Class	Adm No

Candidate Name: ____________________

2024 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **13th Sep 2024**

2 hours

Candidates answer on separate paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission 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. If additional space is required, you should use the page at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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.

Question	A			B	**Total**
	1	2	3	4 / 5	
Marks	19	23	18	20	**80**

Section A

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

1 The halogens are elements in Group 17 of the Periodic Table. The name “halogen” translates to “salt producer”, due to their tendency to form salts readily in the presence of Group 1 metals such as sodium.

(a) **(i)** Citing relevant data values, state and explain the trend of reactivity of the halogens as oxidising agents. [3]

Electrode reaction	**$E^\ominus$ / V**
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

any 3, equation not required [1]

Down Group 17, reactivity of the halogens decreases. [1]

Down the group, $E^\ominus$ value becomes less positive and the halogens are less readily reduced. [1]

Examiners’ Comments:

- Many candidates can use the correct concept to explain.
- Most common mistakes include the use bond energy to explain, not linking back to the question on reactivity, and not giving at least 3 $E^\ominus$ values to state the trend.
-

(ii) Outline a procedure to demonstrate the relative reactivities of chlorine and bromine, given only the following reagents to choose from:

Cl_2(aq) Cl^-(aq) Br_2(aq) Br^-(aq)

[2]

To a test tube containing 1 cm^3 of Br^-(aq), add 1 cm^3 of Cl_2(aq). [1]
sufficient, but can also do the reaction between Cl^- and Br_2

The colourless solution will turn orange as the more reactive Cl_2 displaces Br^- to produce Br_2. [1]

Examiners’ Comments:

- Few candidates gave succinct procedure despite the question using “outline” as a command word.
- A number of candidates also did not mention the initial colour of the solution for the observation.

(b) Gaseous PCl_3 and PCl_5 exist in an equilibrium.

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

At 250 °C, the K_c for this equilibrium has a value of 26.0.

(i) A sample of solid PCl_5 is added into a sealed 2 dm^3 container at 250 °C, and the solid quickly sublimes. After equilibrium was established, there was found to be 0.20 mol of Cl_2.

Determine the initial mass of solid PCl_5 added. [4]

Let y be the initial $[PCl_5(g)]$.

[ ] / mol dm^{-3}	$PCl_3(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$PCl_5(g)$
initial	0		0		y
change	$+x$		$+x$		$-x$
equilibrium	x = 0.10		x = 0.10		$y-x$ = y-0.10

ICE table with correct algebraic formulas [1]

x = 0.20 / 2 = 0.10 mol dm^{-3}

$K_c = \frac{[PCl_5(g)]}{[PCl_3(g)][Cl_2(g)]}$ [1]

$26.0 = \frac{y-0.1}{0.1^2}$

y = 0.36 mol dm^{-3} [1]

initial mass of $PCl_5(g)$ = (0.36 x 2) x [31.0 + 5(35.5)] = 150 g (3sf) [1]

Examiners' Comments:

- A significant number of candidates did not have proper headers and units for their ICE table.
- Some candidates calculated K_c using amount instead of concentration.

(ii) In a modified experiment, some Na(s) was present in the container initially before addition of solid PCl_5 (all other conditions were kept the same).

Explain the effect of this on the position of equilibrium, and the value of K_c. [3]

Na(s) reacts with $Cl_2(g)$ produced, decreasing $[Cl_2(g)]$. [1]

By Le Chatelier's Principle, position of equilibrium shifts to the left to increase $[Cl_2(g)]$. [1]

No change to K_c as temperature remains constant. [1]

Examiners' Comments:

- A number of candidates did not know the species that reacts with Na(s).
- Majority of the candidates lost the second mark as they linked K_c to how POE shifted.

(iii) In the solid state, PCl_5 exists as an ionic solid, with $[PCl_6]^-$ as the anion.

Identify a formula unit of the ionic solid. [1]

$[PCl_4]^+[PCl_6]^-$ [1]

Examiners' Comments:

- Candidates are unfamiliar with the term "formula unit" and some gave just the cation or anion.

(iv) Describe how PCl_5 acts as an acid in the formation of $[PCl_6]^-$, writing an equation to explain your answer. [1]

PCl_5 is a Lewis acid as the P atom accepts a lone-pair from Cl^-.

$PCl_5 + Cl^- \rightarrow [PCl_6]^-$ [1]

Examiners' Comments:

- Majority of the candidates cannot give the correct equation.

(v) Unlike PCl_5, PI_5 does not exist.

Suggest an explanation for why this is the case. [1]

The size / atomic radius of I is larger than C*l*, leading to very large and unfavourable steric hindrance around the P atom. [1]

Examiners' Comments:

- A significant number of candidates did not use the correct correct to explain.

(c) A 25.0 cm^3 sample of water contains chlorine, Cl_2, and monochloramine, NH_2Cl.

The amounts of chlorine and monochloramine in this sample can be analysed using the DPD-FAS titration method, where DPD serves as the indicator and Fe^{2+} the titrant.

The concentration of chlorine is determined first:

Step 1:
Excess of indicator DPD (colourless) is added to the 25.0 cm^3 sample, turning the indicator magenta and reducing Cl_2.

$$\underset{\text{colourless}}{DPD} + Cl_2 \rightarrow \underset{\text{magenta}}{DPD^{2+}} + 2Cl^-$$

Step 2:
The resultant mixture is then titrated against Fe^{2+}.

$$DPD^{2+} + 2Fe^{2+} \rightarrow DPD + 2Fe^{3+}$$

From the same mixture, the concentration of monochloramine is determined next:

Step 3:
A small amount of catalyst is added, catalysing the reduction of NH_2Cl.

$$DPD + NH_2Cl + 2H^+ \rightarrow DPD^{2+} + NH_4^+ + Cl^-$$

Step 4:
The resultant mixture is then titrated against Fe^{2+}, same as Step 2.

$$DPD^{2+} + 2Fe^{2+} \rightarrow DPD + 2Fe^{3+}$$

When 0.0010 mol dm^{-3} of Fe^{2+} was used as the titrant, the titres obtained at the end of Steps 2 and 4 are 15.00 cm^3 and 5.00 cm^3 respectively.

(i) Calculate the amount of Cl_2 in the 25.0 cm^3 water sample. [1]

$n_{Fe2+} = 0.0010 \times \frac{15.00}{1000} = 1.5 \times 10^{-5}$ mol

$n_{Cl2} = \frac{1.5\times10^{-5}}{2} = 7.5 \times 10^{-6}$ mol [1]

Examiners' Comments:
- Candidates did well for this question.

(ii) Calculate the amount of NH_2Cl in the 25.0 cm^3 water sample. [1]

$n_{Fe2+} = 0.0010 \times \frac{5.00}{1000} = 5.0 \times 10^{-6}$ mol

$n_{NH2Cl} = \frac{5.0\times10^{-6}}{2} = 2.5 \times 10^{-6}$ mol [1]

Examiners' Comments:
- Candidates did well for this question.

