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.

[Turn Over

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.

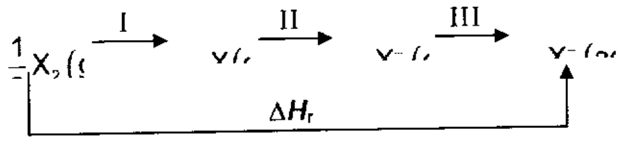

Fig. 1.1

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
C*l*	+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 values of energy term **III**. [2]

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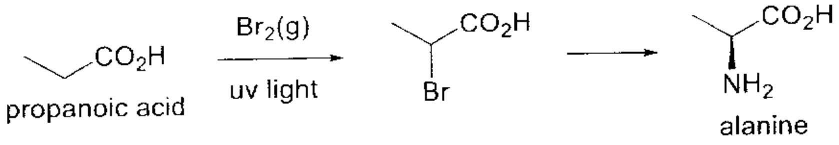
Alanine, which is found in a variety of food sources, is an amino acid that can be derived from propanoic acid. One of the methods to obtain alanine from propanoic acid is illustrated in the pathway below.



(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]

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

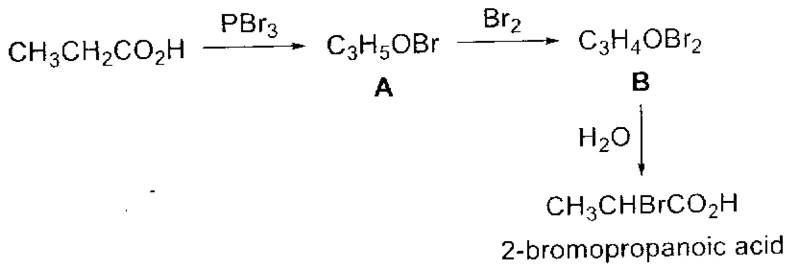
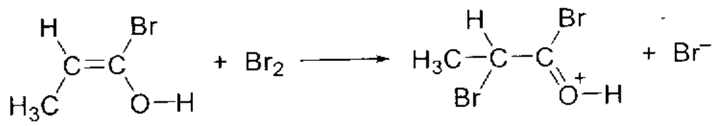


Fig 1.2

(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]

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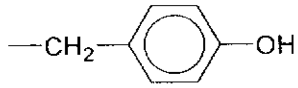
[Total: 20]

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.

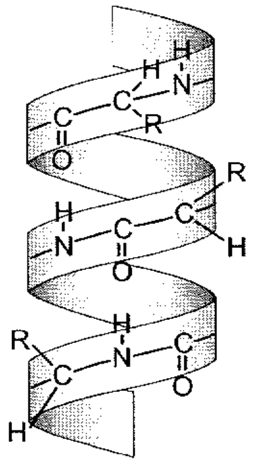


Fig. 2.1

(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]

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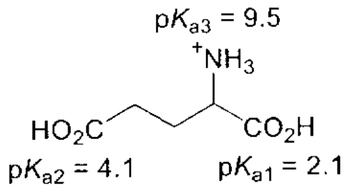
(b) Amino acids are soluble in both dilute acids and dilute alkalis due to the ability to exist as zwitterions.

(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.

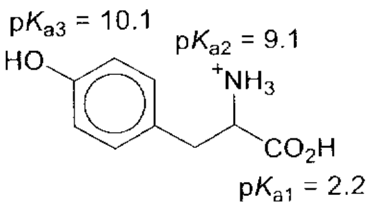


Make use of these pK_a values to suggest

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]

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(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]

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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]

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(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]

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

The methanides, Mg_2C and $A\ell_4C_3$, both undergo hydrolysis in water to yield methane.

(i) Suggest a balanced equation, and state the observations for the complete hydrolysis of *solid* $A\ell_4C_3$ in water. [2]

(ii) Mg_2C is hydrolysed immediately by moisture in the air, while $A\ell_4C_3$ 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≡CCH$_3$.

