EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2021
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME					
CIVICS GROUP	2	0	–		

INDEX NUMBER		

CHEMISTRY

9729/03

Paper 3 Free Response

22 September 2021
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

Section A
Answer **all** the questions

Section B
Answer **one** question.

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

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

For Examiner's Use	
Paper 3	
Section A	
1	/20
2	/20
3	/20
Section B	
4	/20
5	/20
Total	**/80**

This document consists of **32** printed pages.

Section A

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

1 Halogens are powerful oxidising agents, and the oxidising power of halogens may be understood via the energy cycle in Fig. 1.1.

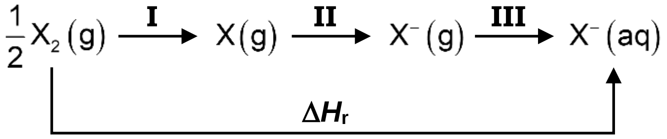


Fig. 1.1

The corresponding values of some of the energy terms are given in Table 1.1.

Table 1.1

	energy term **I** (kJ mol^{-1})	energy term **II** (kJ mol^{-1})	energy term **III** (kJ mol^{-1})
F	+79	–328	–506
Cl	+121	–349	–364
Br	+112	–324	–335
I	+107	–295	–293

(a) **(i)** Name the three energy terms, **I**, **II** and **III**. [2]

(ii) Explain why energy term **I** becomes less endothermic moving down the group from chlorine to iodine. [1]

(iii) Explain the exceptionally low value for energy term **I** of fluorine, in contrast to that of the remainder of the halogens. [1]

(iv) Explain why energy term **II** becomes less exothermic moving down the group from chlorine to iodine. [1]

(v) Using values from the *Data Booklet*, account for the difference in the value of energy term **III**. [2]

(i) **I:** enthalpy change of atomisation **II:** first electron affinity

III: enthalpy change of hydration

(ii) As the valence orbital used in bonding is **more diffused** moving down the group from chlorine to iodine, the **overlap of orbitals is less effective** (moving down the group), leading to less energy being required to break the bond in the diatomic molecule.

(iii) Due to the small atomic size of fluorine (as compared to other halogens), there is **high inter-electron repulsion between the non-bonding electrons** of the 2p-orbitals in the fluorine molecule. This leads to significantly lower bond dissociation energy.

(iv) Since the electron to be gained by the atom is **increasingly further away from the nucleus** and **experiences a decrease in electrostatic forces of attraction between the nucleus and incoming electron**, the first electron affinity becomes less exothermic.

(v) The ionic radii of F^- is **significantly smaller at 0.136 nm,** while the ionic radii of the other halogens are more comparable, with **Cl^- being 0.181 nm**, Br^- being 0.195 nm and I^- being 0.216 nm. As the halide ions have the same charge, the F^- ion has a **significantly higher charge density** due to its significantly smaller ionic radius, and hence has stronger ion-dipole interaction with the surrounding water molecules. Therefore, its hydration energy is significantly more exothermic.

Marker's Comments:

(a)(i)

- The naming of the three energy terms was reasonably well-attempted.
- Common errors include:
  - For energy term **I**: Confusion between enthalpy change of atomisation and that of bond dissociation energy (the value of the two terms are not equivalent, and in fact $\Delta H_{atom} = \frac{1}{2}(\text{Bond Energy of X-X})$.
  - For energy term **II**: Not being specific to the "electron affinity". The term "first" was important in mentioning the electron affinity, as the sign and value of different electron affinity can be different. In the case of halogens, first electron affinity was exothermic, while second electron affinity can be endothermic due to the negatively-charged anion repelling the incoming electron.
  - For energy term **III**: There was a slight confusion between enthalpy of solution and enthalpy of hydration. The enthalpy of solution referred to the dissolution of an ionic substance, and will include overcoming the lattice energy.

(a)(ii)

- Candidates were expected to make specific mention that the orbitals used in bonding for larger halogen atoms (down the group) were **more diffused**, and explain how the more **diffused orbitals led to less effective orbital overlap** when forming a bond.

(a)(iii)

- This was generally poorly attempted. Most candidates did not realise that the **very small atomic size of fluorine** caused high inter-electron repulsion between the non-bonding electrons, which in turn weakened the covalent bond formed.

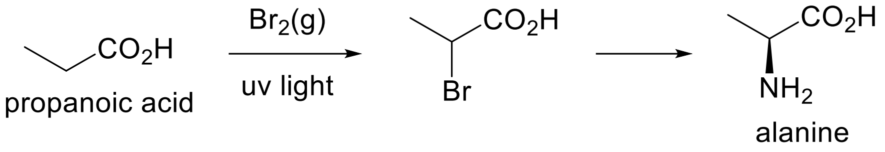
(a)(iv)

- Many candidates seem to be confused and used terms like "more endothermic" when they meant "less exothermic" instead. While it might seem that the two terms were equivalent in meaning, the former was not applicable in a situation where the enthalpy change was always expected to be negative, which is the case for halogens and in the given data. Hence it would only be more appropriate to discuss the magnitude of energy released (how exothermic the reaction was).
- Some students erroneously stated that effective nuclear charge, Z_{eff}, decreased down the group. However, the increase in shielding effects only approximately cancelled out the increase in nuclear charge (and if anything, there seems to be an increase in Z_{eff} instead). Hence, the less exothermic electron affinity down the group (which was given in the data in the table) should only be explained via the decrease in electrostatic forces of attraction (which was due to increasing distance from the nucleus).

(a)(v)

- A handful of candidates were confused and talked about hydrogen halides instead of hydration energy, and continued to discuss bond strength when there was no bond to be broken.
- Some candidates erroneously talked about lattice energy, which was puzzling. There were no oppositely charged ions in this question.
- There were also candidates who quoted atomic radius instead of ionic radius. Candidates are hence reminded to be more meticulous in the reading of the question.

Alanine, which is found in a variety of food sources, is an amino acid that can be derived from propanoic acid. One of the methods to obtain alanine from propanoic acid is illustrated in the pathway below.



(b) **(i)** Outline the mechanism for the formation of 2-bromopropanoic acid via the reaction between propanoic acid and bromine gas. [3]

(ii) In the reaction between propanoic acid and bromine gas, the relative rate of abstraction of primary, secondary and tertiary hydrogen is in the ratio of 2 : 3 : 6.

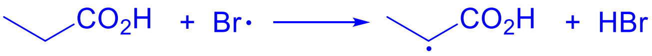
Draw the structures of all mono-brominated products formed, including stereoisomers if any, and state their relative proportion. [3]

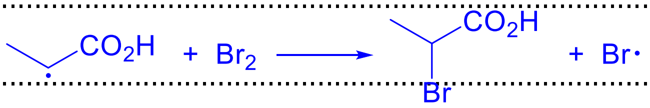
(iii) With reference to **(b)(i)** and using relevant values from the *Data Booklet*, explain why free radical substitution is rarely performed to produce 2-iodopropanoic acid. [2]

(iv) State the reagents and conditions for the formation of alanine, $CH_3CH(NH_2)CO_2H$, from 2-bromopropanoic acid. [1]

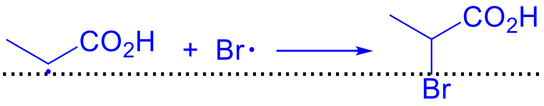
(i) Initiation

Propagation

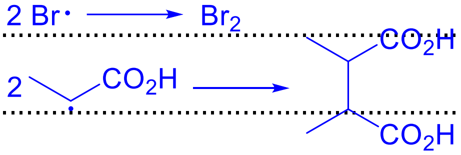




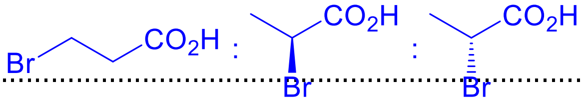
Termination



$2\,Br\cdot \longrightarrow Br_2$



(ii)



3 × 2 : 1 × 3 : 1 × 3

6 : 3 : 3

2 : 1 : 1

(iii) As the **bond enthalpies of H–I and C–H are +299 kJ mol^{-1} and +410 kJ mol^{-1} respectively**, the overall enthalpy change for **the first step of the propagation stage is highly endothermic** at +111 kJ mol^{-1} and likely non-energetically feasible.

