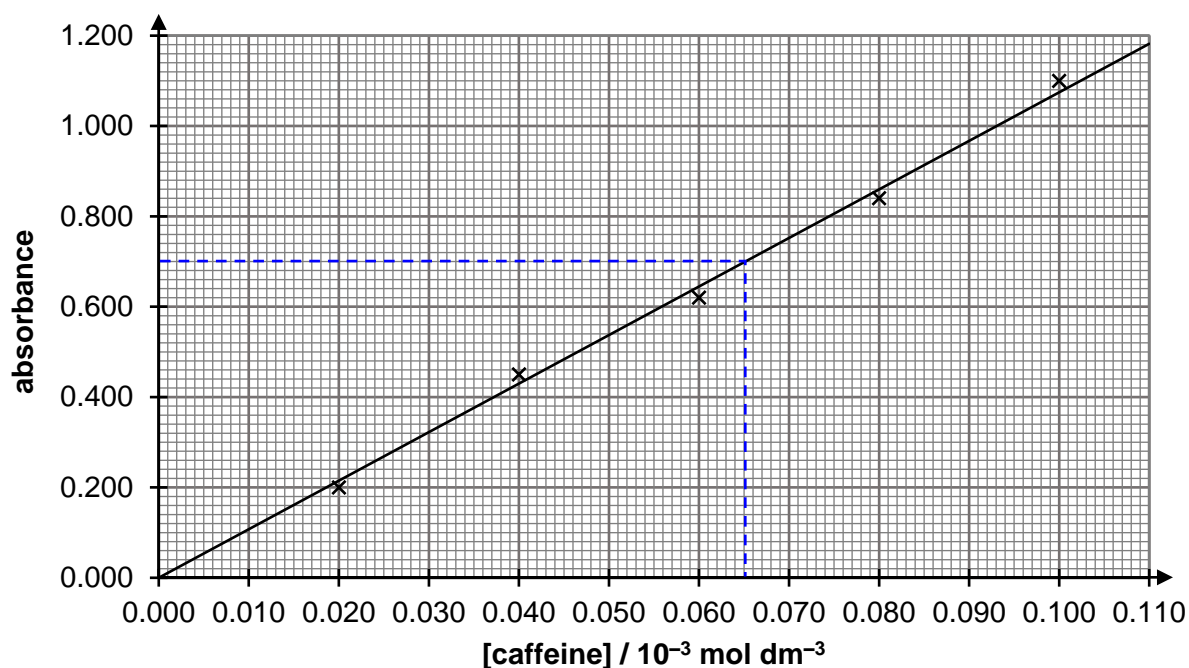
Fig. 4.2

(i) State one assumption made when using spectrophotometry to determine the concentration of caffeine in a sample of tea leaves for example.

One assumption is that caffeine is the **only compound** in tea leaves which

absorbs light at the specific wavelength used in the determination.

or other logical answers that indicate the absorption was due to caffeine only. [1]

Comments:
- This part was poorly attempted. There were incomplete or vague answers.
- Students were expected to show understanding that absorption was due to caffeine only

(ii) The organic phase extract was found to have an absorbance of 0.700.

Using Fig 4.2, determine the concentration of caffeine present in the extract.

6.50×10^{-5} mol dm^{-3} [1]

Comments:
- This part is well done in general.
- Common mistakes involved error in reading the graph. Also mis-interpret or missing out the "10^{-3}" in the x axis.

(iii) The caffeine was extracted using 0.050 dm^3 of trichloromethane and 0.500 dm^3 of water.

Using your answer in **(c)(ii)** and data from Table 4.1, determine the concentration of caffeine remaining in the aqueous phase in mol dm^{-3}.

$$[\text{caffeine}]_{org} = 6.50 \times 10^{-5} \text{ mol dm}^{-3}, \ K_D(\text{trichloromethane}) = 8.3$$

$$[\text{caffeine}]_{aq} = \frac{[\text{caffeine}]_{org}}{K_D} = \frac{6.50 \times 10^{-5}}{8.3}$$

$$= 7.8313 \times 10^{-6} \text{ mol dm}^{-3}$$

$$= 7.83 \times 10^{-6} \text{ mol dm}^{-3}$$
[1]

Comments:
- This part is well done in general.
- E.c.f. was awarded.

(iv) Hence, determine the total mass of caffeine originally present in the sample.
(M_r of caffeine = 194.2)

$$n(\text{caffeine}) = \left[0.065 \times 10^{-3} \times 0.050 \right] + \left[7.8313 \times 10^{-6} \times 0.500 \right]$$

$$= 7.1656 \times 10^{-6} \text{ mol}$$

$$m(\text{caffeine}) = 7.1656 \times 10^{-6} \times 194.2$$

$$= 1.3916 \times 10^{-3} \text{ g}$$

$$= \mathbf{1.39 \times 10^{-3} \, g}$$

[1]

Comments:
- Common mistakes involved using the "Total Volume of 0.550 dm³" for their calculations.
- Many students did not attempt this part.

(d) Instead of extracting caffeine using a single volume of solvent, it is possible to use successive volumes of solvent to extract caffeine from the sample.

The following equation gives $[\text{caffeine}]_n$, the concentration of caffeine *remaining* in V_{aq} dm³ of aqueous phase, after extraction using n V_{org} dm³ portions of organic solvent.

$$[\text{caffeine}]_n = \left(\frac{V_{aq}}{V_{org} K_D + V_{aq}} \right)^n [\text{caffeine}]_0$$

$[\text{caffeine}]_0$ is the original concentration of caffeine in the V_{aq} dm³ of aqueous phase.

An investigation on the efficiency of caffeine extraction was performed using
- one 0.100 dm³ portion,
- five 0.020 dm³ portions, and
- ten 0.010 dm³ portions

of trichloromethane, while keeping the total volume used constant (0.100 dm³).

The initial concentration of caffeine in 0.100 dm³ of the aqueous phase is 1.00×10^{-3} mol dm⁻³.

(i) Using the equation above and data from Table 4.1, complete Table 4.2.

Table 4.2

number of portions of trichloromethane used	concentration of caffeine left in aqueous phase (mol dm⁻³)	% caffeine **not** extracted from aqueous phase
one 0.100 dm³ portion	1.08×10^{-4}	10.8%
five 0.020 dm³ portions	7.51×10^{-6}	0.751%
ten 0.010 dm³ portions	2.37×10^{-6}	0.237%

[3]

Comments:
- This part was poorly done in general. Despite the example given, many were unable to use the equation to correctly calculate the concentration left as well as % not extracted.

    (ii) Comment on the efficiency of extracting caffeine using five 0.020 dm^3 successive portions of trichloromethane.

        Using **more portions of trichloromethane** allows for **more caffeine to be**

        extracted, thus making extraction more efficient.................................[1]

Comments:
- This part was poorly done in general. Some students did not attempt this part at all.
- For students who mentioned data from the table were expected to compare the efficiency between using one portion and ten portions.

    (iii) Extracting caffeine using too many successive portions of trichloromethane is not ideal. Suggest a reason for this.

        When **excessive portions of trichloromethane** is used, the amount of caffeine

        extracted **diminishes and becomes less inefficient**.................................[1]

Comments:
- This part was poorly done in general. Some students did not attempt this part at all.

[Total: 20]

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2019
General Certificate of Education Advanced Level
Higher 2

CHEMISTRY

9729/03

Paper 3 Free Response

20 September 2019

2 hours

Candidates answer on answer booklet.

Additional Materials: Answer Booklet
                         Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on 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 staplers, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

Begin **each question** on a **fresh** page of the answer booklet.

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.

This document consists of **13** printed pages and **1** blank page.

[Turn Over

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

1 Phosphoric(V) acid, H_3PO_4, is widely used in the production of fertilizers and the acidification of foods and beverages such as soft drinks. It behaves as a tribasic acid.

(a) Phosphoric(V) acid can be formed from the reaction of phosphorous(V) oxide, P_4O_{10}, or phosphorous(V) chloride, PCl_5, with water.

   (i) Write an equation for the reaction that occurs when a small amount of PCl_5 is dissolved in water. State the expected observations and the colour of the resultant solution when a few drops of Universal Indicator is added. [2]
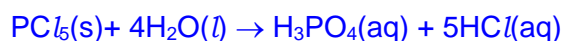
   $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$
   White fumes observed, **red** solution

Comments:
- The equation was generally well-attempted, although some students gave the equation for the reaction with limited water (instead of excess water). This was not accepted as the question stated "small amount of PCl_5".
- Many students missed out the expected observations, or assumed that effervescence would be given out.

   (ii) Phosphorus(V) chloride dissolves in some inert polar solvents to form solutions which conduct electricity. This is due to the presence of the two ions, $[PCl_4]^+$ and $[PCl_6]^-$.
   Draw structure of the $[PCl_6]^-$ ion, indicating the types of bonding within the ion, and state its shape. [2]
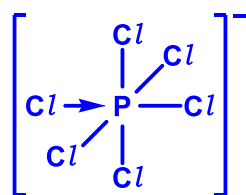
   octahedral

Comments:
- The most common error for the structure omitted the use of one dative bond. Some others used 6 dative bonds which would result in several electron-deficient chlorine atoms.
- The shape around the central atom was generally well-attempted.
- Candidates are advised to learn how to spell specific technical terms (including "octahedral").

(b) In an experiment, 25.0 cm^3 of 0.080 mol dm^{-3} phosphoric(V) acid is titrated against 0.100 mol dm^{-3} NaOH. The initial pH of the solution was 1.69.
Assume that the initial pH is due to the first dissociation of H_3PO_4 only.

(i) Show, by calculations, that H_3PO_4 is a weak acid. [1]

If H_3PO_4 is a strong acid,   *or* $\left[H^+\right] = 10^{-1.69} = 0.02042\,\text{mol dm}^{-3}$
$\left[H^+\right] = 0.080\,\text{mol dm}^{-3}$
$pH = -\lg(0.080) = 1.10 < 1.69$ $< 0.080\,\text{mol dm}^{-3} = \left[H_3PO_4\right]$
Hence H_3PO_4 is a weak acid.   Hence H_3PO_4 is a weak acid.

Comments:
- Calculations alone without any brief comment are not credited.
- Students should not use K_a to show as the use of K_a assumes that H_3PO_4 is a weak acid (i.e. a circular argument).

(ii) The numerical values of the second and third acid dissociation constants of H_3PO_4 are as follows.

$$H_3PO_4\,(aq) \rightleftharpoons H_2PO_4^-\,(aq) + H^+\,(aq) \qquad K_{a1}$$

$$H_2PO_4^-\,(aq) \rightleftharpoons HPO_4^{2-}\,(aq) + H^+\,(aq) \qquad K_{a2} = 6.17 \times 10^{-8}$$

$$HPO_4^{2-}\,(aq) \rightleftharpoons PO_4^{3-}\,(aq) + H^+\,(aq) \qquad K_{a3} = 4.79 \times 10^{-13}$$
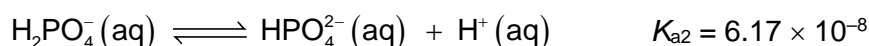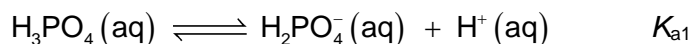
Calculate the equilibrium concentration of H_3PO_4 after the first dissociation and hence, a value of K_{a1}. [2]

Eqm (1)	$H_3PO_4\,(aq)$	$\rightleftharpoons$	$H_2PO_4^-\,(aq)$	+	$H^+\,(aq)$
Initial conc / mol dm^{-3}	0.080		0		0
change in conc / mol dm^{-3}	−0.02042		+0.02042		+0.02042
eqm conc / mol dm^{-3}	0.05958		0.02042		$10^{-1.69} = 0.02042$

equilibrium concentration of H_3PO_4 = **0.0596 mol dm^{-3}**

$$K_{a1} = \frac{\left[H^+\right]^2}{\left[H_3PO_4\right]} = \frac{0.02042^2}{0.05958}$$
$$= \mathbf{7.00 \times 10^{-3}\,\text{mol dm}^{-3}}$$

Comments:
Note: the amt of dissociated H_3PO_4 cannot be ignored as the acid is 25% dissociated.
- Some students did not answer to the question about equilibrium concentration of H_3PO_4. Some students have the misconception that equilibrium concentration of H_3PO_4 = concentration of H^+.

(iii) Calculate the first equivalence volume of NaOH for the titration. [1]

$$\text{amount of NaOH required} = \text{initial amount of } H_3PO_4$$
$$= \frac{25.0}{1000} \times 0.080$$
$$= 2.00 \times 10^{-3} \text{ mol}$$

$$\text{first equivalence volume of NaOH} = \frac{2.00 \times 10^{-3}}{0.10}$$
$$= \underline{\textbf{20.0 cm}^3} \text{ 3 s.f. or 2 d.p.}$$

Comments:
- This question was surprisingly poorly attempted.
- Many candidates have the misconception that since H_3PO_4 does not fully dissociate in water, it would not fully react with NaOH either.
- Correct concept: When H^+ from the dissociation of H_3PO_4 reacts with NaOH, the position of equilibrium (1) shifts to the right, so all H_3PO_4 would react.

(iv) Calculate the pH after the addition of 10.00 cm³ of NaOH. Give your answer to 2 decimal places. [1]

$$\text{At half equivalence point, pH} = pK_{a1} = -\lg\left(7.00 \times 10^{-3}\right)$$
$$= \underline{\textbf{2.15}}$$

Comments:
- Many students did not recognise the solution as a buffer.

(v) Calculate the pH of the resultant solution if 0.20 cm³ of 0.080 mol dm⁻³ HC*l* was accidentally added to the solution in **(b)(iv)**. [2]

$$\text{amount of HC}l \text{ added} = \frac{0.20}{1000} \times 0.080 = 1.60 \times 10^{-5} \text{ mol}$$

$$\text{new amount of } H_3PO_4 = \left(\frac{1}{2} \times 2.00 \times 10^{-3}\right) + 1.60 \times 10^{-5} = 1.016 \times 10^{-3} \text{ mol}$$

$$\text{new amount of } H_2PO_4^- = \left(\frac{1}{2} \times 2.00 \times 10^{-3}\right) - 1.60 \times 10^{-5} = 0.984 \times 10^{-3} \text{ mol}$$

$$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \Rightarrow [H^+] = \frac{\left(7.00 \times 10^{-3}\right) \times \left(\frac{1.016 \times 10^{-3}}{V}\right)}{\left(\frac{0.984 \times 10^{-3}}{V}\right)} = 7.2276 \times 10^{-3}$$

$$pH = -\lg[H^+] = \underline{\textbf{2.14}}$$

(vi) The pH at the second equivalence point of the titration is 9.77. Suggest an equation to account for the basic equivalence point. [1]

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$$

(vii) In total, 50.00 cm³ of NaOH was added during the titration. Using the information given in **(b)**, and your answers in **(b)(ii)** to **(b)(iv)**, sketch the pH–volume added curve for the titration. Label the following key points on the curve.

