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

CHEMISTRY

Paper 3 Free Response

9729/03

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.

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.

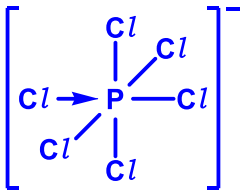
(a) Phosphoric(V) acid can be formed from the reaction of phosphorous(V) oxide, P_4O_{10}, or phosphorous(V) chloride, PCl_5, with water.

(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,
$[H^+] = 0.080$ mol dm^{-3}
$\mathbf{pH = -lg(0.080) = 1.10 < 1.69}$
Hence H_3PO_4 is a weak acid.

or

$\mathbf{[H^+] = 10^{-1.69} = 0.02042\ mol\ dm^{-3}}$
< 0.080 mol $dm^{-3} = [H_3PO_4]$
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}**

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

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]

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

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

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 cm^3 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 cm^3 of 0.080 mol dm^{-3} HCl was accidentally added to the solution in **(b)(iv)**. [2]

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

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

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

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

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

Comments:
- Many students did not recognise the solution as a buffer.
- Among students who did, some forgot to include the volume in the calculation of concentration. Some forgot that both the concentrations of the weak acid and conjugate base would be affected.

(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]

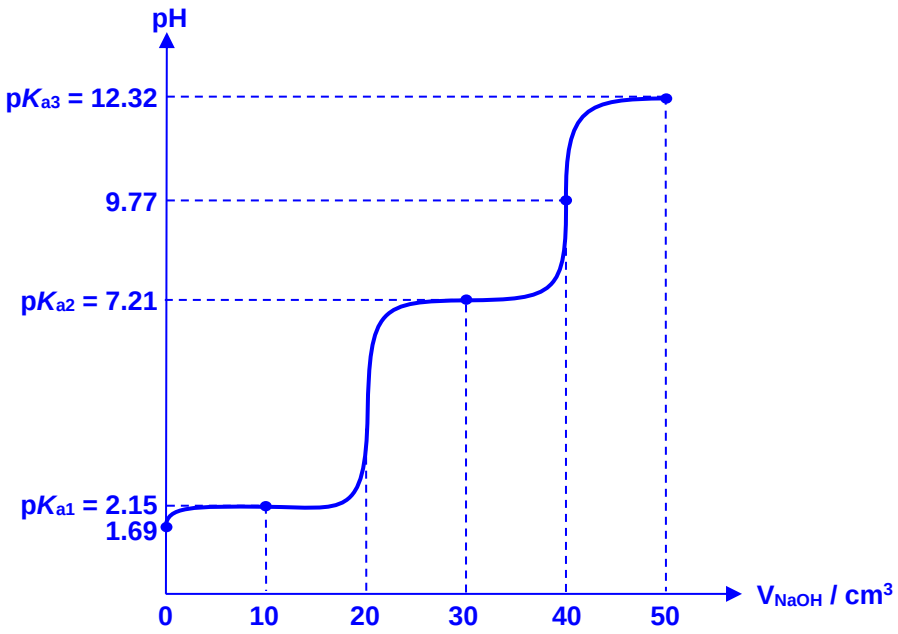
$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$$

Comments:
- Many candidates incorrectly used a non-reversible arrow.
- Some candidates chose the wrong species as the reactant.

(vii) In total, 50.00 cm^3 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**

Comments:
- Despite error carried forward allowed, few candidates were awarded full credit.
- Many students did not label the relevant pH and volume values.
- Many students were penalised for shape if they draw something resembling a straight line (instead of a curve that decreases in gradient) for the initial portion.

(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]

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

Comments:
- This was generally well-attempted.

(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}

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

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

Comments:
- This was generally well-attempted. However, some candidates had calculation errors.

[Total: 18]

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

$$2MnO_4^-(aq) + 5HCHO(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5HCO_2H(aq) + 3H_2O(l)$$

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.

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

[2]

Step 1:

Reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Oxidation: $(V^{3+} + H_2O \rightarrow VO^{2+} + 2H^+ + e^-) \times 5$

$$MnO_4^- + H_2O + 5V^{3+} \rightarrow Mn^{2+} + 5VO^{2+} + 2H^+$$

$E_{cell}^\ominus$ = +1.52 – (+0.34) = **+1.18V**

Since $E_{cell}^\ominus > 0$, reaction is **feasible**.