(iv) **(excess) ethanolic NH_3 and heat** (in sealed tube)

Marker's Comments:

(b)(i)

- Most candidates were able to identify the mechanism as Free Radical Substitution (FRS).
- For the propagation stage, it was critical to **show the regeneration of bromine radicals**. This regeneration of bromine radicals would explain why only a few pulses of *uv* light were required in the initiation stage. As long as the bromine radicals were regenerated, the **overall reaction** between **bromine molecules** (not the bromine radical) **and propanoic acid molecules** would continue. The role of the bromine radical was hence to allow for the bromination.
- Termination occurs as the radicals combine with other radicals to form products (especially when the [radicals] is much greater than the concentration initial reactants). Hence, the reactions listed in this stage must show the consumption of the possible radicals formed. It would thus be insufficient to show only the reaction between a single type of radical.
- For the drawing of arrows to show movement of electrons, it was important to use half arrows to denote the movement of a single electron. A full arrow would indicate the movement of a pair of electrons instead.

(b)(ii)

- The terms primary, secondary and tertiary referred to the environment that the hydrogen atom was found in. In propanoic acid, there were only primary and secondary hydrogens that could be substituted via FRS. The hydrogen in the carboxylic acid functional group will not undergo any reaction, and there would be no acyl bromide formed.
- The relative proportion for the product formed must take into account both the ease of abstraction of hydrogen, and the number of hydrogens available.
- Most students were unable to understand that only **one of the secondary hydrogens needed to be replaced** for the formation of each configuration of the chiral compound obtained, and were hence unable to calculate the correct ratio of product formation.

(b)(iii)

- Although the initiation stage reaction was endothermic, it was not a consideration for the feasibility of the reaction. While the homolytic cleavage of the halogen molecule to produce radicals was endothermic, the energy was provided in the form of *uv* radiation and should not be factored into consideration.
- Calculation should not be made using both steps in the propagation stage. **As long as the first reaction to produce HI does not occur, neither should the second reaction.** Hence, discussion should only be made based on the very first step.

(b)(iv)

- It was important to note that ethanolic NH_3 was used. That meant that NH_3 could be written as NH_3(alc) with some benefit of doubt, rather than (g) or (aq).
- A number of puzzling answers wrote heat in sealed tube with reflux. The examiner did not think such a setup could exist. Hence, students are reminded to revise the reaction conditions diligently.

A more efficient method of synthesising 2-bromopropanoic acid is the Hell-Volhard-Zelinsky (HVZ reaction), shown in Fig 1.2.

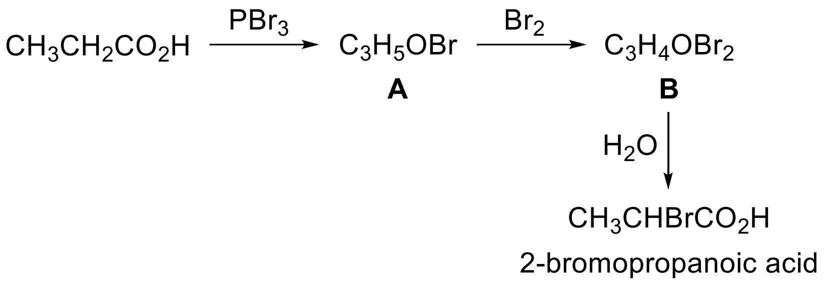
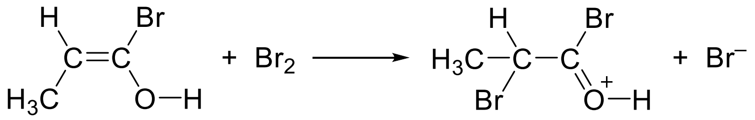


Fig 1.2

(c) **(i)** Draw the structures of **A** and **B**. [2]

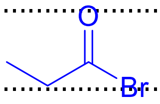
(ii) **A** can undergo isomerisation to give an enol **C** which reacts with bromine to form **B** via a mechanism similar to the electrophilic addition of alkenes, as shown below. Re-draw the step and show the movement of electrons involved. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.



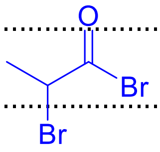
enol **C**

[2]

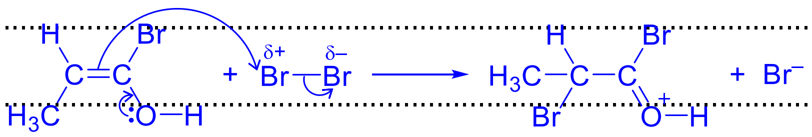
(i) **A** is



B is



(ii)



[Total: 20]

Marker's Comments:

(c)(i)

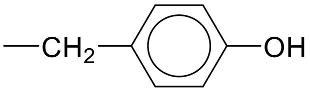
- This question was generally well-attempted, with majority of the candidates being awarded full credit. Some of the structures were poorly drawn (with the wrong bond angles that nearly looked like a straight line) and could be hard to decipher.
- Some students might had misread the question and drew an enol for structure **A**. While Structure **A** could *undergo isomerisation* to give an enol, structure **A** was not the enol.

(b)(ii)

- Students are reminded to **indicate partial charges and lone pairs clearly**. Students are also reminded that arrows should be drawn such that the **arrows reflect movement of electrons from a "source"**, which could either be a bond or a lone pair (instead of from a partially positively charged atom, or a positive charge).
- Students are also reminded to read the question closely. The question had indicated that the movement of electrons was done in **one step**, and hence there was no need to split the mechanism into two steps.

2 Amino acids are the building blocks of proteins. Some examples of amino acids are given in Table 2.1.

Table 2.1

amino acid	formula of side chain (R in $RCH(NH_2)CO_2H$)
glutamic acid	$-CH_2CH_2CO_2H$
lysine	$-CH_2CH_2CH_2CH_2NH_2$
tyrosine	

(a) The three-dimensional form of a local segment of a protein, known as the α-helix, is shown in Fig. 2.1.

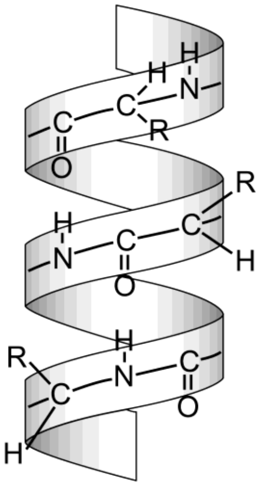


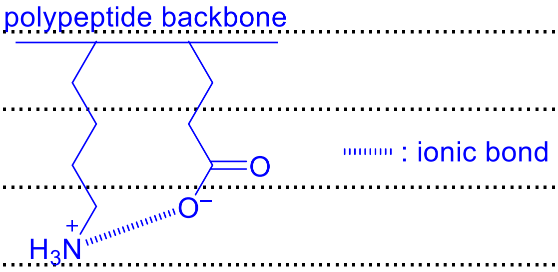
Fig. 2.1

(i) State the type of interaction between the peptide linkages in the α-helix. [1]

(ii) Describe briefly the side chain interaction between glutamic acid and lysine, illustrating your answer with a suitable diagram. [1]

(i) hydrogen bond

(ii) ionic bonds (accept hydrogen bonds)



(a) Marker's Comments:

(i) & (ii) Generally well-attempted, although there were students who did not understand the meaning of "interaction", and discussed about the formation of peptide bonds, or the neutralisation reaction between the basic and acidic groups.

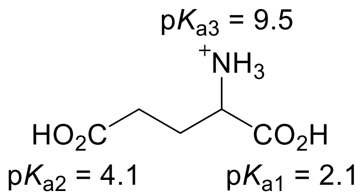
Common mistake for (ii):

- Most students did not realise that the $-NH_2$ and $-COOH$ groups will be ionised to form $-NH_3^+$ and $-COO^-$ at physiological pH. While BOD was given for this assessment, students need to remember that they should reflect the acidic and basic groups of amino acids in their ionised form.

(b) Amino acids are soluble in both dilute acids and dilute alkalis due to the ability to exist as zwitterions.

(i) Explain a physical property of amino acids that arise due to the formation of zwitterions. [1]

(ii) There are three pK_a values associated with glutamic acid: 2.1, 4.1 and 9.5.