- Initial pH
- pH at second equivalence point
- pH at the half-equivalence points

[3]
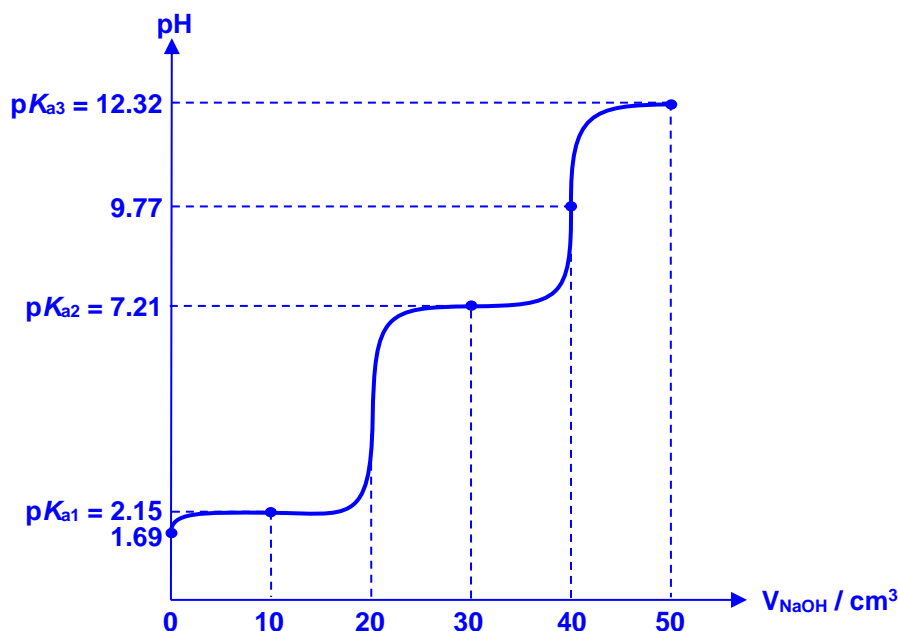
✓ **Label initial point (0.00, 1.62)**
✓ **Label max. buffer capacity (10.00, 2.15)**
✓ **Label second equivalence point (40.00, 9.77)**
✓ **Label all pK_{a2} and pK_{a3} values**
✓ **Correct shape (buffer region should have gentle gradient)**
✓ **Correct axes with units**

(c) Consumption of an excessive amount of soft drinks can cause tooth decay as the acid present in the beverage reacts with $Ca_{10}(PO_4)_6(OH)_2$ present in tooth enamel.

$$Ca_{10}(PO_4)_6(OH)_2(s) + 8H^+(aq) \rightarrow 10Ca^{2+}(aq) + 6HPO_4^{2-}(aq) + 2H_2O(l)$$
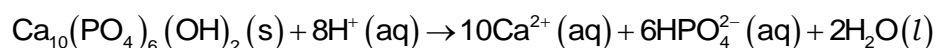
The Ca^{2+} ions lost from enamel can form a precipitate with the PO_4^{3-} ions present in the soft drink.

$$3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightleftharpoons Ca_3(PO_4)_2(s) \qquad K_{sp} = 1.3 \times 10^{-26}$$
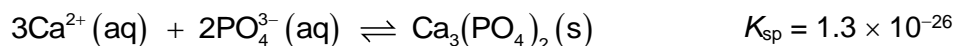
(i) Write an expression for the solubility product, K_{sp}, of $Ca_3(PO_4)_2$, indicating its units.

[2]

$$\boldsymbol{K_{sp} = \left[Ca^{2+}\right]^3 \left[PO_4^{3-}\right]^2 \ mol^5 \ dm^{-15}}$$

(ii) Calculate the solubility of $Ca_3(PO_4)_2$ in water, in $mol \ dm^{-3}$. [1]

Let its solubility be $s \ mol \ dm^{-3}$

$$K_{sp} = \left[Ca^{2+}\right]^3 \left[PO_4^{3-}\right]^2 = (3s)^3 (2s)^2 = 108s^5$$

$$s = \sqrt[5]{\frac{K_{sp}}{108}} = \sqrt[5]{\frac{1.3 \times 10^{-26}}{108}} = \boldsymbol{2.61 \times 10^{-6} \ mol \ dm^{-3}}$$

[Total: 18]

2 (a) The simplest aldehyde, methanal, HCHO, can readily be oxidised to methanoic acid by acidified potassium manganate(VII).

$$2MnO_4^-\left(aq\right)+5HCHO\left(aq\right)+6H^+\left(aq\right)\rightarrow 2Mn^{2+}\left(aq\right)+5HCO_2H\left(aq\right)+3H_2O\left(l\right)$$
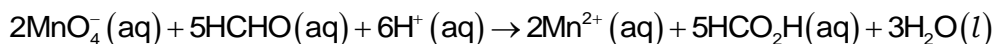
The reaction proceeds very slowly at room temperature. A small amount of vanadium(III) ions, V^{3+}, are added to the mixture to help speed up the rate of reaction.

(i) With reference to data from the *Data Booklet* and that given below, show how vanadium(III) ions act as a catalyst in the reaction.

$$HCO_2H(aq)+2H^+\left(aq\right)+2e^-\rightleftharpoons HCHO(aq)+H_2O(l)\qquad E^\ominus=-0.03\text{ V}$$

[2]

Step 1:
Reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
Oxidation: $(V^{3+} + H_2O \rightarrow VO^{2+} + 2H^+ + e^-) \times 5$

$$MnO_4^- + H_2O + 5V^{3+} \rightarrow Mn^{2+} + 5VO^{2+} + 2H^+$$
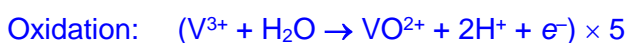
$E^\ominus_{cell} = +1.52 - (+0.34) = \underline{\textbf{+1.18V}}$

Since $E^\ominus_{cell} > 0$, reaction is **feasible**.

Step 2:
Reduction: $(VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O) \times 2$
Oxidation: $HCHO + H_2O \rightarrow HCO_2H + 2H^+ + 2e^-$

$$2VO^{2+} + 2H^+ + HCHO \rightarrow 2V^{3+} + HCO_2H + H_2O$$
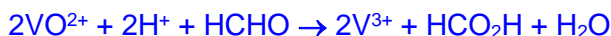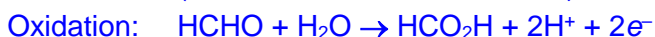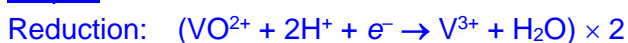
$E^\ominus_{cell} = +0.34 - (-0.03) = \underline{\textbf{+0.37 V}}$

Since $E^\ominus_{cell} > 0$, reaction is **feasible**.

Comments:
- Students are expected to show for **both steps** of catalysis, the $E^\ominus_{cell}$ calculation or qualitatively compare the $E^\ominus_{red}$ values using $E^\ominus_{red}\left(VO^{2+}\middle|V^{3+}\right)$. V^{3+} is also **regenerated** as catalyst.
- This part is generally well done. Common mistake involved using $E^\ominus_{red}\left(V^{3+}\middle|V^{2+}\right)$.

(ii) Hence suggest another transition metal ion that can catalyse the reaction between methanal and acidified potassium manganate(VII). [1]

Fe^{2+} or other transition metal ion with $-0.03\text{ V} < E^\ominus_{red} < +1.52\text{ V}$

Comments:
- This part is generally well done.
- Common mistakes involved choice of non transition metal ion e.g. Sn^{4+}/Sn^{2+} and lack of consideration that **both** species of their choice should be ions e.g. Cu^{2+}/Cu

(b) Methanoic acid can be oxidised by bromine to carbon dioxide.

$$HCO_2H(aq) + Br_2(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

The kinetics of the reaction was studied and results of the experiments performed are shown in Table 2.1.

Table 2.1

experiment	$[Br_2]$ / mol dm^{-3}	$[HCO_2H]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.0100	0.120	1.8×10^{-4}
2	0.0050	0.240	1.8×10^{-4}
3	0.0050	0.480	3.6×10^{-4}

(i) Determine the order of reaection with respect to Br₂ and to HCO₂H. Explain your reasoning. [2]

Let rate $= k[Br_2]^x[HCO_2H]^y$

Comparing expt 2 and 3, $[Br_2]$ is the same

$$\frac{rate_3}{rate_2} = \frac{3.6 \times 10^{-4}}{1.8 \times 10^{-4}} = \left(\frac{0.480}{0.240}\right)^y$$

$\Rightarrow y = 1$. ∴ reaction is **first order** with respect to HCO₂H.

Comparing expt 1 and 2,

$$\frac{rate_2}{rate_1} = \frac{1.8 \times 10^{-4}}{1.8 \times 10^{-4}} = \left(\frac{0.0050}{0.0100}\right)^x \left(\frac{0.240}{0.120}\right)$$

$\Rightarrow x = 1$. ∴ reaction is **first order** with respect to Br₂.

Comments:
- This part is generally well done.
- Students were expected to show clearly their working or reasoning using the given data.
- Common mistakes involved the reasoning for order of reaction w.r.t. Br₂ was incomplete or confusing. Some students also "created" 4th experiment which was irrelevant.

(ii) Hence write the rate equation for the reaction, and calculate the rate constant for the reaction including its units. [2]

$$\text{rate} = k[Br_2][HCO_2H]$$

Using experiment 1, $1.8 \times 10^{-4} = k(0.0100)(0.120)$

$$k = \underline{\mathbf{0.150\,mol^{-1}\,dm^3\,s^{-1}}}$$

Comments:
- The rate equation was generally well done. Few students stated wrongly "rate equation = $k[Br_2][HCO_2H]$"
- Most students could calculate the value for k but derived the wrong unit.
- There is ecf from **(b)(i)**.

(iii) Determine the half-life of the reaction in experiment 3. [1]

Since $[HCO_2H] \gg [Br_2]$,

$\text{rate} = k[Br_2][HCO_2H] = k'[Br_2]$, where $k' = k[CO_2H]$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[HCO_2H]}$$

$$= \frac{\ln 2}{0.150 \times 0.480} = 9.63\ s$$

Comments:
- This part was poorly done. Only a few students could correctly deduced that the reaction was pseudo 1st order reaction and worked out the correct $t_{\frac{1}{2}}$ for expt 3.
- No ecf for this part.

A student suggested that using Cl_2 instead of Br_2 will cause the rate of oxidation of HCO_2H to change.

(iv) Explain how the rate of reaction changes, if any, when Cl_2 instead of Br_2 is used. [1]

The rate of reaction would be **faster** as the halogen is **involved in the rate-determining step** and **Cl_2 is a stronger oxidising agent/ more positive $E^{\ominus}_{red}$** compared to Br_2.

Comments:
- Many student were able to link reactivity to oxiding power of halogens. However they missed out the important consideration that the change in halogen will affect rate if halogen is in the rate determining step.
- A few students wrongly state that the reactivity of halogen in redox reactions was related to BE(X–X) or was based on electronegativity.

(v) Outline how you would determine the effect of using Cl_2 instead of Br_2 on the rate of oxidation of HCO_2H, with reference to the results in Table 2.1.

No details regarding use of specific glassware are required. [3]

- Use the **same concentrations** of Cl_2, in place of Br_2, and **HCO_2H** as one of the three experiments in **Table 2.1**.
- Measure the **volume of CO_2 evolved / mass loss for regular time intervals**.
- Determine and compare **initial rate** from the **gradient** of the **volume of CO_2 / mass loss against time graph** at **time = 0**.

Comments:
- This part was well attempted with students understanding the need to keep the experiment conditions the same as that in Table 2.1.
- Full credit was awarded for the correct method (continuous method) as well as correct graph used to determine initial rate.
- Common mistakes involved recording:
  - volume of CO_2 for a fixed period of time
  - time taken for fixed volume of CO_2 / colour of Cl_2 produced/ $AgCl$ ppt formed
  - pH
  - electrical conductivity

(c) Tiglinaldehyde is used as a raw material for the synthesis of many compounds, including isoprene.

tiglinaldehyde   isoprene
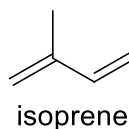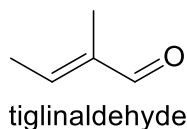
The double bonds in tiglinaldehyde can undergo reduction. When tiglinaldehyde is reacted with $NaBH_4$, which is a source of hydride ions (H^-), compound **A**, $C_5H_{10}O$, is formed.

(i) Deduce the structure of compound **A**. [1]
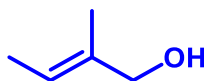
Comments:
- This was generally well done.
- A number of students thought that $NaBH_4$ would react with C=C and left the aldehyde unreacted.

(ii) On the other hand, isoprene does not react with $NaBH_4$. Explain the difference in reactivity between tiglinaldehyde and isoprene with $NaBH_4$. [1]

The carbonyl C in tiglinaldehyde is **electron deficient as it is bonded to an electronegative oxygen atom**, hence it is susceptible to nucleophilic attack by the hydride ions. The **C=C of the alkene in isoprene is electron-rich**, hence it is not susceptible to nucleophilic attack.

Comments:
- Many answers focused on the functional groups present in the compound, without explaning why the functional group would or would not react with the hydride ions from $NaBH_4$.
- A number of students also centred their explanations around why tiglinaldehyde could react with H^-, but completely omitted isoprene, or thought that is was sufficient to mention that isoprene did not have a C=O group, and hence did not react with H^-. It should be noted that when answering similar questions, it is necessary to focus on what a compound has rather than simply stating what it does not have.
- Many answers could recognise the presence of an electron deficient carbonyl carbon, but could not clearly explain how it arose, i.e. C must be bonded to electronegative O. Some incorrectly thought that being bonded to O meant that C was electropositive, as C would not be able to donate its electrons.
- Similarly, when describing the nature of C=C in isoprene, many only focused on the non-polar nature of alkenes, not realising that the electron rich C=C is necessary to explain why H^- would be repelled and not attack the C=C bond.

(iii) Suggest the structure of the compound formed when tiglinaldehyde is reacted with hydrogen in the presence of a platinum catalyst. [1]
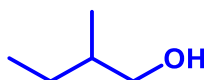
Comments:
- This was generally well done.
- A number of students thought that hydrogen would only be added to the alkene and left the aldehyde unreacted.