Step 2:

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

Oxidation: $HCHO + H_2O \rightarrow HCO_2H + 2H^+ + 2e^-$

$$2VO^{2+} + 2H^+ + HCHO \rightarrow 2V^{3+} + HCO_2H + H_2O$$

$E_{cell}^\ominus$ = +0.34 – (–0.03) = **+0.37 V**

Since $E_{cell}^\ominus > 0$, reaction is **feasible**.

Comments:

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

(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 V < $E_{red}^\ominus$ < +1.52 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 Br_2 and to HCO_2H. Explain your reasoning. [2]

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

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

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{3.6\times10^{-4}}{1.8\times10^{-4}} = \left(\frac{0.480}{0.240}\right)^y$$

$\Rightarrow y = 1$. $\therefore$ reaction is **first order** with respect to HCO_2H.

Comparing expt 1 and 2,

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{1.8\times10^{-4}}{1.8\times10^{-4}} = \left(\frac{0.0050}{0.0100}\right)^x \left(\frac{0.240}{0.120}\right)$$

$\Rightarrow x = 1$. $\therefore$ reaction is **first order** with respect to Br_2.

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. Br_2 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 $k' = k[CO_2H]$

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

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

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 $t_{½}$ 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.

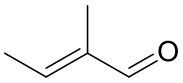
(v) Outline how you would determine the effect of using Cl_2 instead of Br_2 on the rate of oxidation of HCO_2H, with reference to the results in Table 2.1.

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

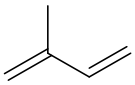
- Use the **same concentrations** of **Cl_2**, in place of Br_2, and **HCO_2H** as one of the three experiments in **Table 2.1**.
- Measure the **volume of CO_2 evolved / mass loss for regular time intervals**.
- Determine and compare **initial rate** from the **gradient of the volume of CO_2 / mass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

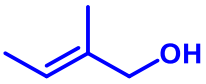


tiglinaldehyde


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.

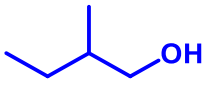
(ii) On the other hand, isoprene does not react with $NaBH_4$. Explain the difference in reactivity between tiglinaldehyde and isoprene with $NaBH_4$. [1]

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.

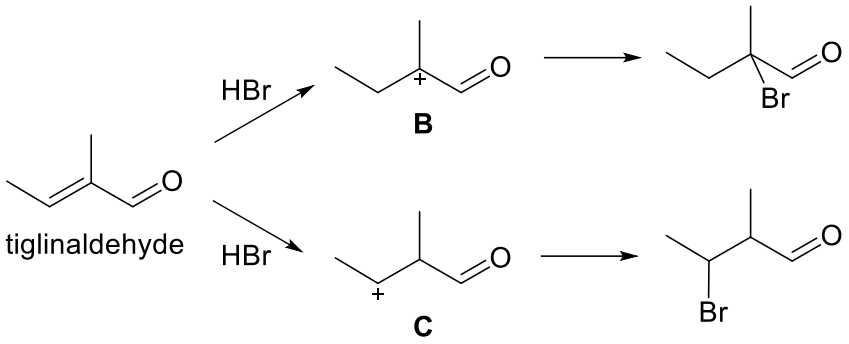
(iii) Suggest the structure of the compound formed when tiglinaldehyde is reacted with hydrogen in the presence of a platinum catalyst. [1]



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**.

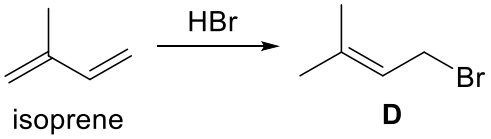
(i) Suggest why carbocation **B** formed is less stable than carbocation **C**. [1]

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.

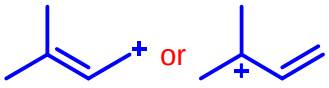
Comments:

- 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**.