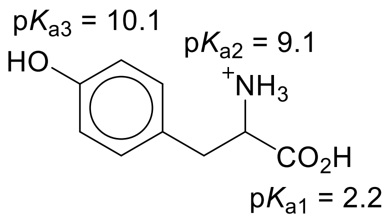


Make use of these pK_a values to suggest

I. the structure of the major species present in a solution of glutamic acid at pH 6.0, and

II. a pH at which the predominant species of glutamic acid is a zwitterion. [2]

(iii) There are three pK_a values associated with tyrosine: 2.2, 9.1 and 10.1.

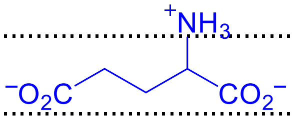


Explain the difference between the pK_{a1} and the pK_{a3} of tyrosine. [2]

(i) **High melting point** due to a large amount of energy needed to **overcome strong electrostatic forces of attraction** between zwitterions ***or***

Soluble in water due to formation of favourable **ion-dipole** interactions

(ii) **I.**



II. **pH 3.1**

(iii) Acid strength: carboxylic acid > phenol

The negative charge on oxygen of the carboxylate anion is **delocalised over** the **two highly electronegative oxygen** atoms resulting in two equivalent resonance structures, while the negative charge on oxygen of the phenoxide anion is **delocalised into the benzene ring**.

The **stabilisation** of the phenoxide **is not as great as** that in the carboxylate ion in which the negative charge is delocalised over 2 highly electronegative O atoms. Hence, the carboxylate anion is resonance-stabilised **to a larger extent** than the phenoxide ion, rendering the carboxylic acid more acidic than the phenol.

(b) Marker's Comments:

(i) Some students discussed the zwitterion being able to act as a buffer. This was not accepted as it is not a property that was possible only because of the formation of a zwitterion.

(ii) Well attempted, most students were awarded full credit for this part.

(iii)

- Many students did not realise that the key reason for the difference was due to the difference in the functional groups involved, and instead chose to discuss the difference in terms of the less significant factor of the distance from the $–NH_3^+$ group.
- Some students who compared the functional groups involved were not precise in the use of the terms e.g. "p orbital is dispersed", "electrons are spread out".
- A number of students wrongly attributed the difference to a **full** delocalisation of the lone pair over the oxygen atoms vs. a **partial** delocalisation of the lone pair into the benzene ring. This is incorrect. The difference is due to the fact that the lone pair is delocalised over **electronegative** oxygen atoms vs. the benzene ring.

(c) Compound **E**, $C_{10}H_{15}O_3N$, is also soluble in both dilute acids and dilute alkalis. One mole of **E** undergoes complete neutralisation with 2 moles of NaOH. However, no gas is evolved when sodium carbonate is added to **E**.

Compound **E** reacts with hot acidified potassium dichromate (VI) to form **F**, which gives a positive result with 2,4-DNPH but not with Tollens' reagent. Upon heating **E** with Al_2O_3, compound **G** is formed. On heating **G** with acidified potassium manganate(VII), the products formed are **H** and **I**, C_3H_6O.

(i) Deduce the structures for each lettered compound, **E** to **I**, and explain the chemistry involved. [10]

(ii) Compound **G** undergoes catalytic hydrogenation when heated with hydrogen gas in the presence of nickel. Describe how nickel acts as a catalyst in this reaction. [3]

(i)

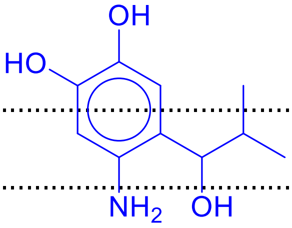
- **E** has more than 6 C atoms and C:H ratio is ~ 1:1 ⇒ **E** contains **benzene**
- **E** undergoes **acid-base reaction** with 2 mole equivalent of NaOH

  ⇒ **E** contains **2 phenol or carboxylic acid** groups (or 1 of each)
- E does not undergo **acid-base reaction** with Na_2CO_3

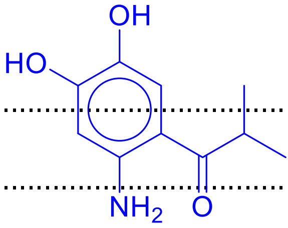
  ⇒ **E** does not contain carboxylic acid, hence it contains **2 phenol OH** groups.
- **F** undergoes **condensation** with 2,4-DNPH ⇒ **F** is a **ketone**
- **F** does not undergo **oxidation** with Tollens' ⇒ **F** is a **ketone**
- **E** undergoes **oxidation** with acidified potassium dichromate(VI) to form ketone **F** ⇒ **E** contains a **secondary alcohol**
- **E** undergoes **elimination** with Al_2O_3, heat to form **G**.

  ⇒ **E** is confirmed to be an alcohol.

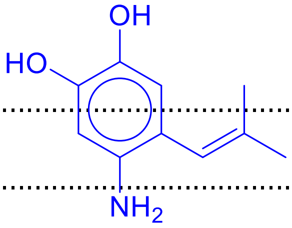
  ⇒ **G** is an **alkene**
- **G** undergoes **oxidation** and acid-base reaction with acidified potassium manganate(VII) to form **H** and **I** ⇒ **G** is confirmed to be an **alkene**.



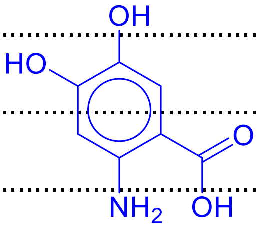
E



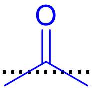
F



G



H



I

(ii) ✓ Nickel provides active sites whereby the reactant molecules may be **physically adsorbed**.

✓ This **increases the local concentration of reactants**

✓ And **weakens the covalent bonds** thus lowering the activation energy for reaction to occur.

✓ The adsorbed product molecules break free from the catalyst surface and leave the surface via **desorption**.

These processes allow nickel to act as a heterogeneous catalyst in this reaction and thus the reaction proceeds at a faster rate via an alternative pathway.

(c) Marker's Comments:

(i) Not well attempted. Many candidates misread the question and assumed that both **H** and **I** have the same molecular formula.

Common conceptual errors included:

- Mistaking that alcohols undergo neutralisation with NaOH
- Wrongly assuming that phenols give CO_2 with carbonates.
- Mistaking the reaction of 2,4-DNPH with carbonyl compounds to be that of oxidation instead of condensation
- Failure to recognise the reaction of alcohol with aluminium oxide
- Mistaking the oxidation using $K_2Cr_2O_7$ to be oxidative cleavage of alkenes.
- Writing **I**, the product of oxidative cleavage using $KMnO_4$, as an aldehyde, without realising that the aldehyde would oxidise further to a carboxylic acid.

There were also candidates who lost credit due to missing points or ambiguous terms:

- Failure to mention about the types of reactions
- Failure to specify the type of alcohol e.g. secondary alcohol
- Using incomplete structures to refer to functional groups e.g. –OH and C=O. Note that the –OH group is present in alcohols, phenols and carboxylic acids; hence, if candidates are referring to alcohols, they should specify it as "alcohol". Similarly, the C=O bond is present not just in carbonyl compounds but also in carboxylic acids and their derivatives.

(ii)

- Although many candidates scored partial credit, not many candidates scored full credit, despite the straightforward nature of the question.
- Candidates are advised to use proper scientific terms e.g. adsorption, increase in concentration (not just "closer proximity"), desorption.

[Total: 20]

3 Carbides are compounds that are formed by a metal or a semi-metal and carbon, which possesses the higher electronegativity. Depending upon the difference in the electronegativities (DEN) between carbon and the metal/semi-metal, several classes of carbides are usually distinguished, among which are the

- salt-like carbides with high DEN and ionic properties, *e.g.* Na_2C_2, Mg_2C_3, Al_4C_3. and
- covalent carbides with small DEN and strong covalent bonding, *e.g.* SiC, B_4C.