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

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

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]

(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:

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

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]

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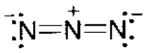
Similar to the carbides, there are also salt-like and covalent nitrides, and the class of salt-like nitrides is similarly divided into different groups. Two of which are those that contains

- 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



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.

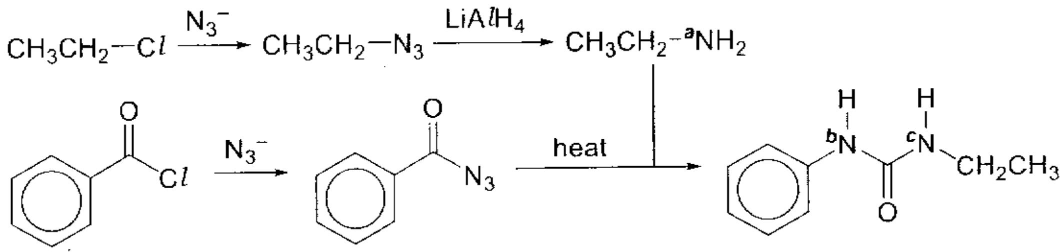


Fig. 3.1

(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]

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(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]

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[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]

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(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.

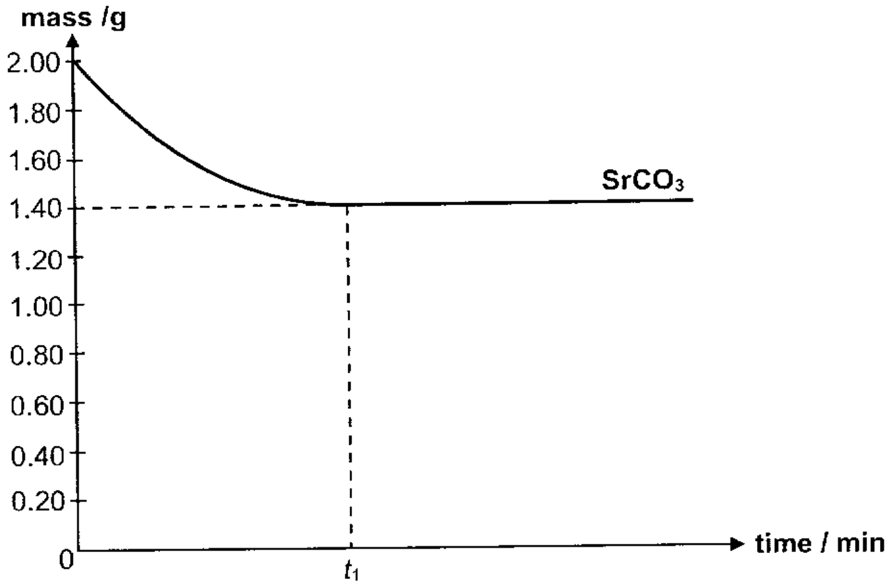

Fig. 4.1

(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 on page 19**, 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]

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(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]

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(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]

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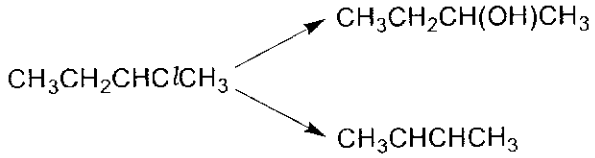
5 **(a)** 2-Chlorobutane can undergo either substitution or elimination with sodium hydroxide under different conditions to form different products.