(d) Tiglinaldehyde reacts with hydrogen bromide to give the products shown.
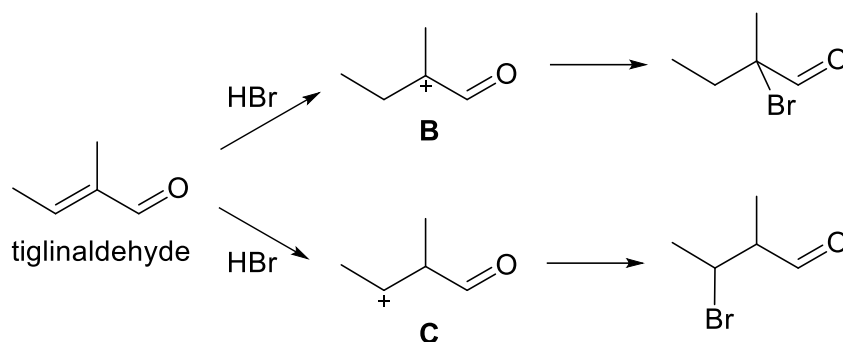
It was found that the major product was formed from carbocation **C**.

(i) Suggest why carbocation **B** formed is less stable than carbocation **C**. [1]

The positive carbon in carbocation **B** is **closer** to the **electron-withdrawing C=O group** compared to that in carbocation **C**. Hence the positive charge on carbocation **B** is **intensified more than** the positive charge on the carbocation **C**, thus making it less stable than carbocation C.

Comments:
- Many answers incorrectly focused on the number of electron donating alkyl groups attached to the each of the + charge carrying carbon in **B** and **C**.
- Some answers attempted to explain the presence of resonance in **B**, and simply state that this would destabilise the cation, without sufficient explanation.
- Weaker answers often did not differentiate the electron withdrawing nature of the C=O group and the electronegativity of the O atom. Some wrongly thought that it was sufficient to mention that the carbonyl C was electron deficient.
- As usual, a number of answers merely stated that the carbocation was stabilised with no reference to how the charge was stabilised, i.e. dispersed.

Isoprene undergoes a similar mechanism with hydrogen bromide to form compound **D**.
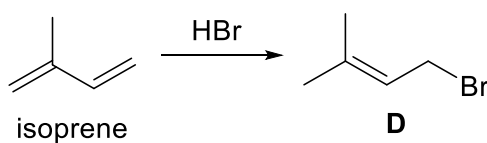
(ii) Suggest a structure for the carbocation intermediate formed in the reaction between hydrogen bromide and isoprene to form compound **D**. [1]
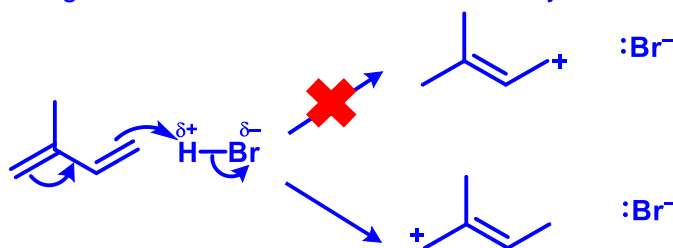
(iii) Hence suggest the mechanism for the formation of compound **D**, clearly showing the formation of the carbocation intermediate in **(d)(ii)** from isoprene. In your answer, you should show all charges and lone pairs and show the movement of electrons by curly arrows. [2]

(e) Ketenes are carbonyl compounds containing C=O directly connected to another carbon atom by a double bond. The simplest ketene is ethenone, CH_2CO.
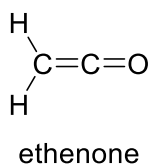
ethenone

(i) State the hybridisation of the carbonyl carbon atom in ethenone. [1]

sp hybridised (2 π bonds)

Comments:
- This was generally well done.
- Do not write sp[1].

(ii) In tiglinaldehyde, the π electrons are delocalised over all four atoms in C=C–C=O. Explain why the π electrons are able to delocalise over C=C–C=O. [1]

Side-on overlap of the parallel/aligned/on the same plane <u>unhybridised p-orbitals</u> **on each C and O atom in C=C–C=O** allows formation of a **continuous π orbital over all four atoms**.

Comments:
- While many could recognise that the p orbitals could overlap, few were able to adequately describe the type of overlap between the parallel orbitals.

(iii) Draw a diagram showing the relevant p orbitals that form the two π bonds in C=C=O, and explain whether delocalisation of π electrons would be able to occur in ethenone. [2]

sp hybridised central C in C=C=O means that the unhybridised **p orbitals of the 2 π bonds are perpendicular / at right angles to each other**. The p orbitals would not be able to overlap to form a continuous π **orbital over all three atoms**.

side-on overlap
to form C–O π bond

C—C—O

side-on overlap
to form C–C π bond
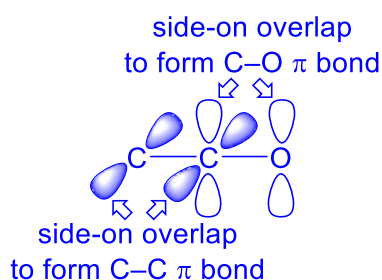
Comments:
- The majority wrongly thought that the p-orbitals of C–C–O could all have a side-on overlap, without considering how the two π bonds were formed. It should be noted that if the p-orbitals of C–C–O could overlap, the bonds between C–C and C–O would be weaker than that of C=C and C=O respectively.

[Total: 23]

3 (a) Selected physical properties of some first row d-block elements are given in Table 3.1.

Table 3.1

element		Sc	Ti	V	Cr	Mn
ionic radius / nm	M(III)	0.075	0.067	0.064	0.062	0.058
	M(IV)	–	0.061	0.058	0.055	0.053
boiling point / ^oC		2748	3285	3350	2690	2060
$E^{\ominus}\left(M^{3+}\big|M^{2+}\right)$ / V		–	–0.37	–0.26	–0.41	+1.54
ΔH_{vap} / kJ mol^{-1}		+333	+425	+460	+342	+221
ΔS_{vap} / J K^{-1} mol^{-1}			+119	+127	+115	+95

ΔH_{vap} : enthalpy change of vaporisation (from liquid to vapour phase)

ΔS_{vap} : entropy change of vaporisation (from liquid to vapour phase)

(i) Account for the trend observed in the boiling points from scandium to vanadium. [1]

Due to the **increase in number of 3d electrons** which can be **delocalised**, resulting in **stronger metallic bonds**, and thus increasing boiling point from scandium to vanadium.

Comments:
- Suprisingly badly attempted.
- A number of students simply state the trend without explaining for the trend.
- A number of students did not read the question carefully and discussed Cr and Mn as well. Many students missed out Ti too, although the question asked for trend *from* Sc to V and not between Sc and V.
- Most students did not make mention about the **type of bonding**, *i.e.*, **metallic bonding**, involved when discussing about boiling point of the TM. A number in fact thought that TM are simple molecular with instantaneous dipole-induced dipole attractions!
- Many students wrote about higher effective nuclear charge as electrons are added to the inner 3d subshell while nuclear charge increases, hence stronger attraction. Effective nuclear charge is used when discussing IE, but not the strength of metallic bonds.
- Students have to understand that strength of metallic bonds is proportional to (**number of electrons delocalised/ionic radii**). Many students simply state that charge density is higher without realising that the higher charge is due to the larger number of valence (3d and 4s) electrons **delocalised**.
- The effect of decreasing ionic radii is not the main factor here and also, many do not realise that the ionic radii here refers to residual cation of differing charges due to the different number of electrons delocalised.

[Turn Over

(ii) Suggest a possible reason for the lower boiling points observed for chromium and manganese compared to vanadium. [1]

Chromium and manganese both possess a **half-filled 3d subshell** which is **extra stable**, hence despite an increase in the number of 3d electrons, these are **less readily delocalised**, resulting in **weaker metallic bonds** and thus lower boiling points.

Comments:
- Very badly attempted.
- Again, many students attempted to use charge density here, but obviously does not work in this case.
- A number of students talked about paired electrons without realising that the 3d subshell is actually all unpaired with a d^5 configuration.
- A number of students mentioned the "partially-filled" 3d subshell, which should be half-filled subshell instead.
- A number of students correctly identified the half-filled 3d subshell, but failed to relate to the stability and hence less readily delocalised, contributing to weaker metallic bonds.

(iii) Trouton's rule states that ΔS_{vap} is almost the same value, about $+88$ J K^{-1} mol^{-1}, for various kinds of liquids at their boiling points. For example, ΔS_{vap} of benzene, methylbenzene and CHCl_3 are $+89.45$, $+87.30$ and $+89.72$ J K^{-1} mol^{-1} respectively.

Based on structure and bonding, suggest a reason why ΔS_{vap} of the d-block elements in Table 3.1 are significantly larger than $+88$ J K^{-1} mol^{-1}. [1]

The ΔS_{vap} are **larger** than that predicted by Trouton's rule due to the **strong metallic bonds** which exists even **in liquid molten metal**. This results in the liquid metals being **more ordered** than the liquid of simple covalent compounds, leading to a **larger increase in entropy** when the metal goes into the gaseous phase.

Comments:
- Very badly attempted.
- Despite given that vaporisation is from liquid to vapour phase, many students mentioned about giant metallic **lattice**, and that the TM is **solid** (at room temperature). They have to realise that vaporisation is basically boiling, which occurs at the boiling point where the TM is in the liquid state.
- Many students realised that TM are held by strong metallic bonds. However, most erroneously related the larger **entropy** change as due to more **energy** needed to overcome these stronger metallic bonds as compared to dispersion forces or permanent dipole-permanent dipole attractions in the given molecules. Entropy is not enthalpy!
- Very few were able to relate the stronger bonds to more orderly structure. Some students wrote about more compact structure, higher density, atoms/nuclei closer together, which benefit of doubt was awarded for the more ordered structure in the liquid phase.
- A number of students wrongly related the larger entropy change to larger entropy of the vapour consisting of ions and electrons.

(iv) Using the data in Table 3.1, calculate ΔS_{vap} of scandium. [1]

During boiling, the system is at **equilibrium** and hence $\underline{\Delta G_{vap} = 0}$.

$$\Delta G_{vap} = \Delta H_{vap} - T_{boiling\,point}\Delta S_{vap} = 0$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{boiling\,point}} = \frac{+333 \times 10^3 \text{ J mol}^{-1}}{2748 + 273 \text{ K}}$$

$$= \underline{+110 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Comments:
- Students have to understanding that the system is in equilibrium during phase changes (e.g. melting, boiling), hence $\Delta G = 0$.
- A handful of students just wrote down +110 without showing any working.
- A number of students also got the units wrong, missing out the K^{-1}.
- The positive sign is also often left out, which was not penalised here.

(b) Ti^{4+} ions exist in white solid titanium(IV) oxide, TiO_2. However, aqueous Ti(IV) sulfate exist in the form of the colourless $TiOSO_4$, instead of $Ti(SO_4)_2$. Similarly, V^{4+} ions exist in solid vanadium(IV) oxide, VO_2. Dissolving the oxide in sulfuric acid gives blue $VOSO_4$, instead of $V(SO_4)_2$.

On the other hand, green $\left[V(H_2O)_6\right]^{3+}$ and violet $\left[Ti(H_2O)_6\right]^{3+}$ are well-established aqueous ions of the +3 oxidation state.

(i) Using the data in Table 3.1, suggest why V^{4+}(aq) and Ti^{4+}(aq) does not exist. [2]

Due to the **high charge** and **small size** of the Ti^{4+} and V^{4+} ions, the **charge density is very high**. This results in **further polarisation** of the **O–H bond** in the coordinated water molecules/ligands, leading to the lost of $2H^+$ and **formation of M=O** (M = Ti, V), lowering the charge density.

Comments:
- Very poorly attempted.
- Despite the question mentioning that Ti^{4+} and V^{4+} exist in the solid and only Ti^{4+}(aq) and V^{4+}(aq) does not exist, many students answered saying that it takes too much energy to remove the 4 electrons. Also, they did not use data from Table 3.1.
- Most students failed to realise that the Ti in $TiOSO_4$ and V in $VOSO_4$ are still in the +4 oxidation state, *i.e.* $(TiO^{2+})(SO_4^{2-})$ and $(VO^{2+})(SO_4^{2-})$, and answered saying that the +3 or +2 oxidation state is more stable.
- Some students thought that the size of the ions are big and the charge density is low.
- The small number of students who realised that the **charge density is (very) high**, some did not relate to the data in Table 3.1, some were unable to relate to the **further polarisation of the O–H bond**, leading to hydrolysis of the Ti^{4+}(aq) and V^{4+}(aq) ions to form the MO^{2+} ion.

(ii) Explain why $TiOSO_4$ is colourless. [1]

Ti(IV) has a **d^0 configuration**. Hence **d-d transition does not occur in TiO^{2+} and visible light is not absorbed**.
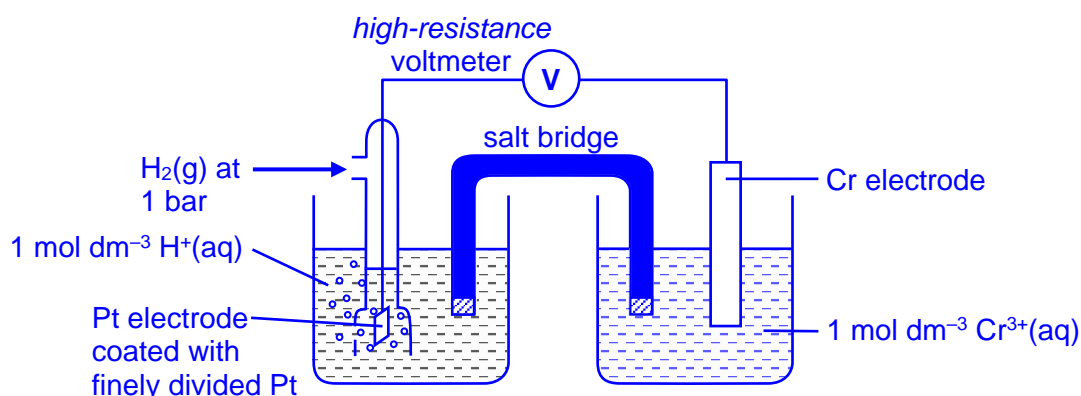
Comments:
- Poorly attempted
- In relation to **(b)(i)**, many students failed to realise that the Ti is in the +4 oxidation state, and hence there are **no 3d electrons** at all!! Some students even think that it has a fully filled 3d subshell.
- Many slipshod phrases, e.g. "no partially filled 3d orbitals", "no partially filled 3d subshell". These do not necessarily mean that there are no 3d electrons as it can be taken to mean also that the 3d subshell is fully filled.
- A number of students thought that there is no d orbital splitting, which is not true as there are still ligands around. Just that there are no 3d electrons to absorb visible light.
- Some students just mentioned that light absorbed does not fall within the visible region, which is technically not wrong (UV light is absorbed to promote electrons from 3p to say 3d/4s orbital). However, no mention is made of the lack of 3d electrons in Ti(IV).