Across period 3, the carbides formed by the elements are:

group 1	group 2	group 13	group 14
Na_2C_2	Mg_2C MgC_2 Mg_2C_3	Al_4C_3	SiC

The class of salt-like carbides is further divided into three groups:

- methanides with C^{4-} anions, *e.g.* Mg_2C and Al_4C_3
- acetylides with C_2^{2-} anions, *e.g.* Na_2C_2 and MgC_2
- allylenides with C_3^{4-} anions, *e.g.* Mg_2C_3

(a) Explain why the DEN decreases across period 3, from Na_2C_2 to SiC. [1]

The DEN decreases across the period, (resulting in a change from salt-like to covalent carbides) since the **atomic radius** of the elements **decreases** from Na to Si, resulting in **stronger attraction** of the nucleus **for the bonding electrons**.

Marker's Comments:

- Generally well-attempted.
- Most candidates who obtain the mark discuss about effective nuclear charge increasing from Na to Si since nuclear charge increases while shielding effect is relatively constant, hence the electronegativity increases from Na to Si.
- Some candidates also simply quoted that electronegativity increases from Na to Si, without explaining why.
- Some candidates erroneously thought that DEN decreases means that the electronegativity of the period 3 elements decreases across the period too.

(b) **(i)** Draw the dot-and-cross diagram of the C_2^{2-} anion and state the hybridisation of the carbon atoms. [2]

(ii) Aluminium oxide, Al_2O_3, is predominantly ionic, but aluminium chloride, $AlCl_3$, is predominantly covalent.

Use data from the *Data Booklet* to suggest why the ionic nature of the bonding in Al_4C_3 is unexpected. [2]

(i)

sp hybridisation

(ii) Anionic radius of C^{4-} is **0.260 nm,** which is **much larger** than **0.181 nm of Cl^-**. Electron cloud of C^{4-} should be **more polarisable** than that of Cl^- and hence lead to **greater covalent character** in the bond between Al^{3+} and C^{4-}. Thus, the ionic nature of the bonding in Al_4C_3 is unexpected.

Marker's Comments:

(b)(i)

- The dot-and-cross diagram was moderately well-attempted.
- Common errors include:
  - Invoking dative bond from one C to the other C. Both being identical carbon atoms, one would expect the two carbon atoms to be similarly bonded, forming a triple bond using 3 valence electrons each, and attaining a negative charge by accepting one electron each.
  - Forgetting to put in the square bracket with 2– charge
  - Failure to differentiate the electrons of the two carbon atoms using different symbols
- The hybridisation was generally well-attempted. Error-carried-forward mark is awarded if the dot-and-cross diagram is wrong, but a *reasonable* hybridisation can be deduced.

(b)(ii)

- Poorly attempted.
- Some candidates failed to realise that Al_4C_3 is $\left(Al^{3+}\right)_4\left(C^{4-}\right)_3$, although the anion is given in the question stem, and instead came up with other anions, e.g. C_3^{4-}

- Most candidates fail to appreciate the given information that $AlCl_3$ is covalent, and use this in their answer. The Al^{3+} being the common cation in all the compounds, does not really make a difference, except noting that it has high charge density due to the high charge and small cationic radius.
- Candidates are expected to compare the *ionic* radius of Cl^- (0.181 nm) and C^{4-} (0.260 nm) from the *Data Booklet*, and conclude that C^{4-} is expected to be more *polarisable* than Cl^-, and hence the $Al–C$ bond should be more covalent than the $Al–Cl$ bond, when in reality, it is in fact more ionic which is unexpected.
- Common errors include
  - Comparing the ionic radius of Al^{3+} (0.050 nm) and that of C^{4-} (0.260 nm), and concluded that because the C^{4-} is larger than Al^{3+}, hence the electron cloud of C^{4-} will be polarised.
  - Simply stating that the C^{4-} anion is large without making any comparison to Cl^-.

(c) The salt-like carbides undergo complete hydrolysis in water as the anions are very strong Brønsted-Lowry bases.

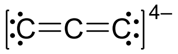
The methanides, Mg_2C and Al_4C_3, both undergo hydrolysis in water to yield methane.

(i) Suggest a balanced equation, and state the observations for the complete hydrolysis of *solid* Al_4C_3 in water. [2]

(ii) Mg_2C is hydrolysed immediately by moisture in the air, while Al_4C_3 is hydrolysed over a few hours in water. Suggest a likely reason for the differences in rate of hydrolysis. [2]

The hydrolysis of the allylenide, Mg_2C_3, in dilute sulfuric acid yields two organic hydrocarbons, of which one is propyne, $HC{\equiv}CCH_3$.

(iii) The structure of the C_3^{4-} anion is shown.



$$[:\!C{=}C{=}C\!:]^{4-}$$

Suggest the mechanism for the formation of propyne from the hydrolysis of Mg_2C_3, assuming that dilute sulfuric acid produces proton, H^+, as the reacting species. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

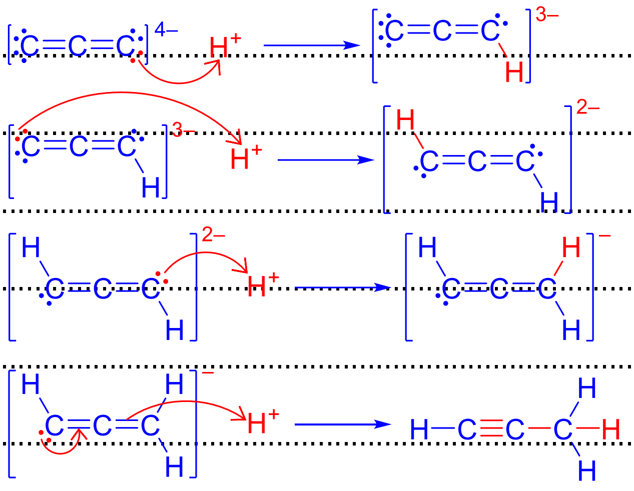
(i) $Al_4C_3(s) + 12H_2O(l) \rightarrow 3CH_4(g) + 4Al(OH)_3(s)$ or

$Al_4C_3(s) + 6H_2O(l) \rightarrow 3CH_4(g) + 2Al_2O_3(s)$

A **white precipitate/residue** of $Al(OH)_3$/Al_2O_3 and **effervescence** of a **colourless gas** (CH_4).

(ii) Due to the **lower charge** and **larger ionic radius** of Mg^{2+}, Mg^{2+} has a **lower charge density** compared to Al^{3+}. The bonding in Mg_2C has **higher ionic character** than that in Al_4C_3, where the **C^{4-} ion reacts rapidly** with water.

(iii)



Marker's Comments:

(c)(i)

- Generally poorly well-attempted.
- Many candidates either did not read that methane is produced, or gave methane as CH_3 instead of CH_4!!
- There is a difference from the "reaction" of $AlCl_3$ with water in that Cl^- is a very very weak base and so will not undergo hydrolysis, whereas the C^{4-} undergoes hydrolysis in this case, similar to O^{2-}, by abstracting H^+ from H_2O.
- The fact for methane, CH_4, is produced from C^{4-} further suggest that the C^{4-} abstract H^+ from H_2O, hence giving OH^- which will combine with Al^{3+} to give $Al(OH)_3$, which can then give Al_2O_3.
- Many students did not read the question carefully and left out the observation.
- Common errors include
  - Not knowing that methane is a gas. (Some thought incorrectly that methane is a pungent gas, although there is no penalty)
  - Thinking that $Al(OH)_3$ or Al_2O_3 is soluble in water (giving an (aq) state symbols in their equation, and not mentioning about it being a (white) solid)

(c)(ii)

- Generally poorly well-attempted.
- Despite the question already mentioning that Mg_2C and Al_4C_3 are salt-like ionic carbides that contains the C^{4-} anion, there are a number of candidates whose answer indicated otherwise.
- Many candidates argued in terms of the lattice energy of Al_4C_3 being more exothermic than that of Mg_2C, and hence more energy is needed to overcome the stronger ionic bonds in Al_4C_3. However, this also means that the $Al(OH)_3$ product will also have a more

exothermic lattice energy compared to $Mg(OH)_2$, hence the hydrolysis of $A\ell_4C_3$ could potentially be more exothermic. Nevertheless, benefit-of-the-doubt is awarded for candidates who answered based on lattice energy. However, the discussion of lattice energy should still make reference to **both** the charge and ionic radius of $A\ell^{3+}$ and Mg^{2+}. Also many students used terms like “lattice energy of $A\ell_4C_3$ is higher than that of Mg_2C”. Either they should refer to the *magnitude* of the lattice energy or use terms like “more exothermic” instead.