(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]

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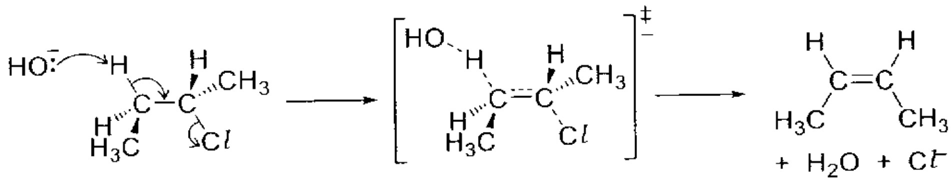
(b) When 2-chlorobutane is reacted with sodium hydroxide, substitution and elimination occur in competition with each other. The single-step elimination mechanism is shown below.



(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

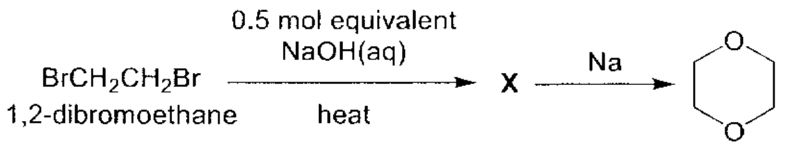
bond	bond energy / kJ mol^{-1}
C–H	410
C–D	415
C–C	350
C–Cl	339

[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]

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



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

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

(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]

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(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 HC*l*, HBr and HI. [2]

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[Total: 20]

Additional answer space

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

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CHEMISTRY

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Section A

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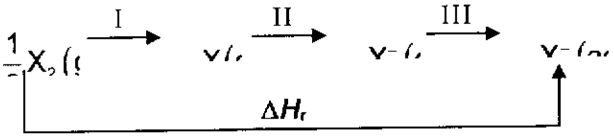

Fig. 1.1

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

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F	+79	–328	–506
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(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/ B(D)E **II**: first electron affinity

III: enthalpy change of hydration

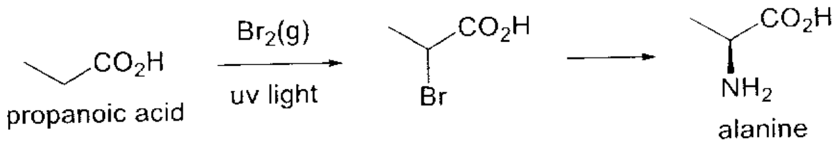
(ii) As the valence orbital used in bonding is **more diffused** moving down the group from chlorine to iodine, the **overlap of orbitals is less effective** (moving down the group), leading to less energy being required to break the bond in the diatomic molecule.

(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.

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.



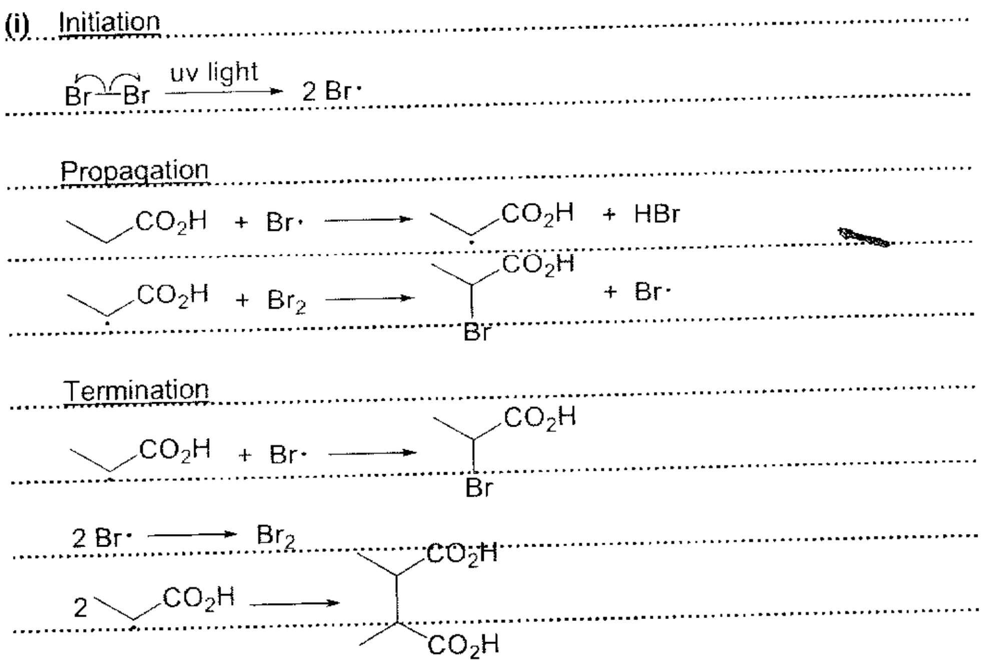
(b) (i) Outline the mechanism for the formation of 2-bromopropanoic acid via the reaction between propanoic acid and bromine gas. [3]