(iii) Hence, determine the total concentration of C*l* atoms (in g dm^{-3}) in the water sample. [2]

total $n_{Cl} = 2(7.5\text{x}10^{-6}) + (2.5\text{x}10^{-6}) = 1.75 \text{ x } 10^{-5}$ mol [1]

$[Cl] = \frac{(1.75\times10^{-5})\times35.5}{25/1000} = 0.0249$ g dm^{-3} (3sf) [1]

Examiners' Comments:

- A significant number of candidates did not multiply the amount of C*l* atoms by 2 even though there are 2 C*l* atoms in Cl_2.

[Total: 19]

2 **(a)** Compound **A**, $C_5H_8O_2$, is neutral. An orange precipitate is observed when 2,4-dinitrophenylhydrazine is added to it, but no precipitate is observed when Fehling's reagent is added.

1 mol of **A** reacts with acidified $KMnO_4$ to produce CO_2 gas and a single organic product **X**. **A** also turns orange acidified $K_2Cr_2O_7$ green, forming another organic product **Y**.

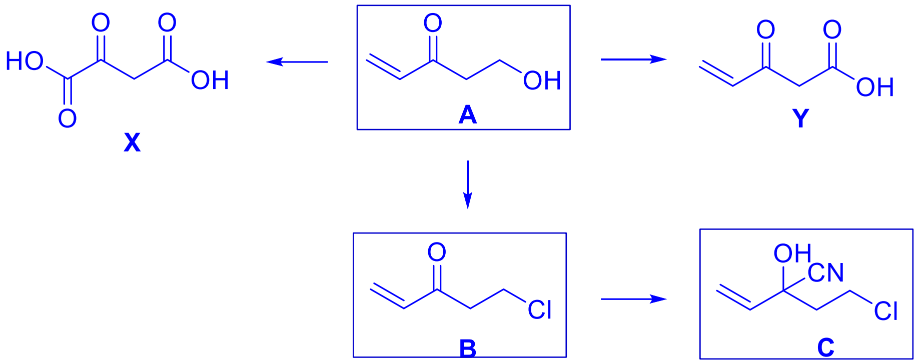
Effervescence of a gas that forms a white precipitate when bubbled through aqueous $Ca(OH)_2$ is observed when Na_2CO_3(s) is separately added to both organic products **X** and **Y**.

A also reacts with PCl_5 to form **B**, C_5H_7OCl. Addition of HCN with trace NaOH(aq) to **B** results in the formation of **C**.

Deduce the structures of compounds **A**–**C**. [6]

Observation	**Deduction** (ToR & Fx Grp)
A has MF $C_5H_8O_2$.	DoU/DBE = $5 - \frac{8}{2} + 1 = 2$ **A** contains 2 double bonds or rings [√]
A is neutral.	**A** does not contain –COOH / carboxylic acid. [√]
Orange precipitate for 2,4-dinitrophenylhydrazine but no precipitate for Fehling's reagent.	Condensation. [√] **A** contains ketone. [√] **A** does not contain aldehyde. [√]
A reacts with acidified $KMnO_4$ to produce CO_2 gas and a single organic product.	Vigorous oxidation / oxidative cleavage. [√] **A** contains terminal C=C / produces ethanedioic acid. [√]
A turns orange acidified $K_2Cr_2O_7$ green.	Oxidation. [√] **A** contains a 1° alcohol / 2° alcohol. [√]
Addition of Na_2CO_3(s) causes effervescence of a gas that forms a white precipitate in aqueous $Ca(OH)_2$.	Acid-carbonate reaction. [√] Both organic products contain –COOH / carboxylic acid, **A** contains a 1° alcohol (cannot be 2° alcohol). [√]
A reacts with PCl_5 to form C_5H_7OCl.	Nucleophilic substitution. [√] **B** contains a 1° alkyl halide (accept 2° if previous part not deduced). [√]
Addition of HCN with trace NaOH(aq) to **B** forms **C**.	Nucleophilic addition. [√] **C** contains hydroxynitrile / cyanohydrin. [√]

12 [√] for [3], 8 [√] for [2], 4 [√] for [1]



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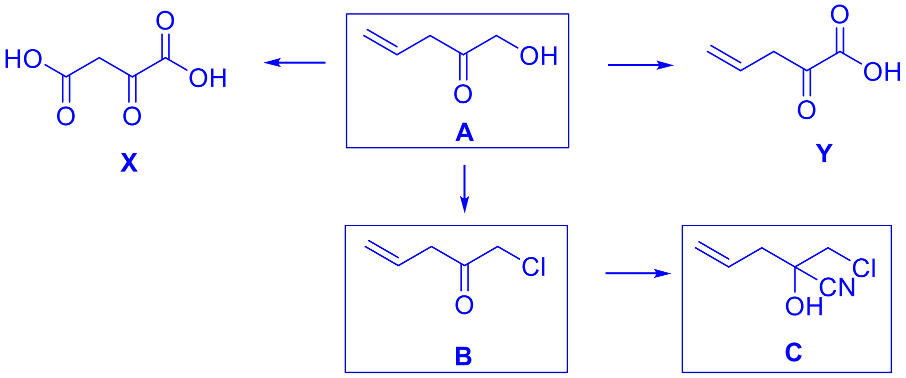

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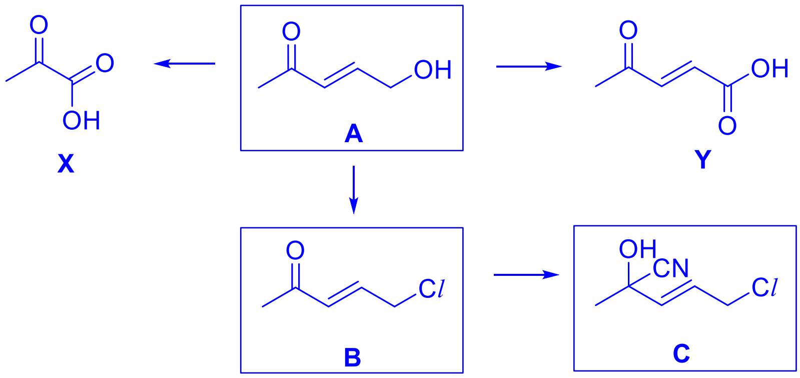
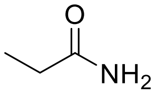


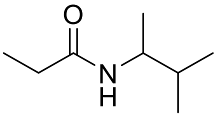
structures [3]

Examiner's comments:

Candidates need to give more details in the deduction of the structures. Most candidates did not include the type of reactions in their answers. A large proportion of candidates also were not familiar with the nucleophilic addition reaction of carbonyl compounds, resulting in giving the wrong structure for C even though their structure for B is correct.