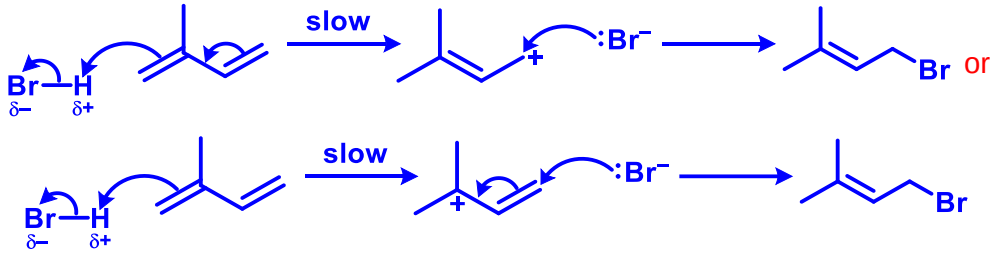
(ii) Suggest a structure for the carbocation intermediate formed in the reaction between hydrogen bromide and isoprene to form compound **D**. [1]



Comments:

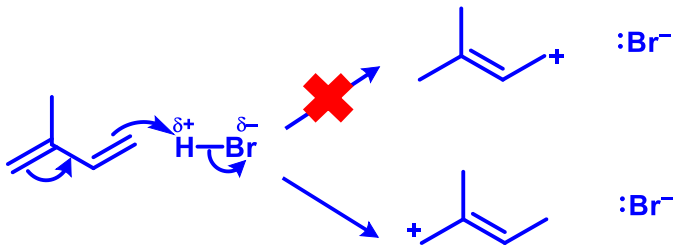
- Many answers showed an attempt to apply their understanding of Markovnikov's rule without considering how the product **D** could be formed from the carbocation. While many could identify that the positive charge on the carbocation would most likely be on the same terminal carbon as the product, fewer failed to realise that the position of the C=C was different from the starting compound.
- A few answers omitted the C=C altogether.

(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]

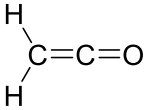


Comments:

- Students were required to apply their knowledge of electrophilic addition to this context. While many could draw the relevant partial charges on HBr and arrows to show the flow of electrons from the alkene to the δ+ H, some attempted to incorrectly show partial charges on the alkene, or thought that electron flow was from H to C=C.
- While many recognised that both double bonds would take part in the reaction at the same time, not all were able to identify which alkene would be the one undergoing electrophilic addition. Many erroneously thought that it would be the less substituted alkene that reacted with H–Br to give the carbocation that was correctly identified in **(d)(ii)**.



(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.

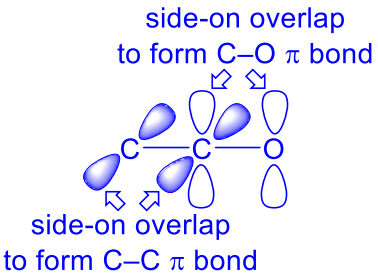
(ii) In tiglinaldehyde, the π electrons are delocalised over all four atoms in C=C–C=O. Explain why the π electrons are able to delocalise over C=C–C=O. [1]

Side-on overlap of the parallel/aligned/on the same plane unhybridised p-orbitals 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**.



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
$E^{\ominus}\left(M^{3+}\middle\vert M^{2+}\right)$ / 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.

(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 $\Delta G_{vap} = 0$.

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

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

$$= \mathbf{+110\ J\,K^{-1}\,mol^{-1}}$$

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]

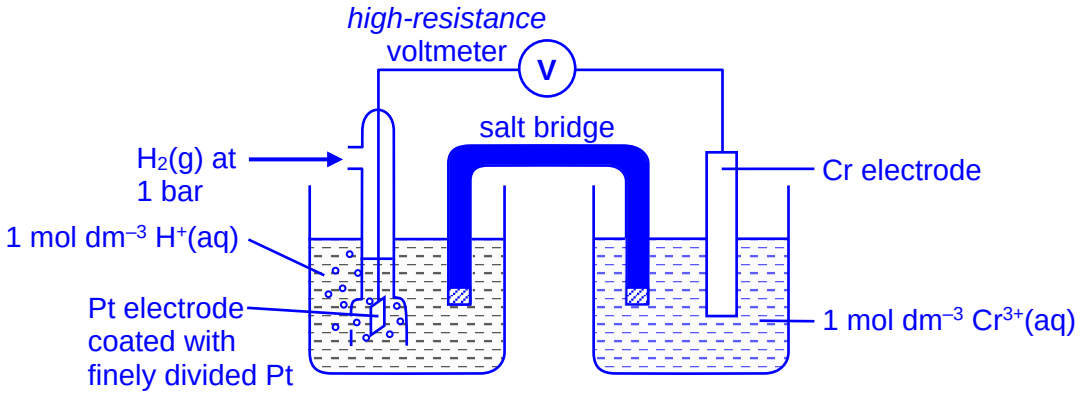
Ti(IV) has a **d^0 configuration**. Hence **d-d transition does not occur in TiO^{2+} and visible light is not absorbed**.

