



ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

Higher 2

CANDIDATE
NAME

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CLASS

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CHEMISTRY

9729/02

Paper 2 Structured Questions

1 September 2021

2 hours

Candidate answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the **spaces provided** on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use		
Q1		9
Q2		9
Q3		24
Q4		20
Q5		13
Total		75

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

- 1 (a) Fig. 1.1 shows a sketch of the logarithm of the first ten ionisation energies, $\log(\text{IE})$, of element **A** against the number of electrons removed.

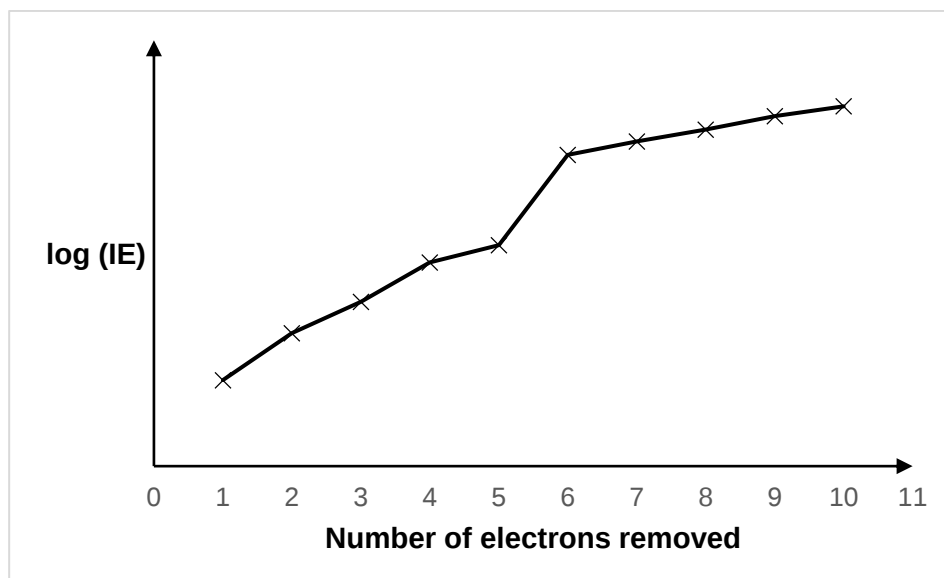


Fig. 1.1

- (i) Write an equation for the *second ionisation energy* of element **A**. [1]



Must have state symbols

- (ii) Explain the following features of Fig. 1.1.

- the general trend in ionisation energy shown in the graph
- the significant jump in values from the 5th to the 6th ionisation energy

[4]

Ionisation energies increased as more electrons were removed. The nuclear charge remained the same, but it attracted a decreasing number of electrons. This led to an increase in the attractive forces on the remaining electrons and hence more energy was required to remove the next electron.

OR

Successive IE increases as remaining electrons will be attracted more strongly to increasingly positively charged ion and hence more energy was required to remove the next electron

The 6th electron is from the inner quantum shell. The decrease in distance of this electron (6th electron) from the nucleus, and less shielding resulted in a

stronger attraction to nucleus, significant increase in the energy required to remove this electron /more difficult to remove this inner shell electron.

(iii) Element **A** is in Period 3.

Identify element **A** using information from Fig. 1.1 and complete its electronic configuration. [1]

Element **A** is phosphorus / P.

$1s^2 2s^2 2p^6 3s^2 3p^3$

(b) Sulfur is another element in Period 3. It forms covalent bonds with other elements in covalent compounds such as SO_2 , SO_3 , SCl_2 .

(i) Describe a covalent bond. [1]

A covalent bond is the electrostatic attraction between a shared / bonding pair of electrons and two positively charged nuclei.

(ii) Predict the intermolecular force which exists between SO_3 molecules. Explain how this force arises. You may use diagrams where appropriate to illustrate your answer. [2]

The SO_3 molecules are held together by instantaneous dipole-induced dipole (id-id) attractions.

In each electron cloud, electrons are constantly moving. The electron density of a cloud can be unsymmetrical at any moment, resulting in an instantaneous dipole.

This dipole can induce a dipole in the neighbouring electron cloud, causing an attraction between them.

OR

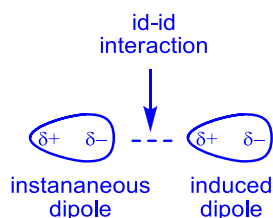


Diagram marks depend on labels used

Label for id-id

Uneven electron cloud

Labels for instantaneous dipole and induced dipole

- 2 Esters are commonly used as artificial flavourings in food products such as cakes and sweets. However, the shelf life of acidic foods containing esters are relatively short as esters are prone to acid-catalysed hydrolysis.