(c) The +3 oxidation state is the most stable and best-known oxidation state for chromium. Salts of chromium(II) are best obtained by the reaction of the appropriate dilute acid with pure chromium metal, with air being rigorously excluded.

(i) Draw a fully labelled diagram of the electrochemical cell you could use to measure the value of $E^{\ominus}\left(Cr^{3+}\middle|Cr\right)$. [2]

$E^{\ominus}\left(Cr^{3+}\middle|Cr\right)$ is the voltmeter reading from the following set-up:

Comments:
- Very poorly attempted. Many students drew a single container instead of two half-cells.
- Students must note that the pressure of $H_2(g)$ is 1 bar and not 1 atm.
- The concentration (1 mol dm^{-3}) is often missing.
- Some students wrote 1 mol dm^{-3} H_2SO_4 or $Cr_2(SO_4)_3$, without realising that this will give 2 mol dm^{-3} of $H^+(aq)$ and $Cr^{3+}(aq)$ instead.

(ii) Using appropriate data from the *Data Booklet*, calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for these two processes:

- $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$
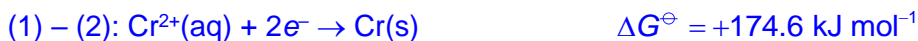
- $Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$ [1]

$$\Delta G^{\ominus} = -nFE^{\ominus} = -3 \times 96500 \times -0.74 = +214230 \text{ J mol}^{-1} = \mathbf{+214\,kJ\,mol^{-1}}$$
$$\Delta G^{\ominus} = -nFE^{\ominus} = -1 \times 96500 \times -0.41 = +39565 \text{ J mol}^{-1} = \mathbf{+39.6\,kJ\,mol^{-1}}$$

Comments:
- A number of students forgot the negative sign for the equation.
- A few students combined the two processes and calculated one single $\Delta G^{\ominus}$.
- A handful of students did not realise that $n = 3$ for the first equation, and a few used 6 for some unknown reason.
- A number of students did not realised that the units for $\Delta G^{\ominus}$ in this case is J mol^{-1}.
- Most students missed out the "+" sign, although they were not penalised here.
- Many students were penalised for their significant figures in the final answer.

(iii) Using your answer to **(c)(ii)**, show that $E^{\ominus}\left(Cr^{2+}\big|Cr\right) = -0.91 \text{ V}$. [2]

$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$ $\Delta G^{\ominus} = +214.2 \text{ kJ mol}^{-1}$ -------- (1)
$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$ $\Delta G^{\ominus} = +39.6 \text{ kJ mol}^{-1}$ ----------- (2)
(1) − (2): $Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$ $\Delta G^{\ominus} = +174.6 \text{ kJ mol}^{-1}$

$$E^{\ominus} = \frac{\Delta G^{\ominus}}{-nF} = \frac{+174.7 \times 10^3}{-2 \times 96500} = -0.905 \text{ V} = \mathbf{-0.91\,V}$$

Comments:
- Most students did not clearly explain how the $\Delta G^{\ominus}$ from **(b)(ii)** were combined to give $\Delta G^{\ominus}\left(Cr^{2+}\big|Cr\right)$. However, benefit of doubts were given.

(iv) From the $E^{\ominus}\left(M^{3+}\big|M^{2+}\right)$ values in Table 3.1, it can be seen that generally the ease of reduction of the M^{3+} to M^{2+} increases from Ti to Mn. Explain this trend using relevant data from Table 3.1. [1]

As the **ionic radius** of the M^{3+} **decreases from Ti^{3+} to Mn^{3+}**, the **attraction** of the M^{3+} for an **incoming electron increases** and hence the **tendency to get reduced** to M^{2+} **increases from Ti to Mn**.

Comments:
- Many students were able to see that the ionic radius decreases, but were not specific which ionic radius they were referring to, M^{3+} or M^{4+}. In this question, they should be looking at the M^{3+} ions.
- Some students talked about the M^{2+} ions getting smaller and hence stronger attraction of nucleus for the valence electrons, thus more difficult to remove an electron and be oxidised to M^{3+}. However, there were no data for radius of M^{2+} in Table 3.1.
- Most students mentioned that due to the decreasing ionic radius (of the M^{3+} ion), the nucleus attract the *valence electrons* more strongly. However, this has no bearing on the ease of reduction as it is the attraction of the nucleus for an **incoming electron** that is important. A few students even gave the idea that the reduction from M^{3+} to M^{2+} happens when one of the valence electron is attracted into the nucleus!

(v) The value of $E^{\ominus}\left(Cr^{3+}\big|Cr^{2+}\right)$ does not follow the general trend described in **(c)(iv)**. Suggest an explanation taking into account the electronic configuration of the $\left[Cr\left(H_2O\right)_6\right]^{3+}$ ion. [1]

Cr(III) has a **$3d^3$ electronic configuration**. The incoming electron has to go into the **higher energy $3d_{z^2}$ or $3d_{x^2-y^2}$ orbitals**, rendering the reduction less favourable.

Comments:
- Very poorly attempted.
- Many students got the electronic configuration of Cr(III) wrong.
- Most student did not realise that the mention of $[Cr(H_2O)_6]^{3+}$ instead of Cr^{3+} is directing them to splitting of the 3d subshell into two sets of orbitals of different energy. Most students mentioned inter-electronic repulsion instead of the electron going to the higher energy orbital when $Cr^{3+}(aq)$ is reduced to $Cr^{2+}(aq)$.
- A few students simply mentioned about higher energy orbital although no reference was made about the splitting or identifying which of the orbitals, for which benefit of doubts was given.

(d) Rechargeable manganese-based aqueous batteries have attracted remarkable attention due to low cost, environmental friendliness and high capacity. One such battery under development is the manganese–hydrogen (Mn–H) battery shown in Fig. 3.1.
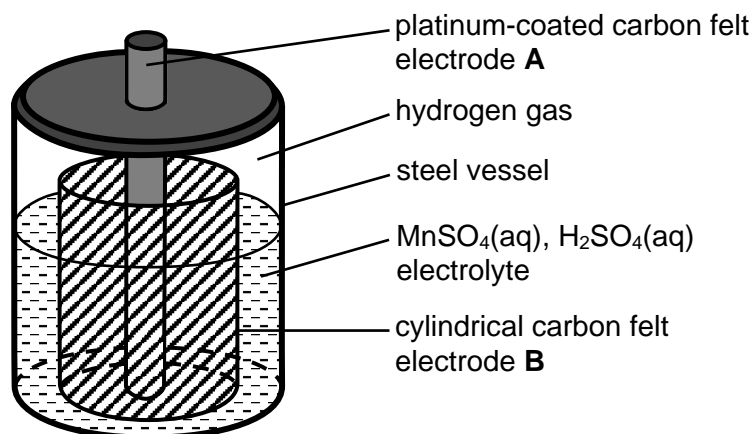

platinum-coated carbon felt electrode **A**

hydrogen gas

steel vessel

$MnSO_4(aq)$, $H_2SO_4(aq)$ electrolyte

cylindrical carbon felt electrode **B**

Fig. 3.1

The electrodes are composed of pieces of carbon felt rolled into a cylindrical shape, placed in the steel vessel containing the electrolyte, under an atmosphere of hydrogen gas.

(i) During charging, hydrogen gas is produced at electrode **A** and MnO_2 is deposited on electrode **B**.

Use the *Data Booklet* to write down the half-equations at the two electrodes during *discharge* and calculate the $E^{\ominus}_{cell}$ of the Mn–H battery. [2]

Electrode **A** : $H_2 \rightarrow 2H^+ + 2e^-$
Electrode **B** : $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$
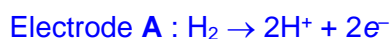
$E^{\ominus}_{cell} = E^{\ominus}\left(MnO_2 | Mn^{2+}\right) - E^{\ominus}\left(H^+ | H_2\right) = +1.23 - 0.00$
$\quad\quad = \underline{\textbf{+1.23 V}}$

Comments:
- Very poorly attempted
- Students did not read the question/diagram carefully:
  - Many students wrote the equations for charging (process described in the question) instead of discharging (asked for in the question)
  - Many students wrote "$\rightleftharpoons$" instead of "$\rightarrow$" for the half-equations during discharge. It should be a definite direction for either charging or discharging.
  - Many students chose $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ instead of $H_2 \rightarrow 2H^+ + 2e^-$ when there is sulphuric acid in the electrolyte.

(ii) Under normal operating conditions, the pressure of hydrogen gas in the steel vessel is slightly more than 1 bar. State and explain the effect on E_{cell} value . [1]

When p_{H_2} is higher than 1 bar, $E\left(H^+|H_2\right)$ will **becomes more negative**, resulting in a **more positive E_{cell}**.

(iii) When the Mn–H battery is charging, oxygen gas may be produced at electrode **B**. Explain, with a relevant half-equation, why this occurs. [2]

A **potential difference larger than $E_{cell}^{\ominus} = +1.23$ V** must be applied across the battery **during charging**. As a result, the oxidation of water :

$$H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

can take place since the potential difference is larger than $E^{\ominus}\left(O_2|H_2O\right) = +1.23$ V .

[Total: 19]

Section B

Answer **one** question from this section.

4 Peroxyethanoic acid is widely used in many areas such as disinfectant, bleaching agent and in organic synthesis processes. Peroxyethanoic acid is commonly synthesised from the oxidation of ethanoic acid by hydrogen peroxide.

peroxyethanoic acid
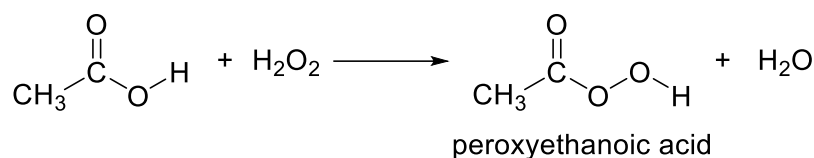
   (a) Suggest why ethanoic acid is a stronger acid compared to peroxyethanoic acid.   [1]

   CH_3COO^- forms 2 equivalent resonance structures with **delocalisation of the negative charge over 2 highly electronegative O atoms** (resonance effect) and hence the conjugate base of CH_3CO_2H is resonance stabilised.

   CH_3COOO^- is not stabilised by resonance as the **negative charge on O atom cannot be delocalised over the C=O group due to the presence of the additional O atom**. Hence, it is only stabilised by a weaker electron-withdrawing inductive effect of the neighbouring O atom.

   So, the $CH_3CO_2^-$ is more stable than $CH_3CO_3^-$ and CH_3CO_2H is a stronger acid than CH_3CO_3H.

   Comments:
   - This part is poorly attempted. Many explained the stability of the ethanoate ion without making comparison to the peroxyethanoate ion.
   - Those who made comparison incorrectly concluded that CH_3COOO^- cannot be resonance stabilised as the carbonyl group was "too far away" or "further away".
   - Many also incorrectly identified CH_3COO group as the electron donating group, hence intensifying the negative charge on the O atom.

Recent studies have been conducted to improve production of peroxyethanoic acid from ethanoic acid in-situ in an electrolytic cell shown in Fig. 4.1.
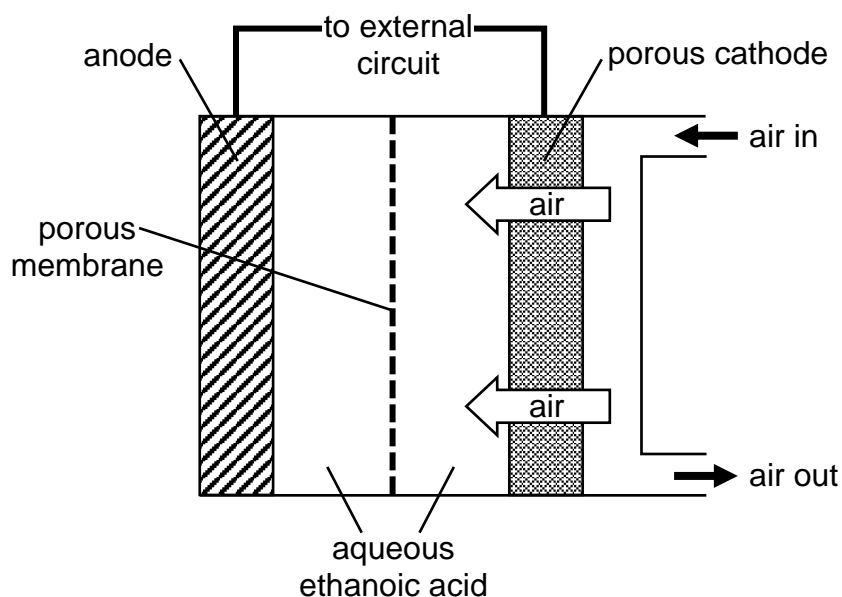
Fig. 4.1

At both the cathode and anode, an oxidising agent is produced which then reacts with ethanoic acid in the solution to form peroxyethanoic acid.

(b) Hydrogen peroxide is formed at the cathode.

  (i) Write an equation to show how hydrogen peroxide is formed at the cathode.   [1]

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

Comments:
- Common mistakes includes giving "$\rightleftharpoons$" instead of a single arrow or attempting to write an incorrect equation for reduction of H_2O.

  (ii) A current of 0.2 A was passed through the cell for 16 hours. Calculate the amount of hydrogen peroxide that was produced at the cathode.   [1]

$Q = I \times t = 0.2 \times 16 \times 60 \times 60$

$\quad = 11520 \text{ C}$

$\text{amount of } H_2O_2 = \dfrac{11520}{96500} \times \dfrac{1}{2} \left(\text{ecf from } \textbf{b(i)} \right)$

$\quad\quad\quad\quad = \textbf{\underline{0.0597 mol}}$

Comments:
- This part is generally well done. Many could recall the equation $n = \frac{Q}{F}$.
- However some failed to consider the mole ratio $H_2O_2 \equiv 2e$ and did not divide by 2 in the calculation of amount of H_2O_2.

(c) A hydroxy *radical*, HO•, is formed at the anode.

    (i) Explain what is meant by the term *radical*. [1]

       A radical is a species that contain an unpaired electron.

Comments:
- Candidates need to recognise that a radical is not limited to only atoms or molecules.
- Answers that describe radicals to have "free electrons" or "extra electrons" in place of "unpaired electron" are not accepted.

    (ii) Construct a half-equation to show how the hydroxy radical is formed from water at the anode. [1]

       Oxidation: $H_2O \rightarrow OH\bullet + H^+ + e^-$

Comments:
- This part is poorly attempted. Many gave $H_2O \rightarrow HO\bullet + H\bullet$ which is not accepted because the reaction fail to show the loss of electrons that should happen at the anode.