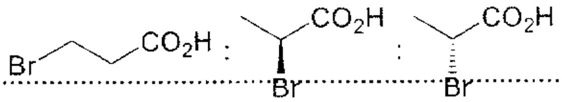
(ii) In the reaction between propanoic acid and bromine gas, the relative rate of abstraction of primary, secondary and tertiary hydrogen is in the ratio of 2 : 3 : 6.

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]



(ii) 

3 × 2 : 1 × 3 : 1 × 3

6 : 3 : 3

2 : 1 : 1

(iii) As the **bond enthalpies of C–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)

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

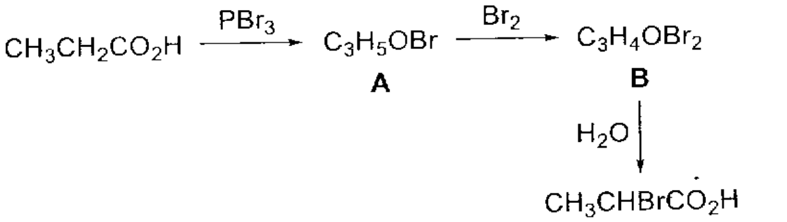
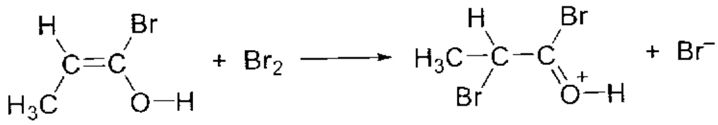


Fig 1.2

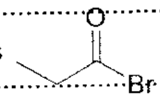
(c) **(i)** Draw the structures of **A** and **B**. [2]

(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.

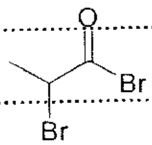


[2]

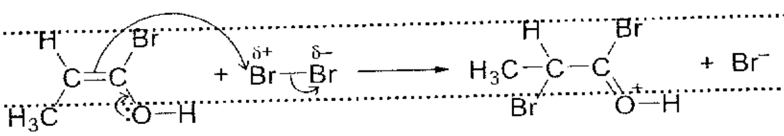
(i) **A** is



B is



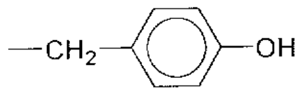
(ii)



[Total: 20]

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.

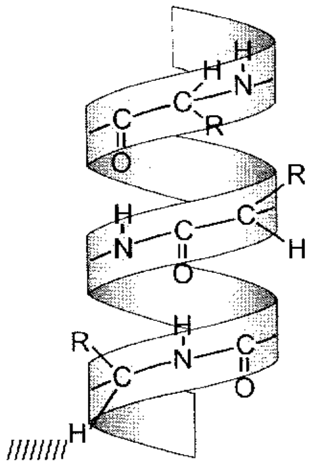


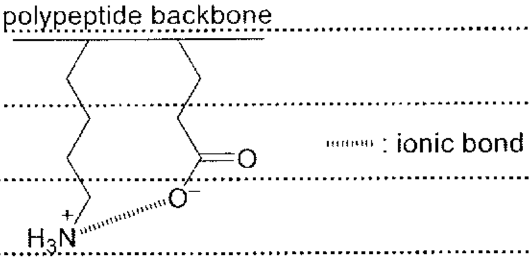
Fig. 2.1

(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

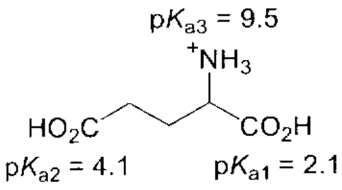
(ii) ionic bonds (accept hydrogen bonds)



(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.