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]

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

$\Delta G^{\ominus} = -nFE^{\ominus} = -1 \times 96500 \times -0.41 = +39565 \text{ J mol}^{-1} = \underline{\mathbf{+39.6 \text{ kJ mol}^{-1}}}$

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 $E^{\ominus}\left(Cr^{2+}|Cr\right) = -0.91 \text{ V}$. [2]

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

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

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

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

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

(iv) From the $E^{\ominus}\left(M^{3+}|M^{2+}\right)$ 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 $E^{\ominus}\left(Cr^{3+}|Cr^{2+}\right)$ 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.

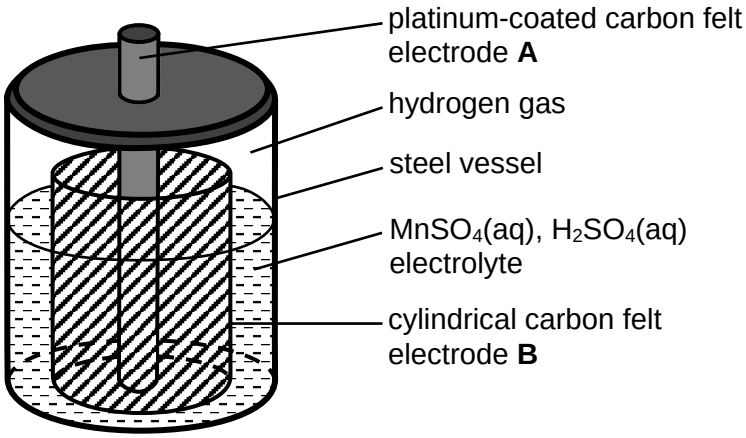


Fig. 3.1

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** : $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$

$$E^{\ominus}_{cell} = E^{\ominus}\left(MnO_2 \middle| Mn^{2+}\right) - E^{\ominus}\left(H^+ \middle| H_2\right) = +1.23 - 0.00$$
$$= \underline{\mathbf{+1.23\ V}}$$

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.

Comments (cont'd):

- Many students chose half-equations involving MnO_4^- or Mn when none of these are given in the question or diagram. Only Mn^{2+} and MnO_2 are given!
- No benefit of doubts given for the calculation of $E_{cell}^{\ominus}$ as students should know that for a discharging battery, the $E_{cell}^{\ominus}$ should be positive, *i.e.* spontaneous.

(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, $\boldsymbol{E\left(H^+|H_2\right)}$ will **becomes more negative**, resulting in a **more positive $\boldsymbol{E_{cell}}$**.

Comments:

- A number of students used the overall cell equation to discuss how the equilibrium is affected. Not that this is wrong, however, they are expected to discuss in terms of changes to either of the electrode potential for the two half-cells and how it impact the E_{cell}.
- Students should explain how changes in the pressure of H_2 will affect the $E\left(H_2|H^+\right)$, and hence E_{cell}.
- There are a few students who used oxidation potential instead and reverses the sign of the $E^{\ominus}$ in the *Data Booklet*. Not that this is strictly wrong, however, this usage is discouraged as at A-level, only reduction potential is used.
- Students have to be more careful with the usage of electrochemistry notation. Once the system is no longer under standard condition, the $\ominus$ symbol should not be present. The usage of $E\left(\text{oxidised form}|\text{reduced form}\right)$ for reduction potential must also be observed.

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

$$\mathbf{H_2O \rightarrow O_2 + 4H^+ + 4e^-}$$

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

Comments:

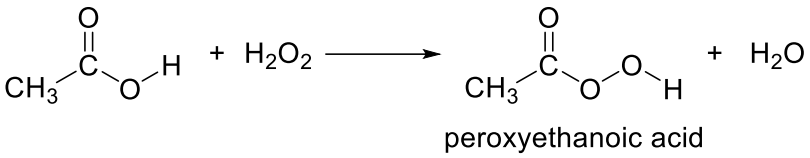
- Most students were able to write the correct equation, although no penalty was made for giving the "$\rightleftharpoons$" sign instead, so long as oxidation of water to O_2 is seen.
- Most students fail to realised that a potential difference larger than $E_{cell}^{\ominus}$ needs to be applied during charging, hence the possibility of oxidation of water.