    (iii) The hydroxy radical reacts with ethanoic acid to form peroxyethanoic acid and water in a two-step radical reaction.

       Each step involves one hydroxy radical, and the second step involves reaction between two radicals.

       Suggest the mechanism for the reaction between the hydroxy radical and ethanoic acid to form peroxyethanoic acid and water. You need not show any curly arrows for the mechanism. [1]

       Step 1: $CH_3CO_2H + OH\bullet \rightarrow CH_3CO_2\bullet + H_2O$
       Step 2: $CH_3CO_2\bullet + OH\bullet \rightarrow CH_3CO_3H$

Comments:
- Candidates who did not give the correct answer for step 1 cannot be awarded the full one mark.
- Many candidates did not understand the question and indicated hydroxy radical as one of the products instead of one of the reactants for step 1.

(d) Hydrogen peroxide is used as a reagent in the Baeyer-Villiger oxidation reaction, which inserts an O atom into a C–C bond adjacent to a carbonyl group.

    An ester can be synthesised from propanone in a single step as shown in Fig. 4.2.
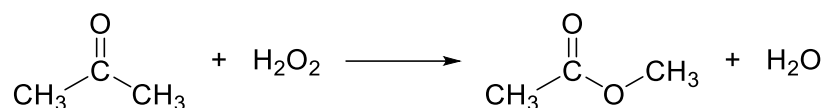
Fig. 4.2

(i) Name the ester formed from the Baeyer-Villiger oxidation of propanone. [1]

methyl ethanoate

(ii) State the oxidation state of the C=O carbon in propanone and the ester respectively. [1]

Propanone: **+2**
Ester: **+3**

The 3-stage synthesis of phenol from benzene, shown in Fig. 4.3, makes use of the Baeyer-Villiger oxidation.
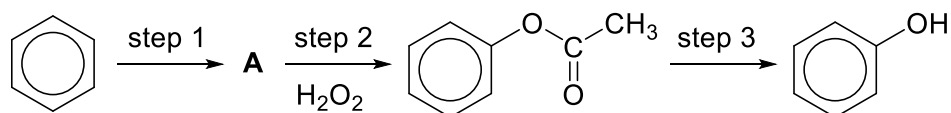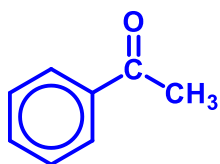

Fig. 4.3

(iii) Suggest a structure for intermediate **A**, and the reagents and conditions for steps 1 and 3. [3]

A
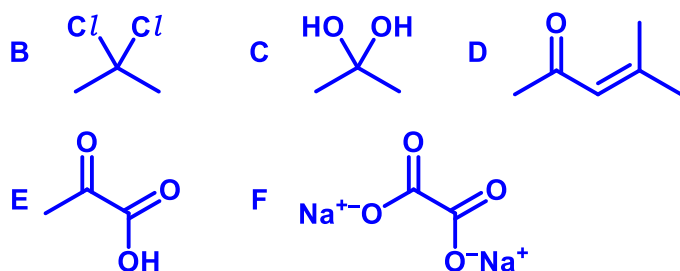
Step 1: $AlCl_3$, CH_3COCl
Step 3: H_2SO_4(aq), heat

(e) A non-chiral compound **B**, $C_3H_6Cl_2$, when heated with NaOH(aq) forms **C**, $C_3H_8O_2$, which then readily loses a molecule of water to form propanone. In the presence of acid, two molecules of propanone reacts to form **D**, $C_6H_{10}O$, with the loss of a water molecule.

D cannot be oxidised by acidified $K_2Cr_2O_7$ but **D** oxidises with hot acidified $KMnO_4$ to give **E**, $C_3H_4O_3$, and propanone only. When warmed with I_2 in NaOH(aq), **E** can react to form organic compound **F** and CHI_3.

Suggest structures for compounds **B**–**F** and explain the all the reactions described.

[9]

observations	deductions
Compound **B**, $C_3H_6Cl_2$, when heated with NaOH(aq) forms **C**, $C_3H_8O_2$	• **B** undergoes nucleophilic substitution to form alcohol (diol) • as seen by decrease in 2 Cl , with increase in 2OH in molecular formula
C, $C_3H_8O_2$ which then readily loses a molecule of water to form propanone	• **C** undergoes **elimination** (of water)
Two molecules of propanone reacts to form **D**, $C_6H_{10}O_2$, with the loss of a water molecule.	• **Condensation** reaction has occurred
D cannot be oxidised by acidified $K_2Cr_2O_7$	D could contain 3° alcohol or ketone
D reacts with hot acidified $KMnO_4$ to give **E**, $C_3H_4O_3$, and propanone only.	• **D** undergoes oxidative cleavage to give E and propanone • **D** contains a C=C

| E can also react with I_2 in NaOH(aq) to form F | • E undergoes oxidation to form F
• presence of CH_3CO- in E |

Comments:
- This part is not well done. Many candidates did not give complete reasoning, often missing out the type of reaction to account for the reactions described in the question.
- Some candidates were confused between elimination (or dehydration) and condensation reactions. Note that condensation reactions involve the combination of two compounds with the removal of a small molecule (e.g. H_2O or HCl) while elimination is the removal of a small molecule (e.g. H_2O or HCl) from a bigger molecule.
- Most candidates managed to deduce structure **D** and **E** by correctly inferring from the observations given.
- Many failed to note that compound **B** is non chiral and gave 1,2-dichloropropane for structure **B** instead.
- Many also failed to realise the basic medium will cause both the carboxylic groups in structure **F** to be deprotonated to give the carboxylate ions instead. The more accurate structure of **F** should include the Na^+ ions as the question requires candidates to suggest structure for organic compound **F**.

[Total: 20]

5 (a) Nickel is a heterogeneous transition metal catalyst that is often used in the catalytic reduction of alkenes to form saturated hydrocarbons.

(i) State one property of transition metals that makes them effective heterogenous catalysts. [1]

They have **partially filled 3d orbitals** which allows the reactant particles to be adsorbed onto the catalyst surface.

Comments:
- Generally okay. Many students were able to identify that for heterogeneous catalysis to occur, there must be partially filled 3d orbitals. Phrasings such as "vacant d orbitals" were also credited.
- Variable oxidation state in this case will not be accepted as it is not a key characteristic of heterogeneous catalysis.

(ii) Outline the mode of action of the nickel catalyst in the reaction. [2]

The reactant molecules are **adsorbed** onto the surface of the catalyst through the **formation of weak bonds** between the reactant molecules and the surface catalyst atoms at the **active sites**. The adsorption **weakens the covalent bonds** within the reactant molecules, **reducing the activation energy** for the reaction / **increases the concentration of the reactant molecules** at the catalyst surface, allowing the reactant molecules to **come into close contact with proper orientation for reaction.**

Comments:
- Generally okay although several answers were not well-elaborated upon. Several students were unable to spell or were confused about the following terms: "adsorb and adsorption".

(iii) Explain, with aid of the clearly labelled Boltzmann distribution, the effect of a catalyst on the rate of reaction. [3]
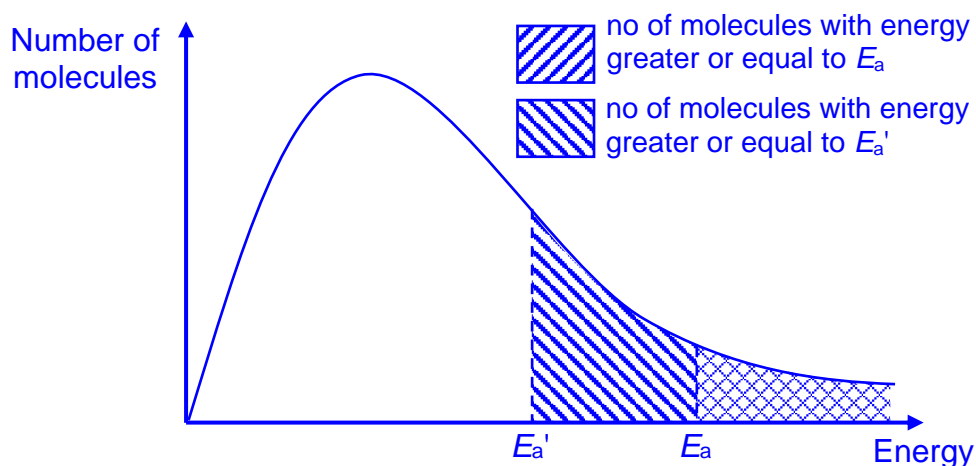
The **activation energy** of the catalysed reaction **is lower**, **more molecules** have energies greater than or equal to the lowered activation energy E_a'. This results in an **increase in the frequency of effective collisions** and the rate of reaction.

Comments:
- Generally okay.
- Some students were not able to draw the diagram well. For example: did not start from zero, axes were not labelled/incorrectly labelled, differentiation of particles were not clear.
- Explanation-wise, many students were not clear that there were more molecules with energies of **at least lowered activation energy**, leaving ambiguity.

(b) Nickel can leak into the environment such as water sources when not disposed of carefully. One way to analyse such leakages is to first isolate nickel(II) ions found in contaminated water sources using chelating agents which act as ligands. A common chelating agent used is ethane-1,2-diamine, $NH_2CH_2CH_2NH_2$ or en for short.

When en is added progressively to a solution of $[Ni(H_2O)_6]^{2+}$, the solution turns from light blue to blue, and finally purple, indicating an octahedral $[Ni(en)_3]^{2+}$ complex is formed.

(i) State the type of reaction that occurred when en is added to a solution of $[Ni(H_2O)_6]^{2+}$. [1]

ligand exchange reaction

Comments:
- Generally well done.

(ii) State the denticity of the en ligand in $[Ni(en)_3]^{2+}$. [1]

en is a **bidentate ligand**.

Comments:
- Generally okay. Many students were not aware that denticity refers to term bidentate and gave a number for the number of bonds involve in bonding instead.
- Some students were not able to spell bidentate correctly, hence not getting the credit.

(iii) Explain why $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ form two different coloured solutions. [3]

The two solutions have different colours despite containing the same nickel(II) ion because of the presence of **different ligands**.

Both the **H₂O and en ligands** split the **five 3d orbitals** of the Ni^{2+} ion into two sets of slightly different energy levels but to **different extents**. Hence $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ ions **absorb different wavelengths of light** from the **visible spectrum for d-d transition to occur**. Consequently, different colours, corresponding to the **complements of the different colours absorbed**, are observed for the two different complex ions.

Comments:
- Generally okay.
- Some students were good at recalling the content related to the question but did not answer the question by referring to the **difference** between the two complexes. These student did not get the credit.
- Some students were extremely confused with the terms, "d orbital splitting, d-d transition, d orbitals and d subshell". There were many incorrect interpretation such as "d-d orbital, d-d splitting, d-d orbital transition etc."
- Some students gave answers related to the amount of energy, which is incorrect as it should be the magnitude of the energy, as this magnitude is related to the wavelength/frequency of the light absorbed by the electron.

(c) **A**, $C_{10}H_{16}O$, exhibits *cis-trans* isomerism but not enantiomerism. **A** forms a silver mirror upon addition of Tollen's reagent. 1 mole of **A** reacts with 2 moles of aqueous bromine at room temperature to give **B**, $C_{10}H_{18}O_3Br_2$, and white fumes.

When heated with $KMnO_4$ and dilute H_2SO_4, **A** gives **C**, $C_5H_8O_3$, **D**, C_3H_6O, and a gas that forms a white precipitate when bubbled through $Ca(OH)_2$.

Both **C** and **D** form a pale-yellow precipitate when heated with NaOH(aq) and I_2(aq). On addition of Na_2CO_3, **C** produces effervescence while **D** does not.

Suggest structures for **A**, **B**, **C** and **D** and explain the reactions described. [9]

Evidence	Deduction
A exhibits *cis-trans* isomerism but not enantiomerism	• **A** contains at least one C=C with 2 different groups on each C atom. • **A** does not contain any chiral centres.
A forms a silver mirror upon addition of Tollen's reagent	• **A** undergoes **oxidation** has an **aldehyde** functional group
1 mole of **A** reacts with 2 moles of aqueous bromine at room temperature to give white precipitate **B** and white fumes	• **A** undergoes **electrophilic addition** • **A** has **2 C=C** groups • **B** is a halohydrin (contains **Br and OH groups**), white fumes is **HBr**.
A react with $KMnO_4$ to form **C** and **D**, and produces a gas that	• **A** undergoes **oxidation**

forms a white precipitate with Ca(OH)$_2$	• 2 C atoms are lost, producing **CO$_2$**. • **Ethanedioic acid** is a product of oxidation
Both **C** and **D** gives a pale yellow ppt when heated with NaOH(aq) and I$_2$(aq).	• Both **C** and **D** undergoes **oxidation / positive iodoform test**. • **C** and **D** contains a **methyl ketone** group **(not alcohol)**
Upon addition of Na$_2$CO$_3$, **C** produces effervescence while **D** does not.	• **C** undergoes **acid-carbonate reaction** while **D** does not. • **C** contains a **CO$_2$H** group

A is ⟨structure⟩ or ⟨structure⟩ or

⟨structure⟩

B is ⟨structure⟩ or ⟨structure⟩ or

⟨structure⟩ OH/Br ... Br/OH **(Markovnikov's rule does not apply)** Br/OH ... OH/Br

C is ⟨structure⟩

D is ⟨structure⟩
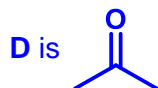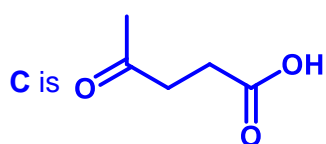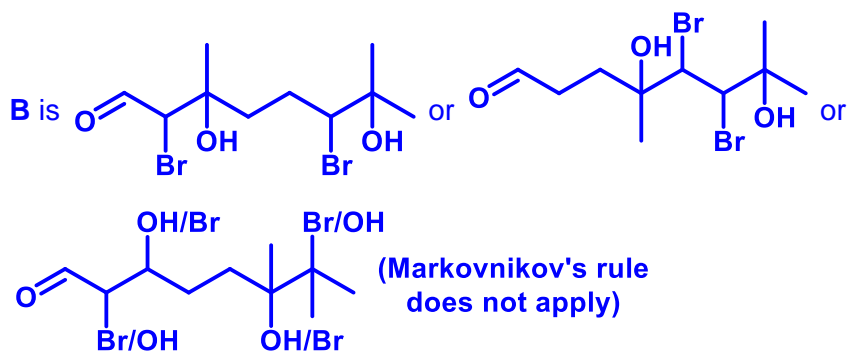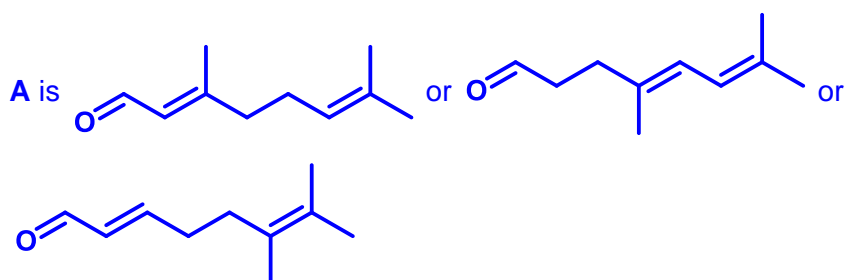
[Total: 20]

Comments:

- Generally okay.
- Many students were unable to complete the full deduction for each evidence. Many did not give the type of reaction and only gave the functionality related to the evidence. Hence the credits were not given.
- Most students were unable to identify that ethanedioic acid is formed before being further oxidised to CO_2.
- For *cis-trans* isomerism, many students did not mention that each C in the C=C bond must have 2 different substituent groups, merely mentioning that C=C bond exists.
- For acid-carbonate reaction, students who gave acid-base reaction were given the credit.
- The structures **C** and **D** were correctly identified by most students. For **A** and **B**, most students were not able to get the structures. Should **A** be incorrectly deduced such that it does not fit the evidences, there will not be any error carried forward for **B**.