(b) Suggest a chemical test to distinguish between the following compounds.





[2]

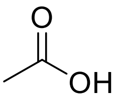
R&C: dilute NaOH, heat [1]

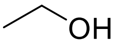
Observations: Pungent gas that turns damp red litmus blue is evolved for 1° amide, but not for 2° amide. [1]

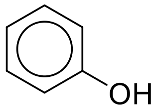
Examiner's comments:

Only a small number of candidates were able to answer this question correctly. Incorrect R&C most commonly given by candidates is the use of dilute acid and heat, failing to realise that this would produce a salt instead of NH_3 and hence unable to turn red litmus paper blue.

(c) Rank the following compounds in order of increasing acid strength, explaining your answer.

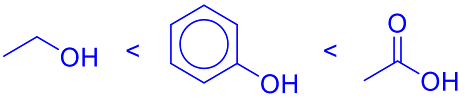






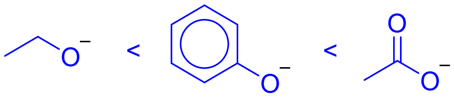
[3]

acidity order:



[1]

conj base stability order:



Strength of acid is determined by stability of conjugate base.

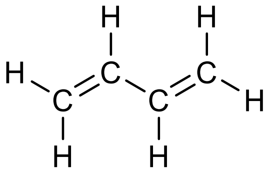
Ethoxide is the least stable as it has an electron-donating alkyl group which intensifies the negative charge on the O atom. [1]

The lone pair on the O atom of ethanoate and phenoxide are both able to delocalise into the C=O and π electron cloud of benzene ring respectively, due to p orbital overlap. This disperses the negative charge on the O atom, stabilising them. Ethanoate is the most stable as this delocalisation is across 2 highly electronegative O atoms, compared to the less electronegative C atoms for phenoxide. [1]

Examiner's comments:

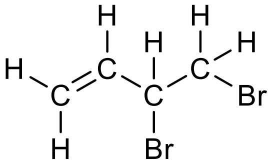
Some candidates did not read the question carefully and listed the compounds in decreasing acid strength instead. Most common mistake includes stating that the inductive effect causes the acid itself (rather than the conjugate bases) to be more/less stable.

(d) Double bonds are said to be conjugated when adjacent p-orbitals of one π bond can align with the p-orbitals of another π bond. Buta-1,3-diene is an example of one such compound with conjugation between its two C=C bonds.

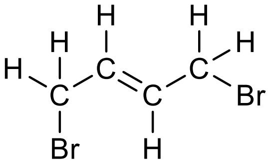


buta-1,3-diene

When 1 mol of Br_2 in CCl_4 is added to 1 mol of buta-1,3-diene, electrophilic addition occurs and products **E** and **F** are formed in an approximate ratio of 50:50.

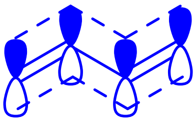


E



F

(i) Draw a suitable diagram to illustrate the conjugation of the two C=C bonds in buta-1,3-diene. [1]

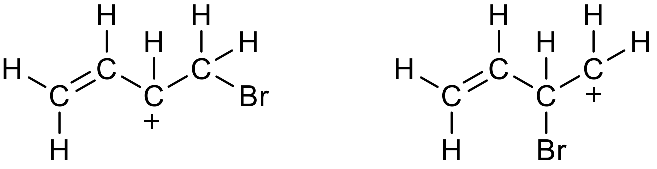


4 parallel p orbitals [1]

Examiner's comments:

Poorly answered.

(ii) Although two carbocation intermediates could have led to the formation of **E**, one is preferred over the other.



preferred intermediate

Explain why this intermediate is preferred. [2]

The preferred intermediate is more stable as it has two electron-donating alkyl groups (as opposed to one for the other intermediate), [1]

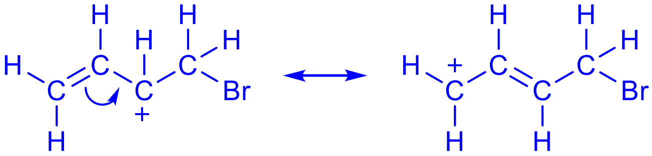
and its positive charge on C is dispersed due to delocalisation from p-orbital overlap with the adjacent C=C (which is not possible in other intermediate). [1]

Examiner's comments:

Some candidates only mentioned there is one more alkyl group, without mentioning the nature of the alkyl group being electron donating. Some also merely stated that the electron donating group stabilises the intermediate, without mentioning how it disperses the positive charge.

(iii) The carbocation intermediate leading to the formation of **F** is produced from the same preferred intermediate in **(ii)**.

By means of suitable curly arrow(s), show the production of the carbocation intermediate leading to the formation of **F**. [1]

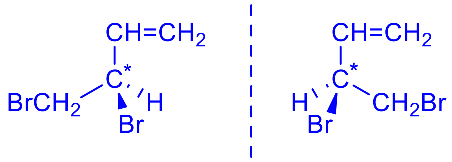


curly arrow and intermediate [1]

Examiner's comments:

Many candidates did not understand the requirements of the questions and drew the electrophilic addition reaction mechanism instead.

(iv) Draw all the stereoisomers of **E**. [1]

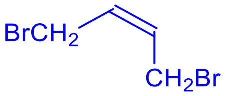


mirror plane [1]

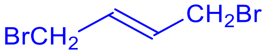
Examiner's comments:

Common mistakes include drawing a completely different structure from E, not drawing the mirror image.

(v) Draw all the stereoisomers of **F**. [1]



cis



trans [1]

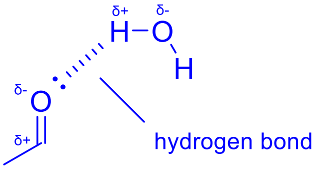
Examiner's comments:

Quite well-answered. Incorrect answers include not drawing the structures in the correct shape (trigonal planar about the 2 C atoms in C=C).

(e) Aldehydes have different solubilities in water.

aldehyde	**formula**	**solubility in water**
ethanal	CH_3CHO	very soluble
pentanal	$CH_3(CH_2)_3CHO$	slightly soluble

(i) By means of a suitable diagram, illustrate why ethanal is very soluble in water. [2]



[1]

Examiner's comments:

The most common misconception noted here is that the H on ethanal is wrongly identified as electron deficient, and hence can form hydrogen bonds with water. Some candidates also identified the interactions formed as ion-dipole interactions instead of hydrogen bond.

(ii) Explain why pentanal is **slightly** soluble in water. [2]

Pentanal is soluble in water as it is also able to form energetically favourable hydrogen bonds with water. Energy released from this is sufficient to overcome hydrogen bonds between water molecules. [1]

However, pentanal is only slightly / not very soluble due to its long(er) non-polar alkyl chain, making its instantaneous dipole-induced dipole interactions with water significant as compared to its hydrogen bonding. [1]

Examiner's comments:

Most candidates only focused on explaining why pentanal is not so soluble and neglected the part about why some can still so dissolve.