- The point here is really that the reaction of the salt-like methanides involve the hydrolysis of the anion, C^{4-}. So in the more ionic methanides like Mg_2C, where the bonding is more ionic, the C^{4-} ions are more “available”, compared to $A\ell_4C_3$ where the covalent character in the bond means that the C^{4-} ion is less “available”.

(c)(ii)

- Generally poorly well-attempted.
- Almost all candidates lump the protonation steps together without realising the implication on the kinetics. Each step in a mechanism is supposed to be an elementary reaction. Drawing four arrows from the C_2^{2-} ion to 4 H^+ is saying that the C_2^{2-} ion collide with 4 H^+ simultaneously in a 4th order reaction, with the correct energy and orientation for reaction to take place, the chances of which is infinitesimally low.
- Some candidates also fail to show and account for the negative charges on the C_2^{2-} ion and the intermediate anions.

(d) MgC_2 was first prepared in 1910 by the reaction of magnesium and ethyne, C_2H_2. At 770 K, MgC_2 starts to transform into Mg_2C_3:

$$2MgC_2(s) \xrightarrow{770\ K} Mg_2C_3(s) + C(s) \qquad \Delta H_r^\ominus$$

The standard enthalpy change of formation of MgC_2 and Mg_2C_3 are +87.9 kJ mol^{-1} and +79.5 kJ mol^{-1}, respectively, at 298 K.

(i) Draw an energy cycle using the information given and use it to determine the standard enthalpy change for the reaction, $\Delta H_r^\ominus$. [2]

(ii) Use your answer to **(d)(i)** and the information given to determine the standard entropy change for the reaction. [2]

(i)

$$\begin{tikzcd}
2MgC_2(s) \arrow[rr, "\Delta H_1^\ominus"] & & Mg_2C_3(s) + C(s) \\
& 2Mg(s) + 4C(s) \arrow[ul, "2\times\Delta H_f^\ominus(MgC_2)"] \arrow[ur, "\Delta H_f^\ominus(Mg_2C_3)"'] &
\end{tikzcd}$$

$\Delta H_1^\ominus = \Delta H_f^\ominus(Mg_2C_3) - 2\Delta H_f^\ominus(MgC_2)$

$= +79.5 - 2(+87.9)$

$= \underline{\mathbf{-96.3\ kJ\ mol^{-1}}}$

(ii) At 770 K, $\mathbf{\Delta G^{\ominus} = 0}$

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$0 = -96.3 \times 10^{3} - 770\Delta S^{\ominus}$$

$$\Delta S^{\ominus} = \frac{-96.3 \times 10^{3}}{770}$$

$$= \underline{\mathbf{-125\ J\,K^{-1}\,mol^{-1}}}$$

Marker's Comments:

(d)(i)

- Generally well-attempted.
- Most common error is that candidates forgot to multiply the $\Delta H_f^{\ominus}(MgC_2)$ by 2 since 2 moles of MgC_2 is involved in the required reaction. Benefit-of-the-doubt is generally given in the cycle itself, but penalised in the calculation of the $\Delta H_r^{\ominus}$.
- Other common errors include
  - Cycle not closed, *i.e.* incomplete cycle
  - Misreading the question and included C_2H_2 in the cycle

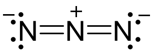
(d)(ii)

- Generally poorly well-attempted.
- However, a number of candidates correctly stated that $\Delta G^{\ominus} = 0$, although the reason is wrong, e.g. that the reaction is a phase change, the system is in equilibrium, etc. Benefit-of-the-doubt is given and there is no penalty. However, candidates should know that in this case, since the reaction only becomes feasible at 770 K means that $\Delta G^{\ominus} > 0$ below 770 K and $\Delta G^{\ominus} < 0$ above 770 K. So the reaction just becomes feasible at 770 K, i.e. $\Delta G^{\ominus} = 0$.
- Common errors include
  - Using the wrong temperature of 298 K. Although the $\Delta H_f^{\ominus}$ given is at 298 K, however, ΔH and ΔS generally do not change much with temperature unless there are phase changes, and so are applicable at 770 K as well.
  - Wrong mathematical manipulation, leading to wrong sign for $\Delta S_r^{\ominus}$.
  - Wrong unit for $\Delta S_r^{\ominus}$, omitting the K^{-1}.

Similar to the carbides, there are also salt-like and covalent nitrides, and the class of salt-like nitrides is similarly divided into different groups. Two of which are those that contains

- the diazenide anion, N_2^{2-}, derived from diazene, N_2H_2, and
- the azide anion, N_3^-, derived from hydrogen azide, HN_3

(e) The structure of the azide anion is shown



$^{-}\!:\!\ddot{N}\!=\!\overset{+}{N}\!=\!\ddot{N}\!:^{-}$

The azide anion is a very good nucleophile in organic reactions, serving as a versatile handle for further transformations. Some reactions involving azides are shown in Fig. 3.1.

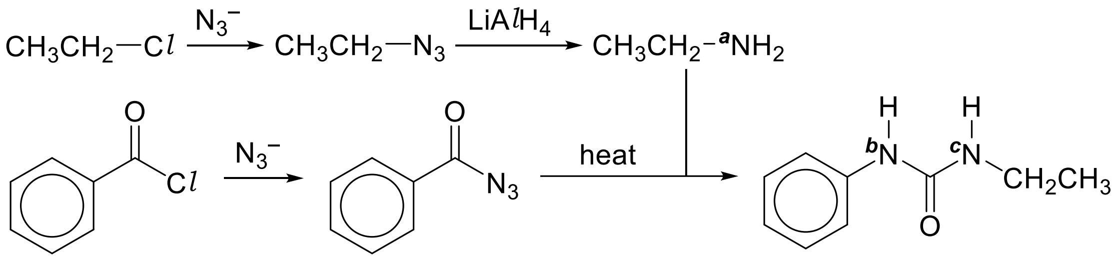


Fig. 3.1

(i) Although $LiAlH_4$ is not able to reduce allenes such as $H_2C=C=CH_2$, it is able to reduce alkyl azides such as $CH_3CH_2N_3$, offering a route to primary amines, as shown in Fig. 3.1.

Assuming that $LiAlH_4$ produces the hydride ion, H^-, suggest a reason why $LiAlH_4$ is able to reduce alkyl azides, taking into consideration the bonding. [1]

(ii) Explain the relative basicity of the three nitrogen atoms, ^aN, ^bN and ^cN in Fig. 3.1. [2]

(i) Although the azide fragment is neutral, however, the **central N** is **electron-deficient** (carries a positive charge, while the terminal N carries a negative charge) and hence will **attract the nucleophilic H^-** of $LiAlH_4$.

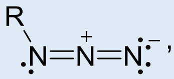
(ii) In increasing basicity: $^bN < {}^cN < {}^aN$.

The **lone pair** of electrons on **^bN** and **^cN** are **effectively delocalised into the C=O**, hence much less available for donation to a H^+ compared to ^aN, resulting in **^aN being the most basic**.

The **lone pair** of electrons on **^bN** is **further delocalised into the benzene ring**, rendering the lone pair on **^bN** less available for donation to a H^+ compared to ^cN, hence **the least basic**.

Marker's Comments:

(e)(i)

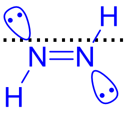
- Generally not well-attempted.
- Most candidates fail to realise that the *central* N in the azide moiety in alkyl azide, , being positively charged will attract the nucleophilic H^- ion.
- Some candidates were not clear which N is the electron-deficient N or mentioned the N with a δ+ charge when the N in fact carries a full positive charge.
- One common error is to mention that the C bonded to the N is electrophilic and is attacked by H^-. However, among the three N in the azide moiety, the N that is bonded to the R group actually remains as the NH_2 group. The remaining two N's are lost as N_2. So the C bonded to the N is not the site of attack.