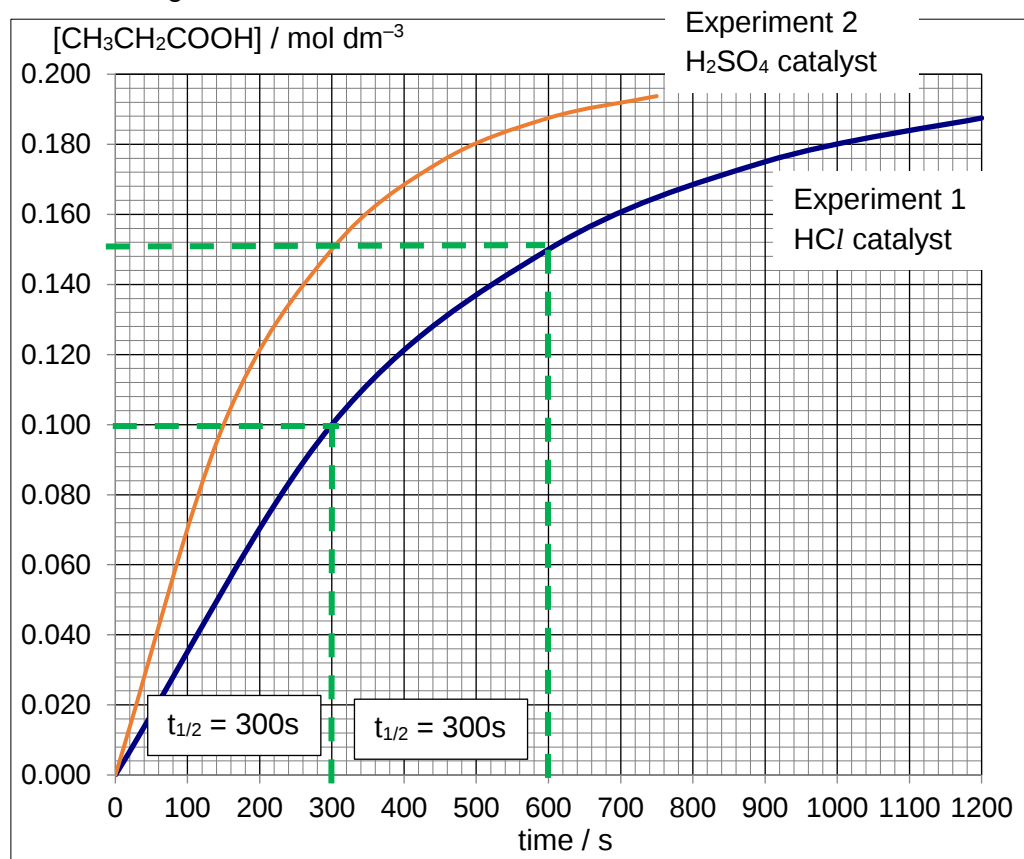
The kinetics of the acid-catalysed hydrolysis of the ester, methyl propanoate, $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$, was investigated in an experiment.

- (a) Write a balanced equation for the hydrolysis of methyl propanoate. [1]



- (b) 0.200 mol of ester was hydrolysed by heating with water and hydrochloric acid catalyst in a 1 dm^3 mixture. In a second experiment, hydrochloric acid was replaced with sulfuric acid of the same concentration. When the reaction is complete, 0.200 mol of propanoic acid is obtained.

The following results were obtained.





- (i) Based on the results obtained, show that the reaction is first order with respect to the ester and first order with respect to H^+ ions. [4]

$$[CH_3CH_2COOH]_{\max} = 0.200 \text{ mol dm}^{-3}$$

Show 2 half life on the graph (either experiment 1 or 2) correctly e.g.

- from 0 $\rightarrow$ 0.100
- from 0.100 $\rightarrow$ 0.150
- does not have to be successive (one after the other e.g. 0.02 $\rightarrow$ 0.11)

Since half life is constant at 300 s (experiment 1) / 150 s (experiment 2), reaction is first order with respect to [ester].