[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.

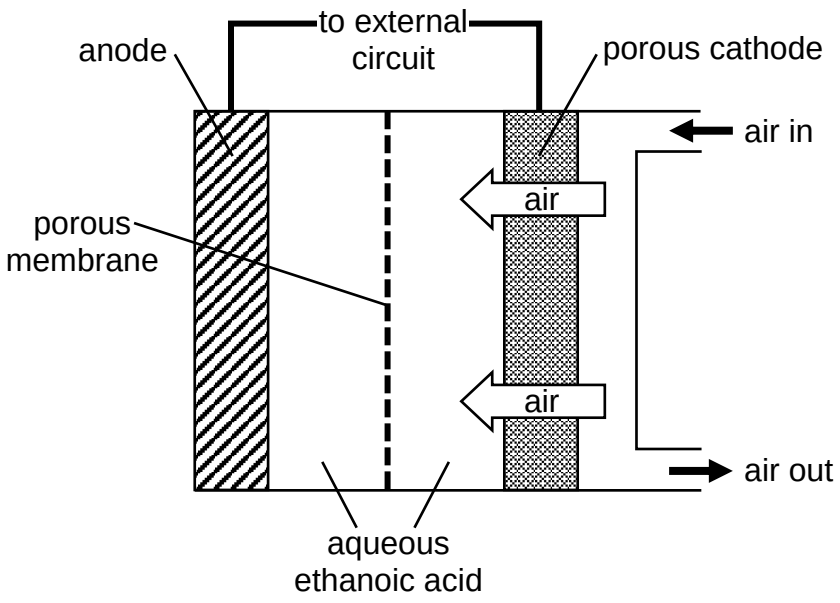


Fig. 4.1

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 "⇌" 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]

$Q = I \times t = 0.2 \times 16 \times 60 \times 60$
$= 11520\ C$

amount of $H_2O_2 = \frac{11520}{96500} \times \frac{1}{2}$ (ecf from **b(i)**)
$= \underline{\mathbf{0.0597\ mol}}$

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.

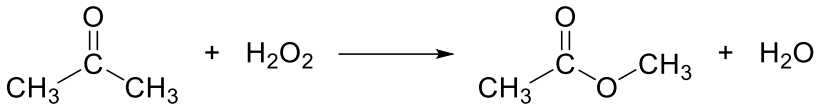


Fig. 4.2

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

methyl ethanoate

Comments:
- Many were confused in identifying the substituent group and gave ethyl ethanoate as the answer instead.

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

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

Comments:
- This part is well done. A small portion of candidates are still writing oxidation state as charge at this point in time! (For instance writing 2+ and 3+ instead of +2 and +3.)

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

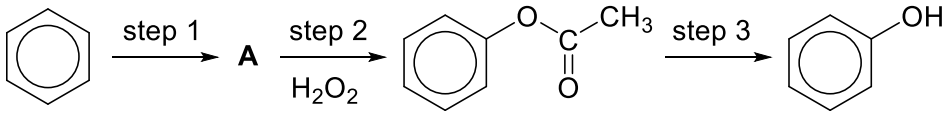
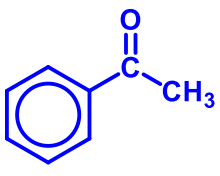


Fig. 4.3

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



A

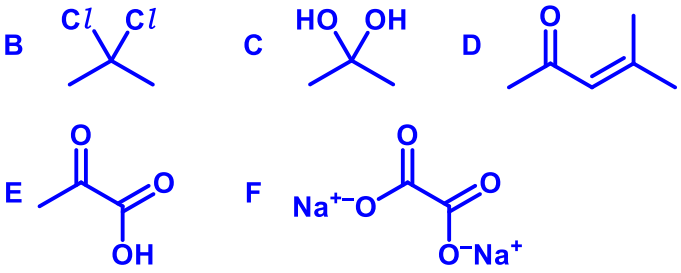
Step 1: $AlCl_3$, CH_3COCl
Step 3: H_2SO_4(aq), heat

Comments:
- A small portion of candidates failed to indicate $AlCl_3$ as the catalyst in step 1.
- Note that conc H_2SO_4 cannot be used for acid hydrolysis. Candidates are expected to state clearly that dilute H_2SO_4 is to be used by writing "**dilute** H_2SO_4" or "H_2SO_4 **(aq)**".
- The use of $LiAlH_4$ is allowed as it can reduce ester to alcohol group.