(e)(ii)

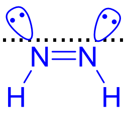
- Generally not well-attempted.
- Many candidates thought incorrectly that the lone pair on ^{b}N is delocalised only into the benzene ring. ^{b}N is bonded to the benzene ring as well as C=O. So the lone pair is in fact delocalised over **both** the benzene ring and C=O, rendering it the least basic.
- Usage of terminology is also often inaccurate. Many candidates said that the N is bonded to electronegative O, when in fact, it is bonded to the C=O group. So the lone pair on N is not available for donation primarily due to its delocalised into the C=O, and not simply due to the inductive effect of O (which does contribute, but minimal).
- Many candidates also think that delocalisation of the lone pair into the benzene ring is more effective. As C atoms are not exactly good at accommodating negative charges as compared to highly electronegative O, hence the delocalisation into the benzene ring is not as effective as delocalisation into the C=O.
- Another common error is that candidates mention that both ^{b}N and ^{c}N are neutral, so they have the same basicity. However, there is still differences in the availability of the lone pair for donation to H^+. Being neutral does not mean that the lone pair of electrons cannot be donated. Just that under normal condition in say water and aqueous acid, the lone pair generally are not available for donation. Under extremely acidic condition, e.g. concentrated H_2SO_4, the amide N can still be protonated.

(f) There are two isomers of diazene, N_2H_2, which can be isolated at low temperature.

Suggest the structures for the two isomers of diazene and explain how they arise.[2]



trans



cis

Cis-trans isomerism arises due to **restricted rotation about the N=N**, while there being **two different groups**, a hydrogen atom and a lone pair of electrons, **on each N**.

Marker's Comments:

- Poorly attempted. Question adapted from **2017 GCE A-Level Paper 3 Question 2(b)**.
- Most candidates were not able to even work out the H–N=N–H linkage. Among those who managed to see the H–N=N–H, thought that it is linear (or drew it so) and hence missed the possibility of *cis-trans* isomerism.
- Among the few candidates who recognise the possibility of *cis-trans* isomerism, the explanation of how the two isomers arises either missed out on the restricted rotation of the N=N or more commonly, the needed to have two different "substituents" (one H and one lone pair) on each N.

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** The thermal decomposition reaction of Group 2 carbonates is considered a reversible reaction. The reversible thermal decomposition of $CaCO_3$ is represented by the following equation.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

50.0 g powdered calcium carbonate is placed in a 1 dm^3 evacuated vessel. The vessel is heated at 1100 K until the reaction has reached equilibrium. The pressure of the vessel was found to be 3.92×10^{-2} atm.

(i) Explain what is meant by *dynamic equilibrium*. [1]

(ii) Write the equilibrium constant K_c, including its units. [1]

(iii) Using the information above, calculate the value of K_c. [1]

(iv) Explain how the equilibrium of the system is affected separately:

- when volume of the vessel is decreased.
- when 25.0 g of solid $CaCO_3$ is added. [2]

(i) It refers to a **reversible process at equilibrium** in which the **rate of the forward and backward reactions are equal, constant and non-zero**.

(ii) $K_c = [CO_2]$ units: **mol dm^{-3}**

(iii) $pV = nRT$

$$[CO_2] = \frac{p}{RT} = \frac{3.92\times10^{-2}\times101325}{8.31\times1100} = \mathbf{0.435\ mol\ m^{-3}}$$

K_c = **4.35×10^{-4} mol dm^{-3}**

(iv) A decrease in the volume of the vessel will cause **the position of equilibrium to shift to the left to decrease the amount of gaseous CO_2 in the system.**

The **position of equilibrium will not change** when solid $CaCO_3$ is added as the concentration of the solid **remains constant.**

Marker's Comments:

(a)(i)

- Most candidates were not able to provide the complete definition for dynamic equilibrium. Most are either missing reversible process at equilibrium and /or rate being non-zero.

(a)(ii)

- Many candidates did not realise that the equilibrium is a heterogeneous equilibrium which there is no need to include the solid terms. Some gave the units in atm even though it is K_c.

(a)(iii)

- Many candidates fail to realise that the units are in mol m^{-3}. Giving the answer immediately in mol dm^{-3} instead with no conversion. Several also were not able to utilise the ideal gas equation proper, converting incorrectly to SI units or omitting conversions altogether.
- Many attempted to solve for a heterogeneous equilibrium with the information given but it is not possible.

(a)(iv)

- Most candidates was able to explain the change in equilibrium position when volume is decreased whether through amount / pressure. Some attempted to explain that the change is necessary to re-equilibrate the volume of the gas which is incorrect.
- Most were unable to explain correctly what happens when excess solid is added and its effect in a heterogeneous equilibrium. Some simply stated that it is not part of the K_c and left it at that without further explanation.

(b) A thermal decomposition experiment was conducted in an open environment where 2.00 g each of powdered $CaCO_3$ and $SrCO_3$ are heated separately at temperature T until their masses are constant, signifying complete reaction.

Fig. 4.1 represents the change of mass that occurred for $SrCO_3$ over time. At time t_1, the decomposition is complete, and the residue has a constant mass of 1.40 g.

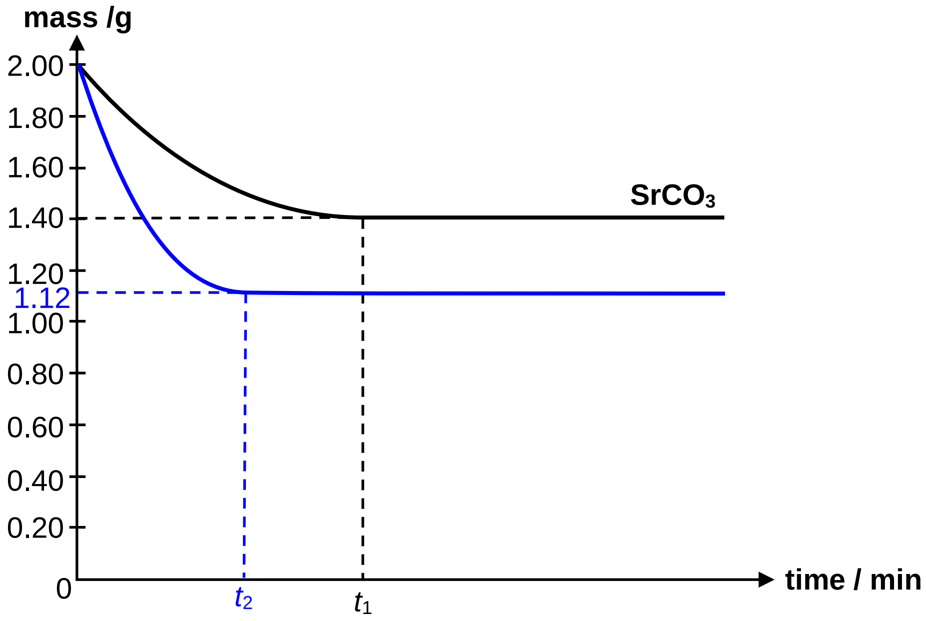


Fig. 4.1

(i) Calculate the mass of the residue left by $CaCO_3$ after thermal decomposition. [1]

(ii) Using your answer in **(b)(i)**, draw **on Fig. 4.1**, the variation in mass when 2.00 g of $CaCO_3$ is heated under the same condition. Use the label t_2 to indicate the time of complete thermal decomposition for $CaCO_3$. [1]

(iii) Explain the difference between the thermal decomposition of these two carbonates. [2]

(ii) amount of CaO = amount of $CaCO_3$

$$= \frac{2.00}{40.1 + 12.0 + 16.0 \times 3}$$

$$= 1.998 \times 10^{-2} \text{ mol}$$

mass of CaO = $1.998 \times 10^{-2} \times (40.1 + 16.0)$ = **1.12 g**

(ii) **[show correct t_2 and increased gradient]**

(iii) Down the group, **ionic radii of Ca^{2+} increases**, **charge density / polarising power** of the cation **decreases**, ability to distort the carbonate electron cloud **decreases**, **C-O bond** in carbonate is **weakened to a smaller extent, hence more difficult to decompose/more thermally**

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Marker's Comments:

(b)(i)

- Generally okay. Students who answered incorrectly did not realise that the amount of CaO after complete decomposition is the same as the amount of $CaCO_3$ initially.

(b)(ii)

- Most students were able to identify that t_2 is before t_1 due to $CaCO_3$ decomposing more rapidly, and that the rate should be faster.
- Some students did not label even though instructed to use the label t_2. No credit is given.