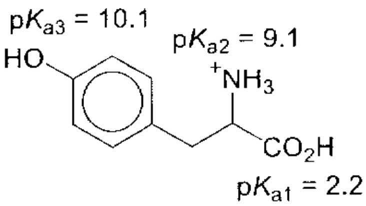


Make use of these pK_a values to suggest

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.

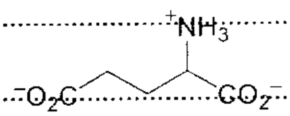


Explain the difference between the pK_{a1} and the pK_{a3} of tyrosine. [2]

(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.

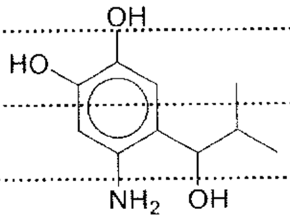
(c) Compound **E**, $C_{10}H_{15}O_3N$, is also soluble in both dilute acids and dilute alkalis. One mole of **E** undergoes complete neutralisation with 2 moles of NaOH. However, no gas is evolved when sodium carbonate is added to **E**.

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.

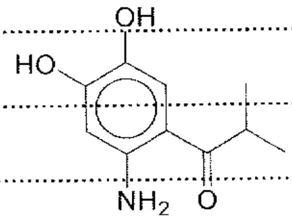
(i) Deduce the structures for each lettered compound, **E** to **I**, and explain the chemistry involved. [10]

(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]

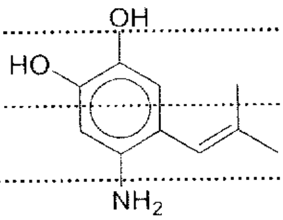
(i)
- E undergoes **acid-base reaction** with 2 mole equivalent of NaOH but not with Na_2CO_3
  ⇒ E contains **2 phenol OH** groups.
- F undergoes **condensation** with 2,4-DNPH but not **oxidation** with Tollens'
  ⇒ F is a **ketone**
- E undergoes **oxidation** with acidified potassium dichromate(VI) 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**.



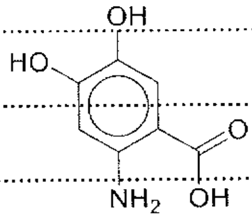
E



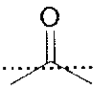
F



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.

[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

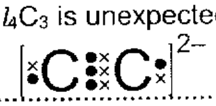
(a) Explain why the DEN decreases across period 3, from Na_2C_2 to SiC. [1]

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**.

(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.

(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≡CCH$_3$.

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

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

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]

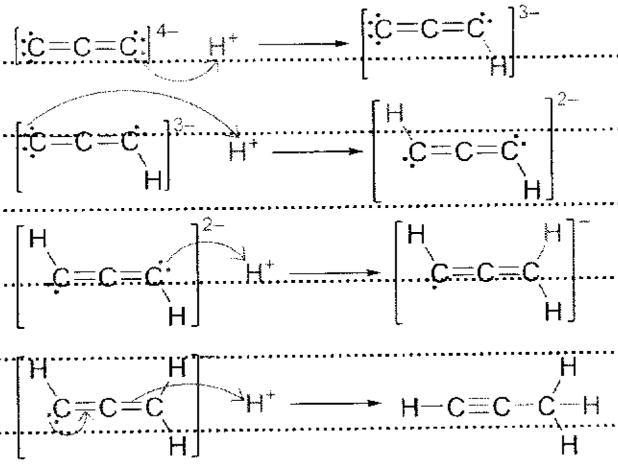
(i) $Al_4C_3(s) + 12H_2O(l) \rightarrow 3CH_4(g) + 4Al(OH)_3(s)$ or

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

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

(i) 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.