CANDIDATE NAME						
CIVICS GROUP	**1**	**8**	–		INDEX NUMBER	

CHEMISTRY

Paper 4 Practical

9729/04

03 September 2019

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidental Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on the work you hand in.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use paper clips, highlighters, 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.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 19 and 20.

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.

Shift
Laboratory

| **For Examiner's Use**	
1	/ 18
2	/ 4
3	/ 19
4	/ 14
Total	/ 55

This document consists of **18** printed pages.

Answer **all** the questions in the spaces provided.

1 Determination of the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$

Copper forms compounds containing Cu^{2+} or Cu^+ ions. Those compounds containing Cu^{2+} ions tend to be relatively stable.

The addition of an excess of potassium iodide, KI, to a solution of Cu^{2+} ions produces iodine, I_2, and a stable precipitate of CuI. To determine the concentration of Cu^{2+} via iodometric titration, it is necessary that all the Cu^{2+} ions are reduced to Cu^+ ions. A brown suspension will be produced, which is an off-white precipitate of CuI in a yellow-brown solution of I_2.

equation 1 $2Cu^{2+} (aq) + 4I^- (aq) \rightarrow 2CuI (s) + I_2 (aq)$
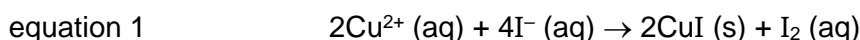
I_2 has a relatively low solubility in water. However, the presence of an excess of I^- ions in the reaction mixture allows the soluble tri-iodide ion, I_3^-, to form as shown by equation 2. This ensures that the I_2 formed as shown in equation 1 is fully dissolved.

equation 2 $I_2 + I^- \rightarrow I_3^-$

The I_3^- ions formed may be titrated against a standard solution of $Na_2S_2O_3$ as shown in equation 3.

equation 3 $I_3^- + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 3I^-$

The solution should be titrated immediately after addition of KI because the I_2 may be adsorbed onto the CuI precipitate, rendering the end-point less sharp.

FA 1 is solid hydrated copper(II) sulfate, $CuSO_4 \cdot nH_2O$, where n is an integer.

You are also provided with
    FA 2, 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$,
    FA 3, 1.00 mol dm^{-3} potassium iodide, KI,
    10% potassium thiocyanate, KSCN,
    1% starch solution.

The presence of thiocyanate ion, SCN^-, in the titration mixture near to the end-point will affect the accuracy of the results. The procedure described is designed to improve on the accuracy.

In this experiment, you will determine the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$. You will titrate a solution of **FA 1** against **FA 2**.

(a) Preparing a solution of FA 1

1. Weigh accurately about 5.00 g of **FA 1** in a pre-weighed weighing bottle.

2. Transfer the solid into a 250 cm³ beaker and reweigh the weighing bottle. Dissolve this solid in about 70 cm³ of deionised water.

3. Transfer the solution to the graduated flask, labelled **FA 1 solution**. Rinse the beaker with deionised water several times, adding each rinsing to the graduated flask.

4. Make up the solution to 250 cm³ with deionised water and mix thoroughly. This solution will be used in both **Question 1(b)** and **2(a)**.

Results

Mass of weighing bottle and **FA 1** / g	9.599
Mass of empty weighing bottle / g	4.596
Mass of emptied weighing bottle / g	4.599
Mass of **FA 1** used / g	5.000

Comments:
- This part was well done in general. This part was well done in general.
- A number omitted to include the mass of empty weighing bottle, as required by the question. Many also did not differentiate between the 'empty' and 'emptied' bottle in their table. It should be noted that there should not be two same headers within a table.
- A small number of students incorrectly referenced mass as "weight".

(b) Titration of solution of FA 1 against FA 2

(i) 1. Fill the burette with **FA 2**.

2. Use a pipette to transfer 25.0 cm³ of **FA 1** solution into a 250 cm³ conical flask.

3. Use a measuring cylinder to add about 15 cm³ of **FA 3** into this flask.

4. Run **FA 2** from the burette into this flask. Near the end-point, when the brown solution becomes pale, add about 1 cm³ of 1% starch solution.

5. Continue adding **FA 2** until the blue-black colour **just** disappears. Add 10 cm³ of 10% KSCN solution using a measuring cylinder.

6. Continue adding **FA 2** slowly. The end-point is reached when the **solution** first becomes colourless. The white precipitate remains.

7. Record your titration results in the space provided on page **4**. Make certain that your recorded results show the precision of your working.

8. Swirl the reaction mixture and filter the mixture. Wash the residue twice with deionised water. Keep the residue for use in **2(a)**. The residue is **FA 4**.

While you are waiting for the mixture to filter, continue with step 9.

9. Repeat points **1** to **7** as necessary until consistent results are obtained.

Titration results

Titration number	1	2
Final burette reading / cm^3	20.00	40.00
Initial burette reading / cm^3	0.00	20.00
Volume of **FA 2** solution used / cm^3	20.00	20.00
	✓	✓

- Table with <u>correct headings</u> (*'burette' must be stated)* and <u>units</u>.
- <u>All burette readings</u> recorded to the nearest 0.05 cm^3
- Titres for end-point must be within 0.10 cm^3

[5]

Comments:
- This part was well done in general.
- Common errors included using 'burette volumes' instead of burette readings, making reference to **FA 1** instead of **FA 2**, and recording volume as 'amount'.
- The accuracy of the titration was poor, with majority of the volumes obtained being significantly higher than the expected volume.

(ii) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

$$\text{volume of } \textbf{FA 2} \text{ used} = \frac{20.00 + 20.00}{2}$$
$$= 20.00 \text{ cm}^3$$

volume of **FA 2** = ...**20.00 cm^3**.......... [1]

Comments:
- This part was well done in general. A small number of students incorrectly rounded their values off to 3 sf, although it was left as 2 dp in their final answer. It should be noted that the average volume calculated should follow the precision of the burette readings, i.e. to 2 dp, without rounding it to 3 significant figures.

(c) (i) Calculate the amount of iodine, I_2, liberated from 25.0 cm^3 of **FA 1** solution.

$$n_{S_2O_3^{2-}} \text{ used} = \frac{20.00}{1000} \times 0.100 = 2.00 \times 10^{-3} \text{ mol}$$

$$n_{I_2} = n_{I_3^-} = \frac{1}{2} n_{S_2O_3^{2-}} = \frac{1}{2} \times 2.00 \times 10^{-3} \text{ mol}$$
$$= 1.00 \times 10^{-3} \text{ mol}$$

amount of I_2 liberated from 25.0 cm^3 of **FA 1** solution = ...**1.00×10^{-3} mol**.......... [1]

(ii) Hence, calculate the amount of copper(II), Cu^{2+}, in 25.0 cm^3 of **FA 1** solution.

$$n_{Cu^{2+}} = 2n_{I_2} = 2 \times 1.00 \times 10^{-3} \text{ mol}$$
$$= 2.00 \times 10^{-3} \text{ mol}$$

amount of Cu^{2+}, in 25.0 cm^3 of **FA 1** solution = ...**2.00 × 10⁻³ mol**.................. [1]

(iii) Determine the amount of $CuSO_4 \cdot nH_2O$ in 250 cm^3 of **FA 1** solution.

$$n_{CuSO_4 \cdot nH_2O} \text{ in 250 cm}^3 \text{ of \textbf{FA 1} solution} = \frac{250}{25} \times 2.00 \times 10^{-3}$$
$$= 2.00 \times 10^{-2} \text{ mol}$$

amount of CuSO$_4 \cdot n$H$_2$O in **FA 1** solution = ...**2.00 × 10⁻² mol**.......... [1]

Comments:
- Part **(c)** was well done in general. Common mistakes included using the wrong stoichiometric ratio for calculation in **(c)(i)** and **(c)(ii)**.

(iv) Use your answer to **1(c)(iii)** to calculate the M_r of $CuSO_4 \cdot nH_2O$, and hence the value of n.
[A_r: H, 1.0; O, 16.0; S, 32.1; Cu, 63.5]

$$M_r(CuSO_4 \cdot nH_2O) = \frac{5.000}{2.00 \times 10^{-2}}$$
$$= 250$$

$$n = \frac{250 - (63.5 + 32.1 + 16.0 \times 4)}{(1.0 \times 2 + 16.0)}$$
$$= 5.022$$
$$\approx 5$$

M_r of CuSO$_4 \cdot n$H$_2$O = ...**250**..................

value of n = ...**5**..................

Comments:
- This part was well done in general.
- A small number of students incorrectly used 5 g as the mass of solid in their calculations instead of using the mass of **FA 1** that was transferred into the beaker for preparation of standard solution. Some incorrectly used the mass of **FA 1** weighed, rather than the mass of **FA 1** used when the two values were different.
- A few students did not follow the question and reversed the order by first determining the value of n, before using it to calculate the M_r of CuSO$_4 \cdot n$H$_2$O.

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Hence, determine the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$.
Show your working.

$$\text{percentage by mass of water of crystallisation} = \frac{5.022 \times (1.0 \times 2 + 16.0)}{250}$$
$$= 36.2\% \ (3 \text{ s.f.})$$

percentage by mass of water of crystallisation = ...**36.2%**................. [3]

Comments:
- This part was well done in general.

(d) Starch forms a dark blue-black complex with the tri-iodide ion, I_3^-. The starch indicator is not added at the beginning of the titration as the resulting complex at high I_3^- concentration is relatively stable, dissociating only slowly.

Predict and explain the effect of adding the starch indicator at the start of the titration on the M_r of $CuSO_4 \cdot nH_2O$ determined in **1(c)(iv)**.

Due to the slow release of I_3^- from the starch-I_3^- complex, the **end-point would have**

exceeded the equivalence point as the titration reaction is slower, leading to a

larger titre volume.

This would lead to a **larger amount of $CuSO_4 \cdot nH_2O$**, hence the M_r of $CuSO_4 \cdot nH_2O$

determined in **1(c)(iv)** would have been **smaller than the actual value**. .... [2]

Comments:
- This part poorly done for the explanation for the titre value being larger than expected.
- Otherwise, most students can conclude the effect of titre value on the M_r of $CuSO_4 \cdot nH_2O$.
- Minority of students mis-read this question.

(e) (i) The solution should be titrated immediately after addition of KI because I_2 may be adsorbed onto the CuI precipitate, rendering the end-point less sharp. Explain how I_2 is adsorbed onto the CuI precipitate.

Similar to the formation of I_3^-, the **I^-** ion in CuI can **donate a lone pair of**

electrons to I_2 to form a dative bond with the I_2 molecule, leading to the

adsorption of I_2 on the surface of the solid CuI. .... [1]

Comments:
- This part was poorly in general.
- Many students wrongly thought that dative bond had occur between Cu^{2+} and I_2. Or that the I_2 forms intermolecular id-id with CuI.

(ii) Hence, explain the effect **1(e)(i)** has on the amount of $CuSO_4 \cdot nH_2O$ determined in **1(c)(iii)**.

Due to adsorption of I_2 onto the CuI precipitate, the **titre reading will be lower**

than expected since there will be **less I_2 to react**. Hence amount of

$CuSO_4 \cdot nH_2O$ determined in **(c)(iii)** would be **smaller than the actual value**. [1]

Comments:
- This part was well done in general.
- Minority of students mis-read this question answered only about the amount of Cu^{2+} or M_r of $CuSO_4 \cdot nH_2O$

(iii) In step 5 of **1(b)(i)**, a colour change was observed when 10% KSCN solution was added to the mixture in the conical flask.

Suggest how the addition of KSCN to the mixture helps to improve the accuracy of titration.

SCN^- **displaces the adsorbed I_2 or I_3^- from the CuI**, allowing essentially **all**

the I_2/I_3^- produced to react in the titration. ....

.... [1]

Comments:
- This part was poorly done in general.
- Many students simply state that addition of SCN^- made the colour change more obvious.
- Some students wrongly thought that K^+ will react with CuI.
- Some students were confused between Cu^+ and Cu^{2+}.

(iv) Similar to the starch indicator, the 10% KSCN solution must not be added too early in the titration, although for a different reason from that given in **1(d)**.

The thiocyanate is also said to be a psuedohalide as it behaves chemically similar to a halide ion, also existing as thiocyanogen, $(SCN)_2$, which is similar to the parent halogen.

Suggest a reason why the KSCN solution should not be added at the start of the titration and the effect this has on the amount of $CuSO_4 \cdot nH_2O$ determined in **1(c)(iii)**.

The I_2 first produced could **oxidise SCN⁻ to (SCN)₂**, itself reduced back to I^-.

This will lead to **lower titre reading** and hence a **smaller amount** of

$CuSO_4 \cdot nH_2O$ in **(c)(iii)** than expected.

....

.... [1]

Comments:
- This part was poorly done in general.
- Many students wrongly thought that $(SCN)_2$ as added instead of SCN^-, hence wrongly concluded the reaction occur with I^-.
- Many students also wrongly thought that SCN^- with react with $S_2O_3^{2-}$ or Cu^{2+}.

[Total: 18]

2 Investigation of inorganic reactions

Note: You should complete **Question 1(b)(i)** before starting **Question 2**.

A reaction in which one species is both reduced and oxidised is known as a disproportionation reaction.