(b)(iii)

- Generally well done. Some students were not clear with the explanation for charge differences in charge density (atomic radius, radius), confusing polarising electron cloud with polarizability of electron cloud and / or breaking the wrong covalent bond (C=O instead of C—O).
- Some attempted to explain using ionic bonding which is incorrect for thermal decomposition.

(c) The numerical value of the solubility products of some calcium-containing salts at 298 K are given below.

Table 4.1

salt	value of solubility product
calcium carbonate, $CaCO_3$	3.36×10^{-9}
calcium fluoride, CaF_2	3.45×10^{-11}
calcium hydroxide, $Ca(OH)_2$	5.02×10^{-6}

(i) Write an expression for the solubility product of calcium carbonate, stating its units. [1]

(ii) Using Table 4.1, calculate a value for the solubility of calcium carbonate. [1]

(iii) Solid calcium nitrate was added slowly to a solution containing 0.200 mol dm^{-3} of sodium fluoride and 0.300 mol dm^{-3} of sodium hydroxide.

Calculate the concentration of fluoride ions remaining in the solution when calcium hydroxide starts to precipitate. [2]

(iv) Describe and explain the difference in solubility of calcium hydroxide in aqueous sodium hydroxide and in water. [2]

(i) **K_{sp} = $[Ca^{2+}][CO_3^{2-}]$ units: $mol^2\ dm^{-6}$**

(ii) $K_{sp} = [Ca^{2+}][CO_3^{2-}] = 3.36 \times 10^{-9}$

$$\text{solubility} = [Ca^{2+}] = [CO_3^{2-}]$$

$$= \sqrt{K_{sp}} = \sqrt{3.36 \times 10^{-9}}$$

$$= \mathbf{5.80 \times 10^{-5}\ mol\ dm^{-3}}$$

(iii) Since CaF_2 and $Ca(OH)_2$ have the same number of ions when dissolved, $Ca(OH)_2$ with the lower K_{sp} will precipitate last.

When $Ca(OH)_2$ starts to precipitate,

$K_{sp}(Ca(OH)_2) = [Ca^{2+}][OH^-]^2$

$5.02 \times 10^{-6} = [Ca^{2+}](0.300)^2$

$[Ca^{2+}]$ = **5.578×10^{-5} mol dm^{-3}**

At this point,

$K_{sp}(CaF_2) = [Ca^{2+}][F^-]^2$

$3.45 \times 10^{-11} = (5.578 \times 10^{-5})[F^-]^2$

$[F^-]$ = **7.86×10^{-4} mol dm^{-3}**

(iv) **$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$**

Sodium hydroxide as compared to water, has **a higher concentration of OH^-**. When $Ca(OH)_2$ is added to NaOH, the **position of equilibrium lies to the left, causing the solubility to decrease**

....

....

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....

Marker's Comments:

(c)(i)

- Generally well done. Some candidates had the wrong superscript for the units or included the wrong term in K_{sp} such as $CaCO_3$ or CaO.

(c)(ii)

- Generally well done. Some candidates forgot their units or rounded to the wrong significant figure, or even missing out their standard form during the conversion.

(c)(iii)

- Generally okay. Students who did not do well did not understand that to find the fluoride ions remaining in the solution when $Ca(OH)_2$ precipitates, one has to find out how much $Ca^{2+}(aq)$ is needed to precipitate $Ca(OH)_2$ first.
- Some had the correct fluoride concentration calculated but chose to use it to subtract from the original concentration of fluoride present. This gave the concentration of fluoride ions that had precipitated out as a result.

(c)(iv)

- Poorly attempted across all candidates. Candidates did not understand what the question was asking. Candidates need to be clear that between water and NaOH, there is a clear distinction in terms of the concentration of $[OH^-]$, where it is higher concentration in NaOH. There is no "*increasing*" of concentration.
- Only when it is identified that there is higher concentration, can one explain that when $Ca(OH)_2$ is added, there will be a shift in where the position of equilibrium lies which impacts the solubility. Should students attempt to explain a change in position of equilibrium instead, benefit of doubt is given for this point.

(d) Calcium carbonate is a sparingly soluble salt.

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

The standard entropy change of formation at 298K for these species are shown in Table 4.2.

Table 4.2

species	$CaCO_3(s)$	$Ca^{2+}(aq)$	$CO_3^{2-}(aq)$
$\Delta S_f^\ominus$ / J K^{-1} mol^{-1}	+91.7	–56.2	–50.0

(i) Calculate the standard entropy change of solution for calcium carbonate. Explain the significance of the sign. [2]

(ii) The standard enthalpy change of solution for calcium carbonate is –10.6 kJ mol^{-1}.

Using your answer in **(d)(i)**, calculate the standard Gibbs free energy of solution of calcium carbonate at 298 K in kJ mol^{-1}. [1]

(iii) Explain how the Gibbs free energy of solution of calcium carbonate will change with increasing temperature.

Assume that the entropy change of solution calculated in **(d)(i)** and the enthalpy change of solution for calcium carbonate is not affected. [2]

(i) $\Delta S_{sol}^\ominus = \sum \Delta S_f^\ominus(\text{products}) - \sum \Delta S_f^\ominus(\text{reactants})$

$= (-56.2 + (-50.0)) - (+91.7)$

$= \mathbf{-198\ J\ K^{-1}\ mol^{-1}}$

Since $\Delta S_{sol}^\ominus$ is negative, it suggests a decrease in entropy due to the due to the **water molecules that were originally free to move become restricted in motion as they arrange themselves around the ions**. Hence, there is less disorder in the system.

(ii) $\Delta G^{\ominus}_{\text{sol}} = \Delta H^{\ominus}_{\text{sol}} - T\Delta S^{\ominus}_{\text{sol}}$

$\Delta G^{\ominus}_{\text{sol}}$ = –10.6 – (298)(–0.198)

= **+ 48.4 kJ mol^{-1}**

(iii) **$\Delta G = \Delta H - T\Delta S$**

Since ΔS and ΔH are negative, with increasing temperature, **$T\Delta S$ becomes more negative / $-T\Delta S$ becomes more positive / $-|T\Delta S| > |\Delta H|$**.

This makes **ΔG more positive**.

Marker's Comments:

(d)(i)

- Poorly attempted. Many students were not able to apply the cycle or memorised the equation incorrectly.
- Many were unable to give the associated explanation to their signs calculated. Often, just resorting to simply saying change in disorder of the system.

(d)(ii)

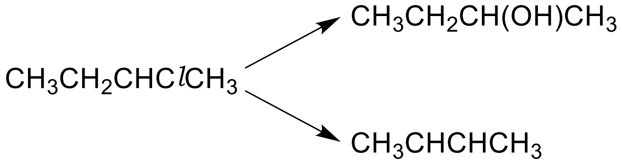
- Generally okay. Some students did not convert to the common energy SI units before applying the formula. i.e. all should either be in J or kJ. Some did not give their answers in kJ mol^{-1} as tasked.

(d)(iii)

- Generally okay with heavy error carried forward marking. As long as the change in the relevant terms in the Gibbs Free Energy equation is given in candidate's responses, and the association to the change in Gibbs Free Energy as a result of increasing temperature, credit will be given.

[Total: 20]

5 **(a)** 2-Chlorobutane can undergo either substitution or elimination with sodium hydroxide under different conditions to form different products.



(i) 2-chlorobutane can undergo substitution via both S_N1 and S_N2 mechanisms to form butan-2-ol. Explain why each of the two mechanisms is possible for 2-chlorobutane. [2]

(ii) To identify the substitution mechanism that 2-chlorobutane undergoes when reacted with sodium hydroxide, two experiments were conducted with different concentrations of sodium hydroxide, keeping all other conditions constant.

State and explain the expected experimental results if the reaction occurred via the S_N2 mechanism. [2]

(iii) Suggest another way to determine if an enantiomerically pure sample of 2-chlorobutane undergoes S_N1 or S_N2 substitution. [1]

(i) S_N1 mechanism may be possible as there are **two electron-donating alkyl groups** bonded to the positively charged carbon in the carbocation intermediate, leading to a **relatively stable carbocation**. S_N2 mechanism may be possible as there are only two relatively **small** alkyl groups attached to the reactive carbon, which **does not lead to much steric hindrance** and will not hinder the approach of the nucleophile.