(ii)



(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:

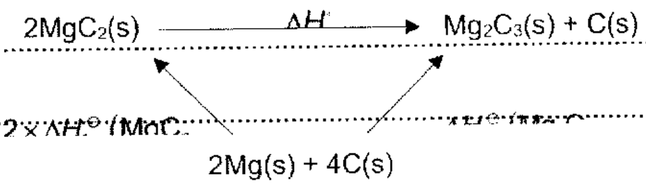
$$2MgC_2(s) \xrightarrow{770\text{ K}} Mg_2C_3(s) + C(s) \qquad \Delta H_r^{\ominus}$$

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)



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

$= +79.5 - 2(+87.9)$

$=$ **-96.3 kJ mol^{-1}**

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

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

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

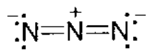
$\Delta S^{\ominus} = \dfrac{-96.3 \times 10^3}{770}$

$=$ **-125 J K^{-1} mol^{-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



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.

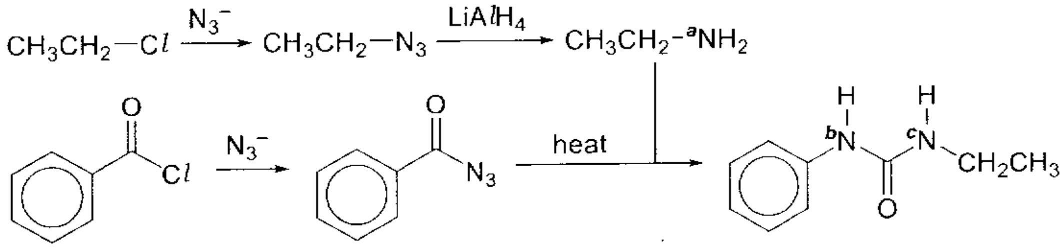


Fig. 3.1

(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 $LiAlH_4$.

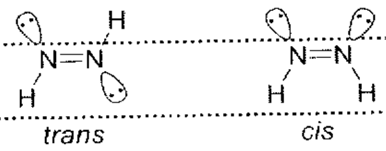
(ii) In increasing basicity: $^{b}N < ^{c}N < ^{a}N$.

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

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

(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]



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**.

[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) $pV = nRT$

$$[CO_2] = \frac{p}{RT} = \frac{3.92 \times 10^{-2} \times 101325}{8.31 \times 1100} = \mathbf{0.435\ mol\ dm^{-3}}$$

(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.**

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(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.