In aqueous solution, $Cu^+(aq)$ ions are unstable as they spontaneously undergo a disproportionation reaction. However, stable Cu^+ compounds may be prepared by precipitation or by forming complex ions. Examples of precipitates are copper(I) iodide, CuI, and copper(I) thiocyanate, CuSCN. Examples of stable complex ions are $[CuCl_2]^-$ and $[Cu(NH_3)_2]^+$, both of which form colourless aqueous solutions.

FA 1 solution is the solution of $CuSO_4 \cdot nH_2O$ prepared in **1(a)**.
FA 2 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FA 4 is the residue from **1(b)(i)**. This solid is copper(I) iodide, CuI.

Carry out the following tests. Carefully record your observations in Table 2.1.

If there is no observable change, write **no observable change**.

Table 2.1

	test	observations
(a)	Add 10 drops of **FA 1** solution to a test-tube.	
	Add 10 drops of 10% KSCN solution dropwise, with shaking.	Blue solution turns **green** initially. When more KSCN is added a **dark green/brown/black ppt** is formed.
	Add **FA 2** slowly, with shaking, until no further change is seen.	The dark green/brown/black ppt turns **white** upon addition of **FA 2**. White ppt **dissolves in excess** **FA 2** to give a **clear colourless solution**. [2]
(b)	Transfer 1 small spatula of **FA 4** into a clean test-tube, using the small plastic spatula.	
	Add **FA 2** slowly, with shaking, until no further change is seen.	White **FA 4 dissolves in excess** **FA 2** to give a **clear colourless solution**. [1]

(c) Suggest an explanation for your observations in **2(a)** and **2(b)** when **FA 2** is added in excess to the mixture.

Cu$^+$ forms a **stable water-soluble complex** with S$_2$O$_3^{2-}$:

$$Cu^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons \left[Cu(S_2O_3)_2\right]^{3-}(aq)$$
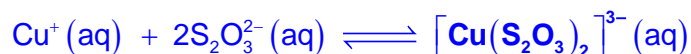
This causes [Cu$^+$(aq)] to decrease, resulting in the **dissolution of the white CuSCN** formed in **2(a)** and the CuI in **2(b)** when the **I.P. falls below the respective K_{sp}** .... [1]

[Total: 4]

3 **Evaluate of the reliability of a gravimetric method in determining the percentage by mass of water of crystallisation in CuSO₄·nH₂O**

FA 1 is solid hydrated copper(II) sulfate, $CuSO_4 \cdot nH_2O$. You are required to determine the percentage of water of crystallisation and the value of n in the salt.

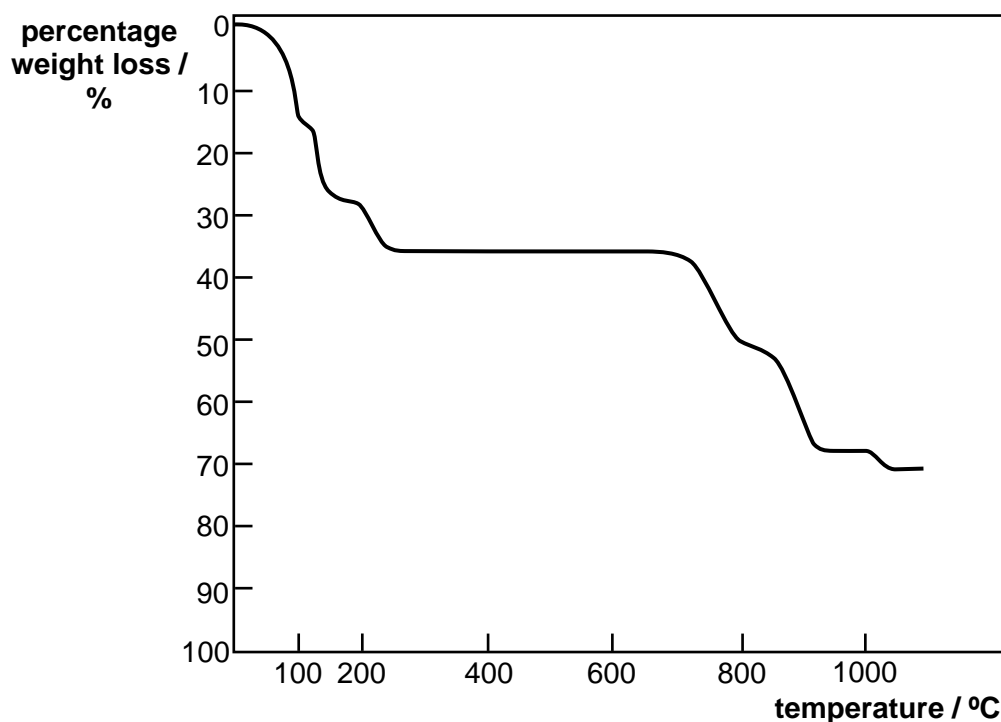When $CuSO_4 \cdot nH_2O$ is heated, the change in percentage weight loss with temperature is as shown in Fig 3.1.

Fig. 3.1

There are four distinct regions of decomposition, listed below along with the approximate temperature range:

$$CuSO_4 \cdot nH_2O(s) \longrightarrow CuSO_4 \cdot H_2O(s) + (n-1)H_2O(g) \qquad 90\text{–}150\ °C$$

$$CuSO_4 \cdot H_2O(s) \longrightarrow CuSO_4(s) + H_2O(g) \qquad 200\text{–}275\ °C$$

$$CuSO_4(s) \longrightarrow CuO(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \qquad 700\text{–}900\ °C$$

$$CuO(s) \longrightarrow Cu_2O(s) + \tfrac{1}{2}O_2(g) \qquad 1000\text{–}1100\ °C$$
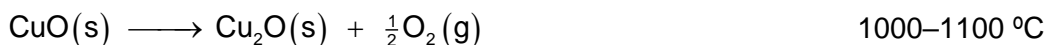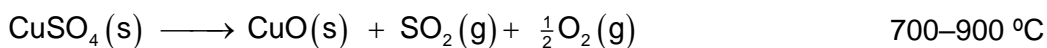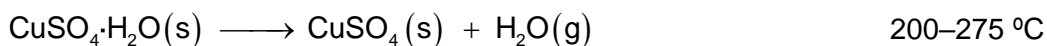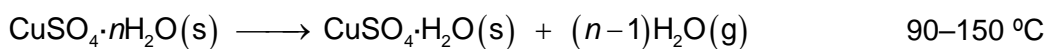
In this question, you will heat to dehydrate the $CuSO_4 \cdot nH_2O$ in **FA 1** and determine the mass of water lost. The data will be used to determine

- the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$,
- the value of n in $CuSO_4 \cdot nH_2O$.

9729/04/J2PE/19

(a) Thermal dehydration of $CuSO_4 \cdot nH_2O$

In this experiment, solid **FA 1** is heated gently in a boiling tube, over a luminous Bunsen flame, until **all** water has been driven off.

1. Weigh accurately between 2.00 g and 2.50 g of **FA 1** in the boiling tube provided. Record your weighings in the space provided below.

2. Heat the tube and content **gently** for 10 minutes.

> Use a **luminous** Bunsen flame with the air-hole **closed** for this purpose. Ensure even heating of the sample and boiling tube.

3. Place the boiling tube into a **dry** 250 cm^3 beaker to cool.

> You may wish to proceed with other experiments while waiting for the boiling tube to cool.

4. Weigh and record the mass of the cooled boiling tube containing the residue.

5. Repeat points 2 (heat gently for 2 minutes subsequently) to 4 as necessary until a constant mass is obtained.

6. **Turn off the Bunsen burner**.

(i) In an appropriate format in the space below, record all weighings.

Mass of empty boiling tube / g	30.883
Mass of boiling tube and **FA 1** / g	32.894
Mass of **FA 1** used / g	2.011
Mass of boiling tube and residue after first heating / g	32.174
Mass of boiling tube and residue after second heating / g	32.171

[4]

Comments:
- This part was surprisingly poorly attempted. Candidates are advised to familiarise themselves with the recording of experimental data in a single table.
- Many candidates did not record the mass of the empty boiling tube.
- Some candidates did not follow the instructions in Step 5. Some other candidates mistook the instruction and repeated steps 1 to 4 instead.

(ii) Using your results, calculate the mass of water vapour evolved.

$$\text{mass of water vapour evolved} = 32.894 - 32.171$$
$$= 0.723 \text{ g } \textbf{[1]}$$

mass of H_2O evolved = ...**0.723 g**........................ [1]

Comments:
- This part was well done in general.

(iii) Using your answer to **3(a)(ii)**, calculate the percentage by mass of water of crystallisation in $CuSO_4 \cdot nH_2O$.

$$\text{mass of } \textbf{FA 1} \text{ used} = 32.894 - 30.883$$
$$= 2.011 \text{ g}$$

$$\text{percentage by mass of water of crystallisation} = \frac{0.723}{2.011}$$
$$= 36.0\% \ (3 \text{ s.f.}) \ \textbf{[1]}$$

percentage by mass of water of crystallisation = ...**36.0%**.................. [2]

Comments:
- This part was well done in general.

(iv) Determine the value of n in $CuSO_4 \cdot nH_2O$.

$$n_{H_2O} = \frac{0.723}{1.0 \times 2 + 16.0} = 0.04017 \text{ mol}$$

$$n_{CuSO_4} = \frac{2.011 - 0.723}{63.5 + 32.1 + 16.0 \times 4} = 8.070 \times 10^{-3} \text{ mol}$$

$$n = \frac{n_{H_2O}}{n_{CuSO_4}} = \frac{0.04017 \text{ mol}}{8.070 \times 10^{-3} \text{ mol}}$$
$$= 4.98$$
$$\simeq 5 \ \textbf{[1]}$$

value of n = ...**5**.................. [2]

Comments:
- This part was not well attempted. Candidates should note that
- n is an integer (as stated in the question paper), and
- they should only use measurements and calculations from the same experiment (instead of using values from Q1).

For Examiner's Use

(b) (i) Solid **FA 1** is a blue crystalline solid. Describe the appearance of the residue after heating.

<u>White / Off-white / Greyish powder</u> .... [1]

> **Comments:**
> - This part is poorly attempted. Majority of the candidates only noted the white colour of the residue, but failed to note the **powder appearance** of the residue.
> - Those who did not ensure heating **until water has been driven off** obtained pale blue or greenish blue residue which is not accepted.

(ii) Explain the difference in colour between solid **FA 1** and the residue.

Despite both containing Cu^{2+} with a **partially filled d subshell**, **water molecules in FA 1 serve as ligands** to bind to Cu^{2+} causing the **d orbitals** to **split into two sets of different energies**, while in residue, **d orbital splitting does not occur** as there are no ligands and the d orbitals in Cu^{2+} are degenerate. **Visible light of a certain wavelength is absorbed by the former** hence appearing the complementary colour, while **visible light is not absorbed by the latter** and the reside **appears white**. .... [3]

> **Comments:**
> - The explanations given lack accuracy and terminologies were not put together correctly.
> - The common errors were as follows.
>   - Many failed to identify the water in **FA 1** act as ligands and the act of heating drives off the water ligands. Hence the residue is anhydrous $CuSO_4$, **not Cu_2O or Cu_2I**. The Cu ion in **both FA 1** and residue contain partially filled d subshell.
>   - Many were casual in the use of the phrase *"d orbital splitting"*. The d subshell or d orbitals split **into two sets of different energies** due to the water ligands in **FA 1**.
>   - Some serious misuse of phrasings seen. For instance, "promotion of d orbitals from lower energy to higher energy?! **It is the d electron that get promoted** from the low energy d orbitals to the high energy d orbitals, not the orbitals.
> - Many also did not realise that **having no d-d transition did not mean no energy is absorbed**. d-s transition can still take place in the residue where **energy can still be absorbed, but not in the visible light range**. Hence the all the wavelengths in visible light is transmitted and residue is white.

(c) The intermediate monohydrate, $CuSO_4 \cdot H_2O$, formed during the dehydration is a white crystalline solid. Using your answer to **3(a)(iv)**, suggest and explain the likely identity of the copper(II)-containing complex ion present in solid **FA 1**.

This suggests that **one of the water molecule** (the last molecule) **is not bound to the Cu^{2+} as ligand**. Hence, the complex is **$[Cu(H_2O)_{n-1}]^{2+}$**. .... [1]

Comments:
- This part was poorly done. Majority of the candidates did not read the question carefully, suggesting only identity of the complex ion without any explanation at all. Hence those who have deduced correctly, but without explanation could not be award the one mark.
- Many could not did not see that if one of the water molecules is left in the intermediate, then the other ($n - 1$) water molecules will act as ligands and copper containing complex ion present in **FA 1** is **$[Cu(H_2O)_{n-1}]^{2+}$**.

(d) One potential source of error in this experiment is further decomposition of the anhydrous $CuSO_4$ residue when temperature goes above 700 ºC as seen in Fig. 3.1.

(i) How would this error affect the calculated results in **3(a)(iii)**?

There would be a **larger lost in mass** than expected, which is ascribed to the water of crystallisation, leading to a **larger percentage by mass** of water of crystallisation calculated in **3(a)(iii)**. .... [1]

Comments:
- This part was well done in general.
- Majority of students were able to relate to the larger mass loss to the SO_2/O_2 gases evolved or the lower/smaller mass of the residue formed.
- Some students say that the "% mass of water of crystallisation will be inaccurate". The effect was not clear and thus penalised.

(ii) Describe two observations that would seen if further decomposition had occurred.

Black solid / residue copper(II) oxide will be seen **OR Brick-red solid / residue** copper(I) oxide will be seen;
Colourless, neutral gas which **rekindles/relights a glowing splint (O_2) evolved;**
Colourless, acidic gas which **turns aqueous acidified potassium manganate(VII) from purple to colourless** evolved (**SO_2**)................................[2]

Comments:
- This part was well-done.
- Majority of students gave the 2 latter gases and the observations from the test of those 2 gases. Some students thought that SO_2 gas was brown in colour.
- Students who gave black solid/residue but identify it to be Cu_2O were penalised.
- Some students did not indicate clearly the colour change for $KMnO_4$ e.g. "decolourise $KMnO_4$".

(e) (i) Comparing the titrimetric method in **1(b)** and the gravimetric method in **3(a)**, which of these two methods is less reliable? Explain your answer.

Gravimetric method; This is because the **temperature** of dehydration **cannot be controlled** using a Bunsen burner, hence it will be **difficult to prevent decomposition** of the anhydrous $CuSO_4$ first formed. **or**
The anhydrous $CuSO_4$ may **absorb moisture from the air during cooling**.
.... [1]

Comments:
- This part proved challenging to most students.
- Those who identified gravimetric method correctly often attributed it to uneven heating or not all H_2O could be evaporated when pg 12 of qns paper step 2 has asked them to ensure this. Many who identified gravimetric method thought they were decomposing the compound in this experiment saying "incomplete decomposition took place.". All these answers were not given credit.
- Out of the 2 explanations above, the 1st one on preventing further decomposition was more commonly given by students. There were few students, which gave the explanation regarding the ability of the anhydrous residue to absorb moisture from the air.