(ii) If the reaction occurred via the S_N2 mechanism, the **initial rate of the reaction will increase proportionally** when concentration of sodium hydroxide used is increased. This is because the rate equation for a S_N2 reaction is rate = k[2-chlorobutane][OH^-], indicating that the **reaction is first order with respect to the nucleophile**.

(iii) Measure the optical activity of the resulting mixture after the substitution reaction. If the **mixture is optically active**, **S_N2** substitution has occurred. If the mixture is optically inactive, S_N1 substitution has occurred.

Marker's Comments:

For (a)(i):

- A number of students merely stated that 2-chlorobutane was a secondary halogenoalkane, without identifying the key features of the alkyl groups that supported the S_N1 (i.e. electron-donating) or S_N2 (i.e. small, not bulky) mechanism.

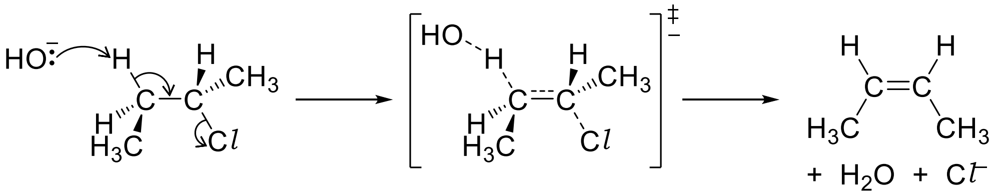
For (a)(ii):

- Generally well attempted. Some students chose to discuss the difference in the optical activity of the products. This was not accepted as it was not relevant to the context given, which involved different concentrations of NaOH being used.

For (a)(iii):

- Well attempted.

(b) When 2-chlorobutane is reacted with sodium hydroxide, substitution and elimination occur in competition with each other. The single-step elimination mechanism is shown below.



(i) What is the role of hydroxide in the elimination reaction? [1]

(ii) The elimination reaction was also carried out using $CH_3CD_2CH(Cl)CD_3$, where D is deuterium, an isotope of hydrogen. Using the relevant information provided in Table 5.1, state and explain why you would expect the rate of this reaction to be slower than that involving 2-chlorobutane.

Table 5.1

bond	bond energy / kJ mol^{-1}
C−H	410
C−D	415

C−C	350
C−C*l*	339

[1]

(iii) When 2-chlorobutane is reacted with ethanoate ion, $CH_3CH_2CH(OCOCH_3)CH_3$ is formed as the major product. However, when 2-chlorobutane is reacted with ethoxide ion, $CH_3CHCHCH_3$ is formed as the major product instead of $CH_3CH_2CH(OCH_2CH_3)CH_3$.

With reference to your answer in **(b)(i)**, explain why this is so. [2]

(i) It is a **base / nucleophile**.

(ii) It will be slower as **more energy** is needed to break the C–D bond in this **elementary reaction** compared to the breaking of the C–H bond.

(iii) Ethoxide ion is a **stronger base** as compared to ethanoate ion as it is the **conjugate base of ethanol, which is a weaker acid compared to ethanoic acid**. Hence, elimination, which requires a base, is favoured over nucleophilic substitution.

Marker's Comments:

For (b)(i):

- Most students identified hydroxide to be a nucleophile. A few students merely described the reaction hydroxide was involved in, which was not sufficient.

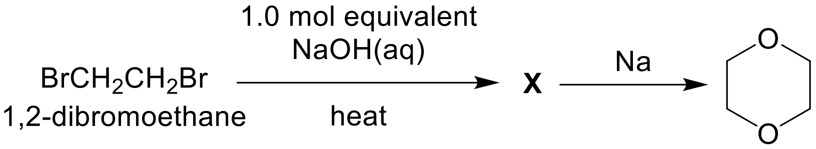
For (b)(ii):

- Almost all students did not score the mark here as they neglected to mention that the breaking of the C–D/C–H bond occurred in an **elementary** reaction (i.e. the only and therefore the **rate-determining** step), which meant that it would affect rate.

For (b)(iii):

- This part was poorly attempted, with many students leaving it blank.
- For students who have identified hydroxide to be a nucleophile, answers that competently compared the availability of the lone pair on the oxygen atom in ethoxide and ethanoate (i.e. strength of nucleophile) were accepted.

(c) 1,4-dioxane can be synthesised from 1,2-dibromoethane via a series of reactions.



(i) Suggest the structure of **X**. [1]

(ii) 2 moles of **X** reacted to form 1 mole of 1,4-dioxane *via* two different reactions. State the two types of reactions involved. [2]

(i) $HOCH_2CH_2Br$ ……………………………………………………………

……………………………………………………………………………………

(ii) Redox and **nucleophilic substitution** ……………………………………

Marker's Comments:

For (c)(i):

- Quite a number of students overlooked the fact that only 0.5 mol equivalent of NaOH was added, and substituted both bromo groups.

For (c)(ii):

- This was poorly attempted. Many students thought that condensation, elimination and/or addition occurred.
- Some students wrongly identified the reaction between the alcohol and sodium to be one of the following: acid-base reaction, neutralisation, oxidation, or reduction.

(d) **(i)** PCl_5 is a common reagent used to produce chloroalkanes from alcohols. It decomposes when heated to form PCl_3 and Cl_2 as shown in the equation below.

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

0.0624 mol of PCl_5 and 0.0707 mol of Cl_2 are placed in a 2 dm^3 vessel maintained at 250 °C and the system was allowed to reach equilibrium. Given that the total pressure at equilibrium is 3.32 atm, calculate the equilibrium constant, K_p at 250 °C, stating the units of K_p clearly. You may assume that the gases behave ideally under the stated conditions. [4]

(ii) State and explain how you would expect the K_p value to change when temperature is increased. [2]

(i)	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial amt/mol	0.0624		0		0.0707
Change in amt/mol	$-x$		$+x$		$+x$
Equilibrium amt/mol	$0.0624 - x$		x		$0.0707 + x$

Total amount of gases at eqm $= (0.0624 - x) + x + (0.0707 + x)$

$$= 0.1331 + x$$

$$pV = nRT$$

$$(3.32 \times 101325) \times (2 \times 10^{-3}) = (0.1331 + x) \times 8.31 \times (250 + 273)$$

$$0.1331 + x = 0.1548 \text{ mol}$$

$$x = 0.02170 \text{ mol}$$

Hence, at equilibrium,

$$p_{PCl_5} = \frac{0.0624 - 0.02170}{0.1548} \times 3.32$$

$$= 0.8729 \text{ atm}$$

$$p_{PCl_3} = \frac{0.02170}{0.1548} \times 3.32$$

$$= 0.4654 \text{ atm}$$

$$p_{Cl_2} = \frac{0.0707 + 0.02170}{0.1548} \times 3.32$$

$$= 1.982 \text{ atm}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{0.4654 \times 1.982}{0.8729}$$

$$= 1.06 \text{ atm}$$

(ii) As the **forward decomposition reaction is endothermic**, when temperature is increased, the **position of equilibrium will shift to the right** to **absorb some heat**, resulting in more products at equilibrium, **increasing the value of K_p**.

Marker's Comments:

For (d)(i):

- Quite a number of students were not able to solve this question as they were not able to link the amounts and partial pressures of gases at the various stages with the equilibrium total pressure.

For (d)(ii):

- This was surprisingly not well done. Many students did not realise that the forward reaction is endothermic, and argued in terms of how a change in temperature will lead to a change in pressure of the system.

(e) Chloroalkanes can also be produced by reacting hydrogen halides with alcohols. Such reactions are usually not conducted at high temperatures as some hydrogen halides have low thermal stabilities.

State and explain the trend in the thermal stabilities of HCl, HBr and HI. [2]

Thermal stability **decreases from HCl to HBr to HI**. This is due to the **decrease in the H–X bond strength down the group**, leading to **less energy** required to break the H–X bond.

Marker's Comments:

For (e):

- Generally well attempted, although there were a number of students who were penalised for suggesting that hydrogen halides are ionic in their answers. There were also a few students who wrote that the atomic radii of the **halides** increase. When referring to the Group 17 atoms, we should use the term **halogen** instead of halide.

[Total: 20]