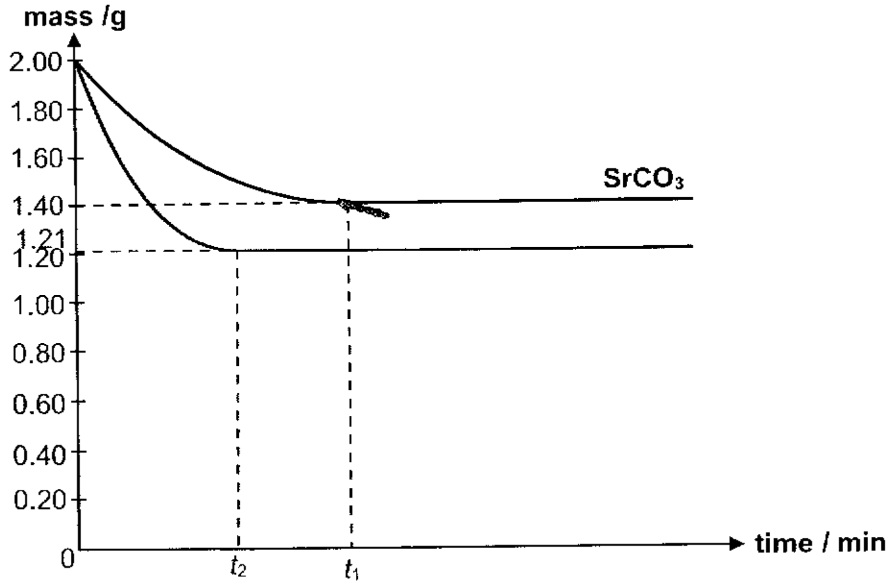


Fig. 4.1

(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 stable**. $CaCO_3$ requires less time for complete 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) $K_{sp} = [Ca^{2+}][CO_3^{2-}] = 3.36 \times 10^{-9}$

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

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

$=$ **5.80×10^{-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) $Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$

Calcium hydroxide is **less** soluble in sodium hydroxide than in water. This is due to the **common ion effect** as the sodium hydroxide contributes **OH^- ions.**

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

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

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

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

$= \mathbf{+\ 48.4\ kJ\ mol^{-1}}$

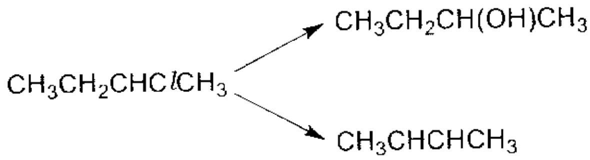
(iii) $\Delta G = \Delta H - T\Delta S$

Since ΔS and ΔH are negative, with increasing temperature, ***TΔS* becomes more negative / –*T*ΔS becomes more positive / –|*T*ΔS| > |Δ*H*|**.

This makes **ΔG more positive**.

[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]

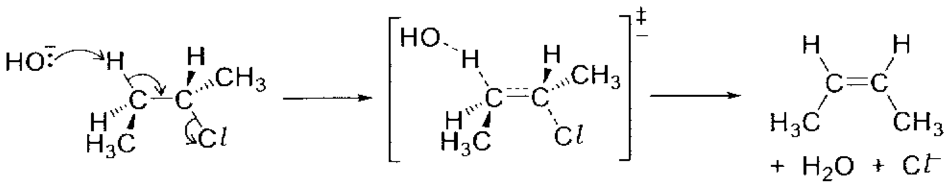
(iii) Suggest another way to determine if an enantiomerically pure sample of 2-chlorobutane undergoes S_N1 or S_N2 substitution. [1]

(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.

(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–Cl	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]

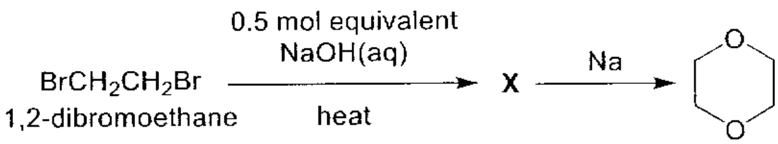
(i) It is a **base / nucleophile**.

(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. or

It is the **rate determining step**.

(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.

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



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

(ii) 1 mole 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**

(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 $= (0.0624-x)+x+(0.0707+x)$

$$= 0.1331+x$$

$$pV = nRT$$

$$(3.32\times101325)\times(2\times10^{-3}) = (0.1331+x)\times8.31\times(250+273)$$

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

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

Hence, at equilibrium,

$$p_{PCl_5} = \frac{0.0624-0.02170}{0.1548}\times3.32$$

$$= 0.8729 \text{ atm}$$

$$p_{PCl_3} = \frac{0.02170}{0.1548}\times3.32$$

$$= 0.4654 \text{ atm}$$

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

$= 1.982$ atm

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

$= 1.06$ 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**.

(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 HC*l*, HBr and HI. [2]

Thermal stability **decreases from HC*l* 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

[Total: 20]

Additional answer space

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