(iii) Explain whether the boiling point of ethanal is higher or lower than that of water. [2]

Lower. [1]

Less energy is required to overcome the weaker permanent dipole-permanent dipole interactions between ethanal molecules compared to the stronger hydrogen bonding between water molecules. [1]

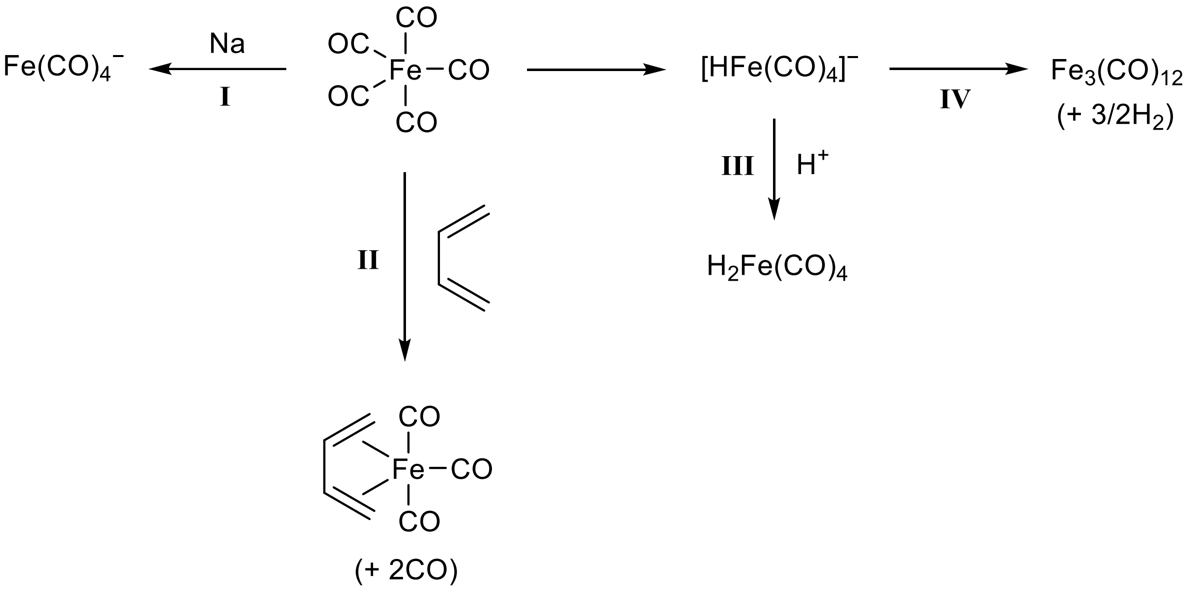
Examiner's comments:

Quite well answered although some gave incomplete answer which did not identify the type of interactions formed and/or overcome. A few candidates also showed misconceptions about breaking covalent bonds during boiling.

[Total: 23]

3 **(a)** Carbon monoxide, CO, is a poisonous, neutral gas that is colourless and odourless. It is also a common ligand in metal complexes. Iron pentacarbonyl, $Fe(CO)_5$, is one such example.

The reaction scheme below shows some reactions involving $Fe(CO)_5$.



(i) Determine the oxidation state of the Fe atom in $Fe(CO)_5$. [1]

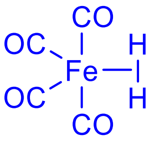
0 [1]

Examiner's comments:

Only a handful were able to give the correct answer. Most common wrong answer is +5.

(ii) The $[HFe(CO)_4]^-$ complex contains a hydride ion, H^-, and the $H_2Fe(CO)_4$ complex contains a H_2 ligand.

Given that $H_2Fe(CO)_4$ is still a penta-coordinate complex, draw the structure of $H_2Fe(CO)_4$. [1]



[1]

Examiner's comments:

Accepted a wider range of answers which include those who drew the 2 H together as H_2. Some candidates did not read the question carefully and gave an octahedral structure instead.

(iii) Identify the type of reactions taking place for Steps **I–IV** in the reaction scheme, focusing on the iron complex. [4]

I: reduction [1]
II: ligand exchange [1]
III: acid-base / neutralisation [1]
IV: condensation [1]

Examiner's comments:

Accepted redox for I although the question mentioned focusing on the iron complex. Some incorrect terms include using ligand displacement instead of ligand exchange. The last two reactions were poorly answered.

(b) CO reacts with oxygen to form CO_2, a known pollutant.

To tackle the harmful effects of CO_2 on the environment, two possible approaches are to

1) Cut down on CO_2 emissions, such as from the burning of fossil fuels, and to
2) Capture CO_2 from the atmosphere.

(i) In some countries, environmentally-friendly electrolysis factories directly utilise electricity generated from windmills to carry out the chemical reactions.

Identify how energies are changed from one form to another in one such electrolysis factory. [1]

Kinetic / Wind → Electric → Chemical [1]

Examiner's comments:

Poorly answered. Many candidates stated chemical to electrical.

To capture CO_2 from the atmosphere, a device called a "humidity-swing" can be used. It consists of a polymeric membrane with key organic functional groups on the carbon chain.

The functional groups, together with H_2O from the atmosphere, enable the reversible collection of CO_2.

(ii) Write an equilibrium equation for the reaction of CO_2 with H_2O. Include state symbols in your answer. [1]

$CO_2(g) + H_2O(g \text{ or } l) \rightleftharpoons H_2CO_3(aq)$ [1]

Examiner's comments:

Poorly answered. Many candidates did not know the product of the reaction. Some gave the correct product but stated that it exists as a gas.

(iii) Suggest a possible functional group that enables the collection of CO_2. [1]

Amine [1]

Functional group should be basic to react with H_2CO_3.
$R_3N + H_2CO_3 \rightarrow R_3NH^+HCO_3^-$ (resultant ionic product holds the "CO_2" in membrane)

Examiner's comments:

Poorly answered. Many gave carboxylic acid or alkene as the answer.

(iv) Explain the harmful effects of CO_2 on the environment. [2]

CO_2 is a greenhouse gas which traps heat on earth / prevents heat from escaping earth. [1]

This then leads to global warming / a rise in temperatures worldwide, which results in harmful effects such as melting of ice caps and rising sea levels (which floods low-lying coastal regions) / killing of biodiversity which are unable to adapt to the higher temperatures. [1]

Examiner's comments:

Poorly answered. Many candidates incorrectly stated that CO_2 depletes ozone layer. Some also wrongly attributed acid rain to CO_2. Out of those who answered correctly about CO_2 being a greenhouse gas which traps heat, some failed to explain explicitly how this impact the environment.

(c) A student carries out an electrolysis experiment at home using a high voltage battery as the power source, metal nails as the electrodes, and dilute sulfuric acid as the electrolyte.