(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 3º 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 HC*l*) while elimination is the removal of a small molecule (e.g. H_2O or HC*l*) 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.

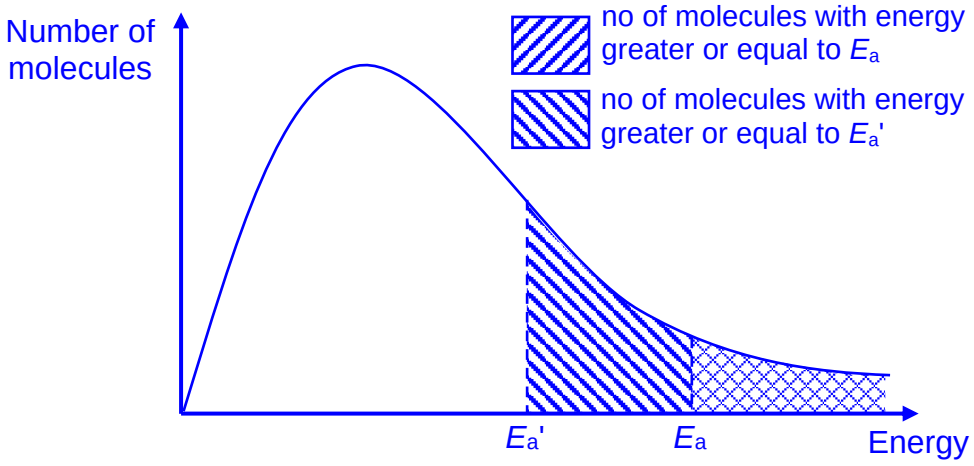
Comments:
- Generally okay. Many students were able to identify that for heterogeneous catalysis to occur, there must be partially filled 3d orbitals. Phrasings such as "vacant d orbitals" were also credited.
- Variable oxidation state in this case will not be accepted as it is not a key characteristic 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 **H_2O 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.

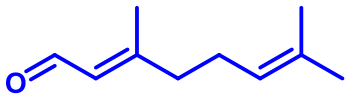
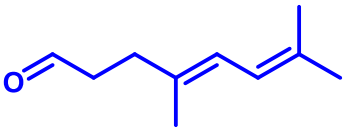
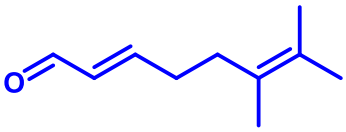
When heated with $KMnO_4$ and dilute H_2SO_4, **A** gives **C**, $C_5H_8O_3$, **D**, C_3H_6O, and a gas that forms a white precipitate when bubbled through $Ca(OH)_2$.

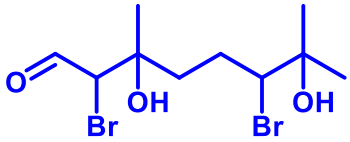
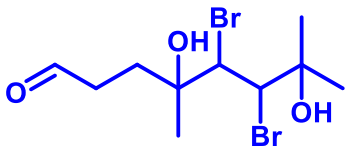
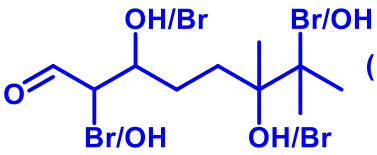
Both **C** and **D** form a pale-yellow precipitate when heated with NaOH(aq) and I_2(aq). On addition of Na_2CO_3, **C** produces effervescence while **D** does not.

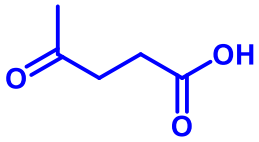
Suggest structures for **A**, **B**, **C** and **D** and explain the reactions described. [9]

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_2CO_3, **C** produces effervescence while **D** does not.	• **C** undergoes **acid-carbonate reaction** while **D** does not. • **C** contains a **CO_2H** group

A is  or  or 

B is  or  or  **(Markovnikov's rule does not apply)**

C is 

D is 

[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**.