(ii) Suggest one way in which the reliability of the method identified in **3(e)(i)** can be improved.

Carry out the dehydration of CuSO₄·_n_H₂O in a vacuum oven under controlled temperature of 400 ºC (≤ 700 ºC) **_or_**

Cool the anhydrous CuSO₄ in a **desiccator** .... [1]

Comments:
- This part was also challenging to majority of the students.
- The answer given in this part should align to method or explanation given in **(e)(i)** for credit to be given i.e. they should be discussing on the gravimetric method.
- Students who propose idea of temperature controlled environment OR oil/sand bath were given credit. Water bath was rejected since it will no longer exist when at a temperature of 200 ºC or higher. Those who mention this but mention "to ensure complete decomposition" were penalised since we are dehydrating and not decomposing it.
- Students who mention "cool residue in a dry (or not humid) environment" or to "stopper the residue during cooling to avoid absorbing moisture in the air" were also given credit.

[Total : 19]

4 Planning

Besides the titrimetric method in **1(b)**, the amount of Cu^{2+} in a sample can be determined by gravimetric method involving precipitation of copper(I) thiocyanate, CuSCN.

The essential experimental conditions are:

1. *slight acidity* of the solution with respect to hydrochloric acid, since the solubility of the precipitate increases appreciably with decreasing pH;

2. *boiling* with ammonium hydrogensulfite, NH_4HSO_3, a *reducing agent*, to first reduce copper(II) to copper(I);

$$2Cu^{2+}(aq) + HSO_3^-(aq) + H_2O(l) \longrightarrow 2Cu^+(aq) + HSO_4^-(aq) + 2H^+(aq)$$
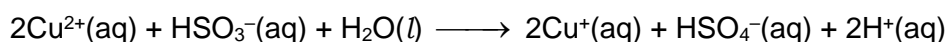
3. precipitation using a *slight excess of ammonium thiocyanate*, NH_4SCN, since a large excess increases the solubility of the copper(I) thiocyanate due to the formation of a thiocyanate complex.

$$Cu^+(aq) + SCN^-(aq) \longrightarrow CuSCN(s)$$
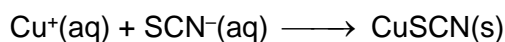
Isolation of the precipitate is achieved by filtering through a sintered-glass crucible shown in Fig. 4.1, which does not require the use of filter paper. At the same time, the crucible serves as a *container* to hold the precipitate during weighing and drying.
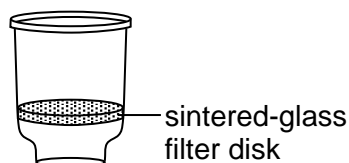

sintered-glass
filter disk

Fig. 4.1

The precipitate is washed with dilute NH_4SCN solution, containing a little NH_4HSO_3 to prevent any oxidation of the copper(I) salt. This is followed by washing with ethanol.

The precipitate (in the crucible) is dried by heating in a hot air oven at 110–120 $^\circ$C.

In the question, you are to plan a procedure that would allow you to determine the percentage purity of a sample of $Cu(NO_3)_2 \cdot 3H_2O$.

You can assume that you are provided with:
*   3.00 g of solid copper(II) nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$ (solubility : 267 g / 100 cm^3 of water),
*   10 cm^3 of 1.00 mol dm^{-3} hydrochloric acid, HC*l*,
*   150 cm^3 of 0.10 mol dm^{-3} ammonium hydrogensulfite, NH_4HSO_3,
*   150 cm^3 of 0.25 mol dm^{-3} ammonium thiocyanate, NH_4SCN,
*   50 cm^3 of ethanol,
*   sintered-glass crucible,
*   the equipment normally found in a school or college laboratory.

(a) Assuming that 2.50 g of $Cu(NO_3)_2 \cdot 3H_2O$ is used. Determine the minimum volume of 0.10 mol dm^{-3} ammonium hydrogensulfite, NH_4HSO_3, that is needed to convert all the Cu^{2+}(aq) into Cu^+(aq).

[A_r: Cu, 63.5; O, 16.0; N, 14.0; H, 1.0]

$$n_{Cu(NO_3)_2 \cdot 3H_2O} = \frac{2.50}{63.5 + 2(14.0 + 16.0 \times 3) + 3(1.0 \times 2 + 16.0)} = \frac{2.50}{241.5} = 0.010352 \text{ mol}$$

$$\text{mininium } n_{HSO_3} \text{ required} = \frac{1}{2} \times n_{Cu^{2+}} = \frac{1}{2} \times 0.010352 = 0.005176 \text{ mol}$$

$$\text{mininium } V_{NH_4HSO_3} \text{ required} = \frac{0.005176}{0.10} = 0.05176 \text{ dm}^3 \approx 51.80 \text{ cm}^3$$

minimum volume of 0.10 mol dm^{-3} NH_4HSO_3 needed = ...**51.80 cm^3**........ [1]

Comments:
- This part was well done in general.
- Despite the equation and hence 2:1 mole ratio of $Cu^{2+}:HSO_3^-$ being given, a handful of students still use a wrong 1:1 stoichiometry in the calculation.
- A number of students also evaluated the numerical answer for $n(Cu(NO_3)_2 \cdot 3H_2O)$ wrongly despite writing down the correct string of A_r corresponding to the formula.

(b) Determine the minimum volume of 0.25 mol dm^{-3} ammonium thiocyanate, NH_4SCN, needed to precipitate all the Cu^+(aq) produced in **4(a)**.

$$n_{Cu^+} = n_{Cu^{2+}} = 0.010352 \text{ mol}$$

$$\text{minimium } n_{SCN^-} = n_{Cu^+} = 0.010352 \text{ mol}$$

$$\text{mininium } V_{NH_4SCN} \text{ required} = \frac{0.01035}{0.25} = 0.04141 \text{ dm}^3 = 41.50 \text{ cm}^3$$

minimum volume of 0.25 mol dm^{-3} NH_4SCN needed = ...**41.50 cm^3**........ [1]

Comments:
- This part was generally badly attempted as most students round *down* the volume of NH_4SCN needed instead of rounding *up* as question ask for the minimum volume.
- Accepted 41.60 cm^3 if student uses n(Cu^+) = 0.0104 mol and 41.40 cm^3 if student uses n(Cu^+) = 0.01035 mol. Otherwise, students are expected to round up to 41.50 cm^3 if they use n(Cu^+) with 5 or higher significant figures.
- Again, despite the 1:1 stoichiometry for the precipitation reaction being given, a handful of students used a 2:1 molar ratio of $Cu^+ : SCN^-$ instead.

(c) Plan an investigation to determine the percentage purity of a 2.50 g sample of $Cu(NO_3)_2 \cdot 3H_2O$ based on the gravimetric method described above.

For Examiner's Use

In your plan, you should include brief details of:
- the apparatus you would use,
- the quantities you would use,
- the procedure you would follow,

Procedure:

1. Weigh out **accurately about 2.50 g** of $Cu(NO_3)_2 \cdot 3H_2O$ into a clean and dry **weighing bottle** using an **analytical balance**.

2. Dissolve the solid in **50 cm^3 of deionised water** in a **250 cm^3 beaker**

3. Add **1 cm^3 of 1.00 mol dm^{-3} HCl** by means of a **10 cm^3 measuring cylinder**

4. Add in **70 cm^3 of 0.10 mol dm^{-3} NH$_4$HSO$_3$** by means of a **100 cm^3 measuring cylinder**.

5. Bring the solution to **boil over a Bunsen flame** for 5 minutes.

6. Turn off the Bunsen burner.

7. Add in **42 cm^3 of 0.25 mol dm^{-3} NH$_4$SCN slowly** to the mixture using a **50 cm^3 measuring cylinder, stirring with a glass rod**.

8. Allow the mixture to stand for 30 minutes at room temperature.

9. **Weigh** and **record** the **mass** of a **clean and dry sintered-glass crucible** using an **analytical balance**.

10. Filter the mixture through the sintered-glass funnel, and **wash the precipitate 3 times** with a mixture consisting of **10 cm^3 of 0.25 mol dm^{-3} NH$_4$SCN** and **1 cm^3 of 0.10 mol dm^{-3} NH$_4$HSO$_3$**.

11. **Wash** the precipitate **3 times with 10 cm^3 portions of** cold **ethanol**.

12. **Heat** the crucible and precipitate in a **hot air oven** at **110–120 °C** for **1 hour**.

13. **Cool** the crucible in a dessicator. **Weigh and record** the **mass of the cooled crucible with the precipitate** using an **analytical balance.**

14. Repeat step 12 and 13 until **constant mass** of the crucible with precipitate is obtained within ±0.01g. .... [10]

Comments:

- This first part up till the precipitation of CuSCN was fairly well attempted.
- The latter part pertaining to isolation of the precipitate and obtaining the mass of the dry precipitate was generally poorly attempted.

Precipitation

- Despite given 3.00 g of solid $Cu(NO_3)_2 \cdot 3H_2O$ in the list and asked to determine the percentage purity of a 2.50 g sample, with the calculations in **4(a)** and **4(b)** dealing with 2.50 g of $Cu(NO_3)_2 \cdot 3H_2O$, a sizable number of students did not weigh out the desired mass of $Cu(NO_3)_2 \cdot 3H_2O$ as the first step (mark ref 44). Very commonly, the use of a weighing balance was not mentioned.
- Some students erroneously weighed the $Cu(NO_3)_2 \cdot 3H_2O$ into the crucible, possibly mis-reading the information "At the same time, the crucible serves as a *container* to hold the precipitate during weighing and drying".
- Quite a significant number of students prepared 250 cm³ of a standard solution from the 2.50 g of $Cu(NO_3)_2 \cdot 3H_2O$ and pipetted out (or in the worst case, using a measuring cylinder to measure out) 10/25/50 cm³ of the solution for subsequent reaction. They should use all the 2.50 g of $Cu(NO_3)_2 \cdot 3H_2O$.
- Among the students who prepared a standard solution, the better ones scaled the volume of NH_4HSO_3 (mark ref 46) and NH_4SCN calculated in **4(a)** and **4(b)** accordingly, which is still acceptable. Many failed to realise that they need to scale the two volumes and ended up using far excess of the two reagents. They did not realise that excess NH_4SCN will actually cause the ppt to dissolve due to formation of a complex. Students were not penalised though (mark ref 48).
- A number of students forgot to add HC*l* to acidify the solution, or more commonly, added too much HC*l* (maximum accepted is 5 cm³; but adjusted if students add in water to dilute the solution) despite being told "slight acidity", or a few used the wrong acid (mark ref 45).
- A large number of students did not mention boiling and just describe heating the solution (mark ref 47). The heat source was also often not mentioned. Thermostatically controlled water bath is not accepted as water bath is not used to boil aqueous solution. A very small number used reflux, which is not needed for aqueous/non-organic system.
- A number of students also did not heat the solution at all and proceeded with addition of NH_4SCN. Although technically the Cu^{2+} would not have converted to Cu^+ fully, students were not penalised for the subsequent parts.
- Many students added the NH_4SCN in far larger excess, without realising that the precipitate is actually soluble in excess of the reagent. However, they were not penalised giving benefit of doubt (mark ref 48).
- Some students did not use the values obtained in **4(a)** and **4(b)** in their plan at all.

<u>Isolation of Precipitate</u>

- Most students did not understand that the sintered glass crucible is used to hold the ppt despite being told "At the same time, the crucible serves as a *container* to hold the precipitate during weighing and drying". Hence, most students did not pre-weigh the sintered glass crucible prior to filtration (mark ref 49).

- The idea that washing needs to be carried out with small volumes of the solution at least 2 times is also missing in almost all the students' scripts. However, this was only penalised once for either the $NH_4HSO_3+NH_4SCN$ mixture (mark ref 50) or ethanol (mark ref 51). The absence of specific volume of the solutions used in washing was also not penalised.

- Most students understand the need to dry the precipitate in the oven, although a few heated the precipitate in a Bunsen flame.

- Most students did not mention the need to allow the heated crucible and ppt to cool before weighing (mark ref 52). Benefit of doubts were given should the student not mention the crucible but just made reference to heating the ppt.

- Only very few students appreciated the need to heat till constant mass (mark ref 53). Even then, those who realised the need, did not state the level of precision for constant mass in general, although they were not penalised.

- Many students thought of repeating the whole precipitation and isolation of precipitate, especially those who prepared a standard solution and took out aliquots for the precipitation, which is not the case for gravimetric determination.

<u>Overall</u>

- Very commonly, students did not give details on the volume of solution and choice of apparatus for the difference steps. One mark overall is deducted in these cases.

(d) Assuming that m g of CuSCN is obtained from 2.50 g of $Cu(NO_3)_2 \cdot 3H_2O$ sample in **3(c)**. Express the percentage purity of the sample in terms of m.

$[A_r$: Cu, 63.5; S, 32.1; O, 16.0; N, 14.0; C, 12.0; H, 1.0]

$$n_{CuSCN} = \frac{m}{63.5 + 32.1 + 12.0 + 14.0} = \frac{m}{121.6} \text{ mol}$$

$$n_{Cu(NO_3)_2 \cdot 3H_2O} = n_{CuSCN} = \frac{m}{121.6} \text{ mol [1]}$$

$$m_{Cu(NO_3)_2 \cdot 3H_2O} = n_{Cu(NO_3)_2 \cdot 3H_2O} \times \left[63.5 + 2(14.0 + 16.0 \times 3) + 3(1.0 \times 2 + 16.0) \right]$$

$$= \frac{m}{121.6} \times 241.5 \text{ g}$$

$$\text{percentage purity} = \frac{\frac{m}{121.6} \times 241.5}{2.50} \times 100\% = \mathbf{79.4}\textbf{\textit{m}}\mathbf{\% \text{ [1]}}$$

[2]

Comments:
- This part was fairly well attempted in general. Other methods of obtaining the % purity were accepted as well.
- Quite a handful of students thought erroneously that $n(Cu^{2+}) = 2n(Cu^+)$.
- One common mistake is to determine the mass of Cu in the precipitate (instead of the mass of $Cu(NO_3)_2 \cdot 3H_2O$) and divide by 2.50 g (the mass of $Cu(NO_3)_2 \cdot 3H_2O$ used) to find the % purity.
- Another commonly observed mistake is to give $100m/2.50\%$ as the % purity without realising that the m g refers to CuSCN and 2.50 g refers to $Cu(NO_3)_2 \cdot 3H_2O$ (despite being given in the question), which are different compounds altogether.

[Total : 14]