The electrolysis set up is shown in Fig. 3.1.

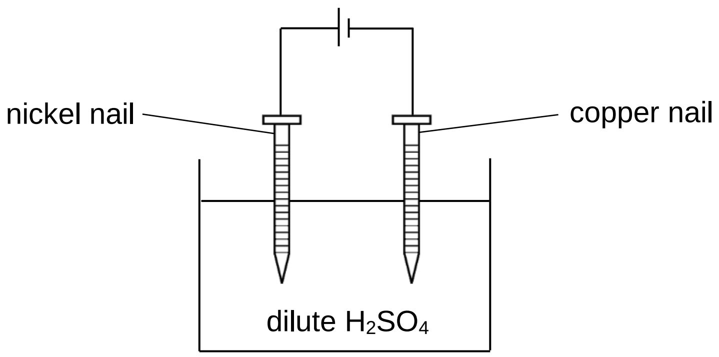


Fig. 3.1

The electrode reactions that took place are as follows.

At nickel anode: $Ni \rightarrow Ni^{2+} + 2e^-$
At copper cathode: $2H^+ + 2e^- \rightarrow H_2$

(i) With reference to relevant electrode reactions from the *Data Booklet* for **all** species present in the electrolysis set up, explain why the above electrode reactions have taken place preferentially. [4]

At nickel anode (positive terminal):

Only anions (cations do not migrate to positive anode), H_2O, and the electrode are considered.

Species must appear on RHS of Data Booklet for [O]

electrode reaction	**E^o / V**	**remarks**
$S_2O_8^{2-}$ / SO_4^{2-}	+2.01	
O_2,H^+ / H_2O	+1.23	
Ni^{2+} / Ni	-0.25	most negative, preferentially oxidised [1]

[1] citing correct 3 reactions and E^o values (penalty for extra contradictions)

At copper cathode (negative terminal):

Only cations (anions do not migrate to negative cathode) and H_2O are considered (metal electrode cannot undergo reduction).

Species must appear on LHS of Data Booklet for [R]

electrode reaction	**E^o / V**	**remarks**
H^+ / H_2	0.00	most positive, preferentially reduced [1]
H_2O / H_2,OH^-	-0.83	

[1] citing correct 2 reactions and E^o values (penalty for extra contradictions)

Examiner's comments:

Poorly answered. Many candidates listed down a laundry list of reduction potential but did not state which to consider at which electrode. Some also compared Ni and Cu and concluded Ni is oxidised because it has a more negative reduction potential compared to Cu.

(ii) Given that the high voltage battery generates an average current of 2 A, determine the amount of H_2 gas produced in one day. [2]

$Q = It = n_{e-}F$

$n_{e-} = \frac{(2\times24\times60\times60)}{96500} = 1.790$ mol [1]

$n_{H2} = ½ \times 1.79 = 0.895$ mol (3sf) [1]

Examiner's comments:

Quite well-answered. Those who lost marks thought that the n in the equation is the amount of H_2 instead of amount of electron.

(iii) The actual amount of H_2 gas produced in one day from the electrolysis reaction is lower than the value calculated in **(ii)**.

Suggest a likely reason for this. [1]

The nickel nail reacts directly with H^+ in the electrolyte ($E^\ominus_{cell} = +0.25 \text{ V} > 0$) [note that this actually produces H_2 too].

OR

The Ni^{2+} produced at the anode could have formed an insoluble ppt of $NiSO_4$, coating the nickel anode and stopping the electrolysis reaction.
(not actually true as $NiSO_4$ is very soluble, but students are not expected to know this)

Do not accept H_2SO_4 being too dilute / insufficient H^+ as H_2O will then be reduced with the same e^- to H_2 mole ratio.
Do not accept battery run flat / unsteady current as the average current was given for the one day elapsed.

Examiner's comments:

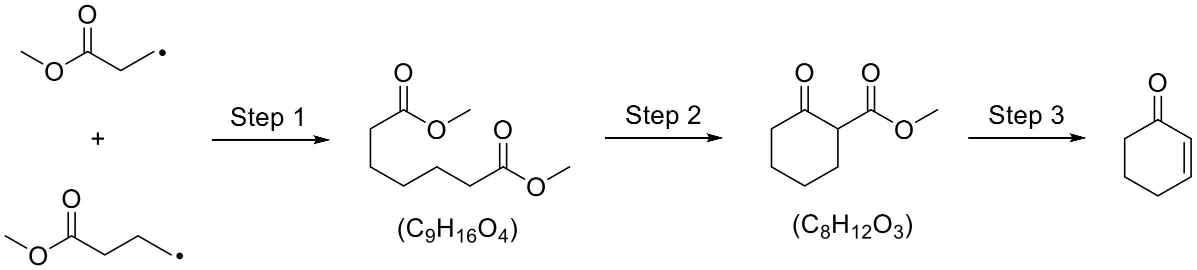
Poorly answered. Many stated that the current is not steady or that the concentration of H^+ is lower.

[Total: 18]

Section B

Answer **one** question from this section.

4 **(a)** A 3-step reaction scheme is as shown.



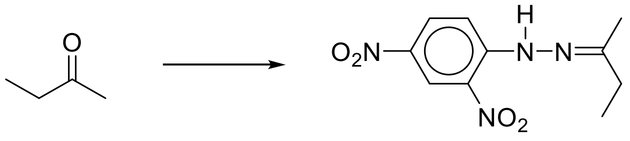
Identify the *types of reaction* that are occurring in Steps 1, 2 and 3. [3]

Step 1: (radical) addition [1] do not accept "termination" as not FRS mech
Step 2: condensation / nucleophilic (acyl) substitution [1]
Step 3: elimination [1]

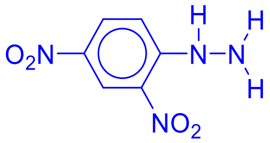
Examiners' Comments:
- A significant number of students could not identify the novel types of reaction in this question based on their definitions.
- The most common mistake made was thinking that Step 1 was "termination" (only applicable for the last stage of the FRS mechanism, which may not be how the radicals were generated) or "free radical substitution" (no substitution here, although radicals are involved).

(b) For each of the reactions below, state the reagents and conditions required:

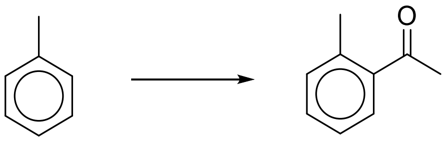
(i)



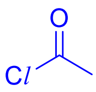
[1]

 / 2,4-dinitrophenylhydrazine, heat [1]

(ii)

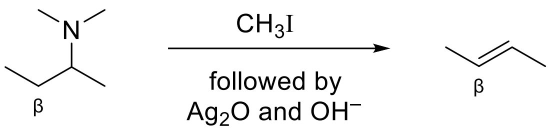


[1]

 / ethanoyl chloride, $AlCl_3$ / $FeCl_3$ catalyst, [1] r.t.

Examiners' Comments:
- Students who memorised their R&Cs were able to do well for this question.
- Common mistakes include omitting heat/warm for **(i)** and not specifying exactly which acyl chloride (RCOCl) was used for **(ii)**.

(c) The Hoffman Degradation reaction converts amines into alkenes. An example of this reaction is shown below, with the beta (β) carbon labelled.



The reaction mechanism consists of 2 steps:

- In step 1, CH_3I acts as the electrophile, reacting with the tertiary amine to form a quaternary ammonium cation and I^-.
- In step 2, a hydroxide ion then removes a proton from the beta carbon of the quaternary ammonium cation, forming a C=C bond and releasing a tertiary amine in the process.

(i) Define the term *electrophile*. [1]

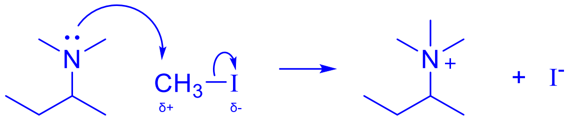
Cations or electron deficient molecules that can form a new covalent bond by accepting an electron pair. [1]

Examiners' Comments:

- A significant number of students who attempted this question missed out some keywords.

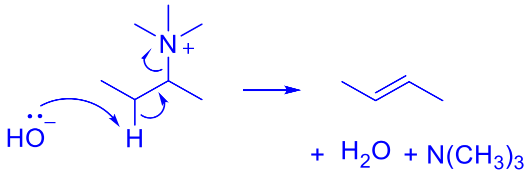
(ii) Draw the mechanism of the Hoffman Degradation reaction shown above, including relevant charges, dipoles, and curly arrows in your answers. [3]

Step 1:



lp + curly arrows + partial charges [1] TS not required
intermediate [1]

Step 2:

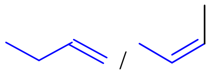


lp + curly arrows [1]

Examiners' Comments:

- Majority of students who attempted this question were unable to obtain the full 3m.

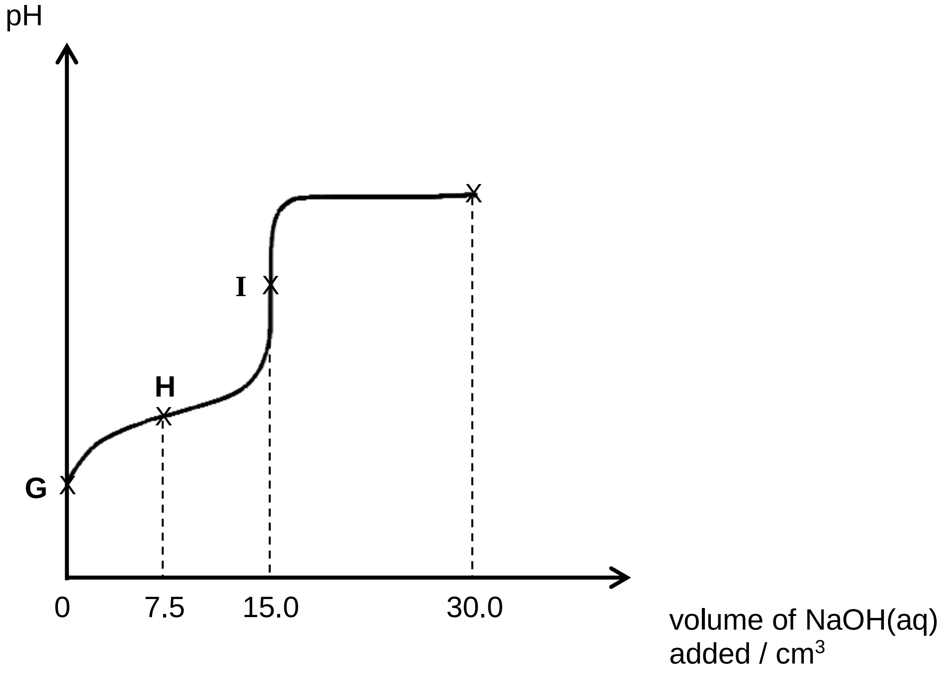
(iii) Suggest the structure of another carbon-containing product from this reaction. [1]

 [1]

Examiners' Comments:

- 2,3-diiodobutane is not possible as there is no I_2 in the reaction.

(d) 25.0 cm^3 of a 0.100 mol dm^{-3} monoprotic acid, HA, was titrated against NaOH(aq) to obtain the following pH curve. The pK_a value associated with HA is 3.75.



(i) Calculate the pH at point **G**. [1]

Initial $[H^+] = \sqrt{(0.100)(10^{-3.75})}$ = 0.004216 mol dm^{-3}
Initial pH = -lg(0.004216) = 2.38 (3sf) [1]

Examiners' Comments:

- Generally well done.
- Weaker students had the misconception that $n_{H+} = n_{HA}$ despite it being a WA.

(ii) Representing the acid as HA, identify the two species present in high concentration at point **H**. [1]

HA and A^- [1]

Examiners' Comments:

- Not as well done as expected, with many still giving answers such as H^+ (HA is a weak acid so any unreacted HA will only give low $[H^+]$) and OH^- / NaOH (which is the limiting reagent at point **H** and is fully reacted).

(iii) Hence, write two chemical equations to explain the shape of the pH curve at point **H**. [2]

$HA + OH^- \rightarrow A^- + H_2O$
$A^- + H^+ \rightarrow HA$ [1]

Since small quantities of acid or base added are reacted away, the solution is able to resist pH changes, leading to the relatively flat curve / smaller gradient at point **H**. [1]

Examiners' Comments:

- A majority of students were unable to recognise that the question was asking about the buffer region. Of the students who did, a significant number used equilibrium arrows, despite it being an acid-base reaction and not a weak acid/base dissociation.
- Almost all students also did not link the equations to an explanation of the shape at **H**.

(iv) Determine the pH at point **I**. [2]

At EP, major species present is A^-.
$n_{A^-} = n_{HA} = 0.100 \times \frac{25}{1000} = 0.0025$ mol
$[A^-]$ at EP = $\frac{0.0025}{(25+15)/1000} = 0.0625$ mol dm^{-3} [1]

Concentration / mol dm^{-3}	A^-	+	H_2O	$\rightleftharpoons$	HA	+	OH^-
Initial	0.0625		-		0		0
Change	$-x$		-		$+x$		$+x$
Equilibrium	$0.0625-x$ ≈ 0.0625		-		x		x

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$
$$\frac{1\times10^{-14}}{10^{-3.75}} = \frac{x^2}{0.0625}$$
$x = 1.874 \times 10^{-6}$ mol dm^{-3} = $[OH^-]$
pH = $14 + \lg(1.874\times10^{-6}) = 8.27$ (3sf) [1]

Examiners' Comments:

- A majority of students were still unable to solve this question, with many not being to identify that the major species present at EP is A^-, which is salt hydrolysis (of a weak base).

(e) SO_4^{2-}(aq) was added dropwise to a 1 dm^3 solution containing 0.10 mol dm^{-3} Pb^{2+}(aq) and 0.20 mol dm^{-3} Sr^{2+}(aq) ions. After some time, $PbSO_4$ and $SrSO_4$ are precipitated.

The K_{sp} values of $PbSO_4$ and $SrSO_4$ are 6.30×10^{-7} and 3.20×10^{-7} respectively.

(i) Determine the concentration of SO_4^{2-} in the solution when $PbSO_4$ just begins to precipitate. [2]

For ppt to begin to form, $Q(PbSO_4) = K_{sp}(PbSO_4)$ [1] understanding of $Q > K_{sp}$ for ppt
$[Pb^{2+}][SO_4^{2-}] = 6.30 \text{ x } 10^{-7}$
$(0.10)[SO_4^{2-}] = 6.30 \text{ x } 10^{-7}$
$[SO_4^{2-}] = 6.30 \text{ x } 10^{-6}$ mol dm^{-3} [1]

Examiners' Comments:
- Most students were able to solve this question. Some students were still confused between this "precipitation" type question (mixing of soluble ions) and "solubility" type questions (dissolving an ionic solid into a solution).

(ii) Calculate the $[Sr^{2+}]$ remaining when $PbSO_4$ just begins to precipitate. [1]

$[SO_4^{2-}] = 6.30 \text{ x } 10^{-6}$ mol dm^{-3}

Some $SrSO_4$ would have already ppt before $PbSO_4$ due to its lower solubility, so $[Sr^{2+}]$ would have changed.

For saturated $SrSO_4$ solution, $Q(SrSO_4) = K_{sp}(SrSO_4)$
$[Sr^{2+}]_{remaining}[SO_4^{2-}] = 3.20 \text{ x } 10^{-7}$
$[Sr^{2+}]_{remaining}(6.30\text{x}10^{-6}) = 3.20 \text{ x } 10^{-7}$
$[Sr^{2+}]_{remaining} = 0.05079$ mol dm^{-3} [1]

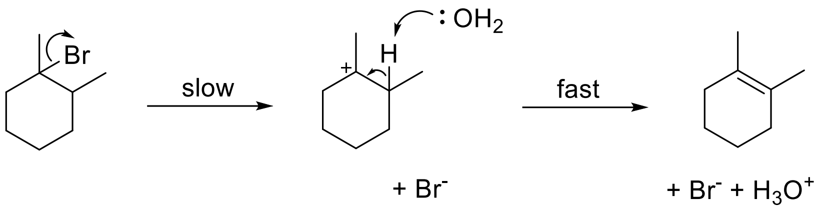
Examiners' Comments:
- This question was poorly done, with many students being confused between $[Sr^{2+}]_{remaining}$ (dissolved) and $[Sr^{2+}]_{ppt}$. By definition, whenever K_{sp} is used for calculations, the concentration value obtained has to be that dissolved in the solution.
- Some students jumped ahead of themselves and mistakenly calculated for **(iii)** in this step.

(iii) Hence, determine the mass of $SrSO_4$ precipitated when $PbSO_4$ just begins to precipitate. (M_r of $SrSO_4$ = 183.7) [1]

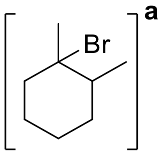
$[Sr^{2+}]_{ppt} = 0.20 – 0.05079 = 0.1492$ mol dm^{-3}
$n_{Sr2+ppt} = 0.1492$ mol
$m_{SrSO4ppt} = 0.1492 \text{ x } 183.7 = 27.4$ g (3sf) [1]

[Total: 20]

5 **(a)** Tertiary alkyl halides in ethanolic solvents can undergo elimination reactions to form alkenes. The 2-step reaction mechanism of a tertiary alkyl halide is as follows:



The generic rate equation for the above reaction is:

rate = *k*  [H_2O]^b

(where **a** and **b** are the respective orders of reactions)

(i) Determine the values of **a** and **b** based on the reaction mechanism given. [1]

a = 1, **b** = 0 [1]

(ii) Explain how you arrived at your answer in **(i)**. [1]

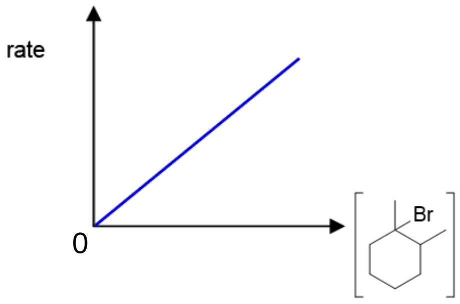
The rate-determining slow step contains 1 molecule of the tertiary alkyl bromide and no molecules of water. [1]

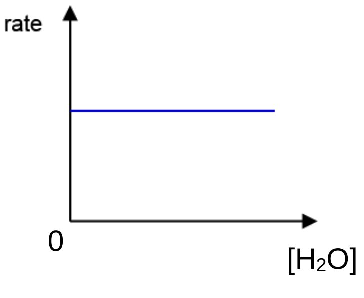
Examiners' Comments:

- The majority of students were able to draw links to the S_N1 (substitution, nucleophilic, 1st order) mechanism they have learnt before. However, this is not a N.S. mechanism and students should not say that it is one.
- Many students were also able to focus on the slow rds. However, did not specify the specific number of molecules involved in the rds.

(iii) An experiment is conducted to verify the values of **a** and **b**.

Based on your answer in **(i)**, sketch the corresponding rate-concentration graphs that would be obtained for the tertiary alkyl bromide and water. [1]



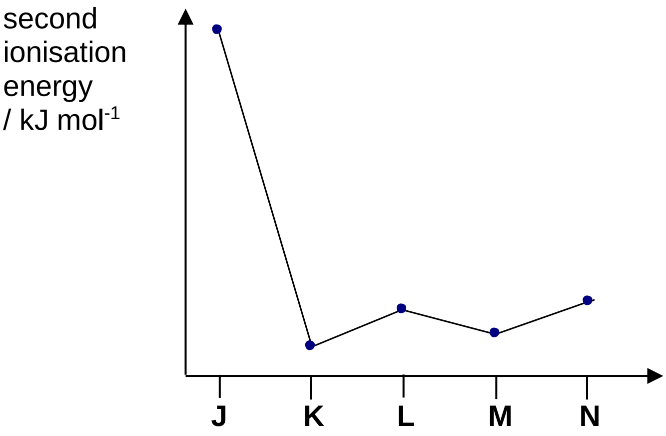


[1] ecf from (i)

Examiners' Comments:

- A significant number of students could not recall the rate-conc graph shapes.

(b) The second ionisation energies of consecutive Period 3 s-block and p-block elements **J–N** are given in the graph below.



(i) Define *second ionisation energy*. [1]

The energy required to remove 1 mol of electrons from 1 mol of singly-charged gaseous cations to form 1 mol of doubly-charged gaseous cations. [1]

Examiners' Comments:

- A significant number of students missed out on one or more keywords.

(ii) Identify element **L** and write the equation to describe its second ionisation energy. [1]

L is A*l*.

$Al^{+}(g) \rightarrow Al^{2+}(g) + e^{-}$ [1] no double penalty from **(i)** for state symbols

Examiners' Comments:

- A large majority of students could identify the element, but missed out the crucial state symbols of the chemical equation.

(iii) By considering the electronic configurations of **J**$^{+}$ and **K**$^{+}$, explain the drastic decrease in second ionisation energy between element **J** and **K**. [2]

J^{+}: $1s^2\ 2s^2\ 2p^6$

K^{+}: $1s^2\ 2s^2\ 2p^6\ 3s^1$ [1] no ecf from **(ii)**

The valence ($3s^1$) electron of **K**$^{+}$ experiences a stronger shielding effect due to it having an additional filled inner shell of electrons. Attraction between the nucleus and the valence electron is lower and less energy is required to remove the electron. [1]

Examiners' Comments:

- A significant number of students missed out on one or more keywords.

(c) *Hess' Law* is frequently used to determine the enthalpy change of reactions that cannot be carried out simply via experiment.

(i) Define *Hess' Law*. [1]

The enthalpy change for a reaction depends only on the initial and final states of the system, and is independent of the reaction pathway taken. [1]

Examiners' Comments:

- Majority of students could not recall this definition.

(ii) The *enthalpy change of hydration* of an ion is defined as the energy released when 1 mol of the gaseous ion dissolves in an infinite volume of water.

Suggest why an "infinite volume of water" is required to determine the enthalpy change of hydration. [1]

There must be sufficient water molecules to fully form ion-dipole interactions with all the 1 mol of gaseous ions such that there are no longer any interactions between the ions themselves. [1]

Examiners' Comments:

- Most students were able to answer this question, although the phrasing could be improved.

(iii) Suggest why the standard enthalpy change of hydration of an ion is difficult to determine with an experiment. [1]

It is difficult/dangerous/expensive to handle/produce free gaseous ions. **OR**
A complex calorimeter will be required to perform the experiment. [1]

(iv) To determine the standard enthalpy change of solution of solid Li*Cl*, an experiment was conducted by dissolving 1.00 g of the solid into 20.0 cm^3 of water (assume "infinite"). The temperature of the solution increased from 298 K to 308 K.

Calculate a value for the standard enthalpy change of solution of solid Li*Cl*. [2]

Q = mcΔT = (20.0)(4.18)(308-298) = 836 J [1]

$\Delta H^{\ominus}_{sol}(\text{Li}Cl) = -\frac{Q}{n_{LiCl}} = -\frac{836/1000}{1.00\ /\ (6.9+35.5)} =$ -35.4 kJ mol^{-1} (3sf) [1]

Examiners' Comments:

- Generally well done. A significant number of students still included the mass of the solid.

(v) The lattice energy of $\mathrm{LiC}l$ is –830 kJ $\mathrm{mol^{-1}}$.

Draw an energy cycle to determine a value for the sum of standard enthalpy changes of hydration of $\mathrm{Li^+}$ and $\mathrm{C}l^-$. [3]

$$\begin{tikzcd}
\mathrm{LiC}l\mathrm{(s)} \arrow[rr, "\Delta H^\ominus_{\mathrm{sol}}(\mathrm{LiC}l) = -35.4"] \arrow[dr, swap, "\begin{matrix}\text{-L.E.}\\ = +830\end{matrix}"] & & \mathrm{Li^+(aq)} + \mathrm{C}l^-\mathrm{(aq)} \\
& \mathrm{Li^+(g)} + \mathrm{C}l^-\mathrm{(g)} \arrow[ur, swap, "\Delta H^\ominus_{\mathrm{hyd}}(\mathrm{Li^+}) + \Delta H^\ominus_{\mathrm{hyd}}(\mathrm{C}l^-)"] &
\end{tikzcd}$$

[1] species + closed cycle [1] values + arrow direction

$\Delta H^\ominus_{\mathrm{hyd}}(\mathrm{Li^+}) + \Delta H^\ominus_{\mathrm{hyd}}(\mathrm{C}l^-) = -830 + (-35.4) = -865$ kJ $\mathrm{mol^{-1}}$ (3sf) [1]

Examiners' Comments:

- An unexpectedly large number of students could not recall this common energy cycle.

(d) Magnesium reacts with steam but not cold water, while calcium reacts even in cold water.

(i) Without reference to any data values, explain the difference in reactivities of magnesium and calcium with water. [2]

$\mathrm{M + 2H_2O \rightarrow M(OH)_2 + H_2}$ [1]
equation not required, mark for demonstrating understanding that $\mathrm{M^{2+}}$ is product

Down Group 2, both nuclear charge and shielding increases, so effective nuclear charge does not change significantly. Number of filled principal quantum shells increases and valence electrons are further from the nucleus, leading to weaker attraction between the nucleus and electrons. Less energy is required to remove the valence electrons to form $\mathrm{Ca^{2+}}$ than $\mathrm{Mg^{2+}}$, thus Ca is more reactive. [1]

Examiners' Comments:

- Generally well done, but a significant number of students missed out on one or more keywords.

The reactivities of magnesium sulfate and calcium sulfate can be compared by determining their thermal decomposition temperatures. In this reaction, O_2, SO_2 and SO_3 gases are evolved.

(ii) It is known that the ratio of O_2:SO_2 gas evolved is 1:2.

Write a balanced chemical equation for the thermal decomposition of magnesium sulfate. [1]

$3MgSO_4 \rightarrow 3MgO + O_2 + 2SO_2 + SO_3$ [1]

Examiners' Comments:

- Many students missed out info from the question stem that SO_3 was also a product.

(iii) Explain whether magnesium sulfate or calcium sulfate has a higher thermal decomposition temperature. [2]

$CaSO_4$ has the higher thermal decomposition temperature. [1]

Ca^{2+} has a larger ionic radius than Mg^{2+} and thus a lower charge density, polarising the SO_4^{2-} electron cloud less. The S–O bond is weakened to a smaller extent and requires more energy to break. [1]

Examiners' Comments:

- A significant number of students were still imprecise in their answers e.g. "Ca has larger ionic radius than Mg" / "calcium has higher atomic radius than magnesium".
- Some students have the misconception that the bond being weakened is the ionic bond (or even worse, mentioning bond energy, which is for covalent bonds) between the cation and anion.

[Total: 20]