Show 2 tangent to curve at $t=0$ clearly and calculate gradient of both tangent to curve

When $[H^+] \times 2$, initial rate $\times 2$, reaction is 1st order with respect to $[H^+]$

OR

Show 2 half life of the other experiment on the graph clearly

$$\text{rate} = k[\text{ester}][H^+]$$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[H^+]}$$

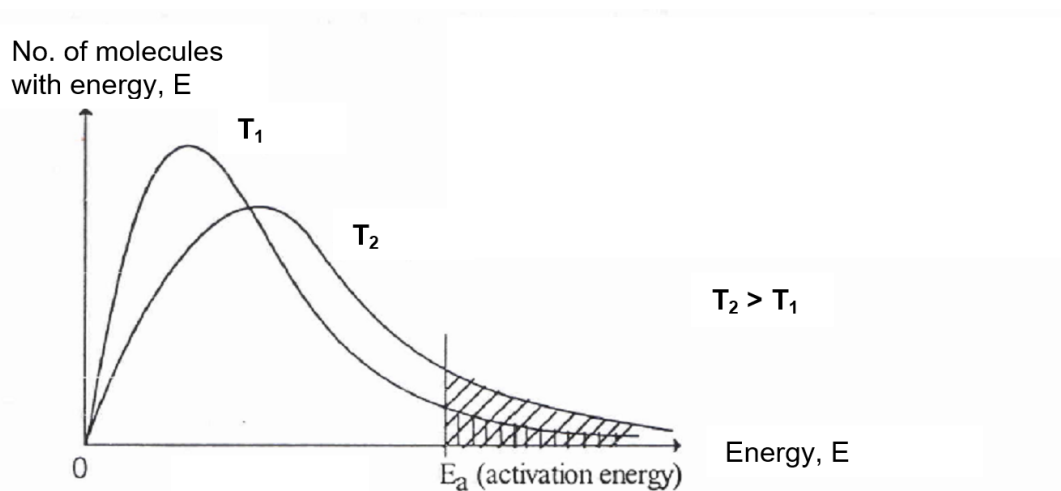
When $[H^+] \times 2$, half life $\times \frac{1}{2}$

Reaction is 1st order with respect to H^+

- (ii) State the units of the rate constant, k . [1]

$$\text{Units of rate constant } k = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

- (c) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature changes the rate of ester hydrolysis. [3]



Note: E_a does not shift as temperature changes.

When temperature is increased, the molecules gain kinetic energy and move about faster. This increases the number of molecules having energy greater than or equal to activation energy. As a result, the frequency of effective collisions increases. Reaction rate thus increases.

[Total: 9 marks]

- 3 Scuba diving is an extreme sport where divers carry their own source of breathing gas to explore the open sea.

Table 3.1 lists the compositions by volume of two breathing gases used by scuba divers.

Table 3.1

Mixture	Composition by volume
Nitrox	32% oxygen, 68% nitrogen
Heliox	21% oxygen, 79% helium

- (a) (i) State one assumption of the kinetic theory as applied to an ideal gas. Hence, deduce, with reasons, whether Nitrox or Heliox shows greater deviation from ideal gas behaviour.

[2]

The intermolecular forces between the gas particles are negligible/insignificant.

Nitrox shows greater deviation as nitrogen has a larger electron cloud size than helium, so its intermolecular forces/ id-id are less negligible /more significant.

OR

The particle size/volume is negligible as compared to the size/volume of the container.

Nitrox shows greater deviation as nitrogen molecule is larger than helium atom, so its particle size/volume is less negligible/ more significant.

- (ii) Use of the *Data Booklet* is relevant to this question.

A canister of breathing gas has a density of 435 g m^{-3} at standard temperature and pressure (s.t.p). Calculate the average molar mass of the mixture.

Hence, with reference to Table 3.1, deduce the identity of the breathing gas. **[3]**

$$pV = nRT$$

$$pV = \frac{m}{M} RT$$
$$M = \frac{mRT}{pV} = \frac{\rho RT}{p} = \frac{(435)(8.31)(273)}{10^5}$$

$$= 9.87 \text{ g mol}^{-1}$$

The breathing gas is Heliox.

- (b) At sea level, the atmospheric pressure is 1 atm. In the sea, there is an increase in pressure of 1 atm for every 10 m of depth below the surface. For example, at 10 m, the pressure on the diver's body is 2 atm and at 20 m, the corresponding pressure is 3 atm.

When a diver inhales from the gas canister, the air that enters the diver's lungs is at the surrounding pressure.

For safety reasons, divers should not inhale oxygen at partial pressures greater than 1.3 atm, as this may lead to oxygen toxicity, causing seizures and death.

- (i) A scuba diver takes a deep breath from his oxygen gas canister to fill up his lungs to 6 dm^3 at a depth of 15 m. Calculate the volume that will be occupied in his lungs by this amount of air at the surface. **[2]**

Pressure at 15 m = 2.5 atm

Amount of air remains constant.

$p_1V_1 = p_2V_2$, where p_2 is 1 atm

$$(2.5)(6) = (1)(V_2)$$

$$V_2 = 15 \text{ dm}^3$$

- (ii) “Never hold your breath when surfacing” is a fundamental rule of scuba diving. [1]

With reference to your answer in (b)(i), explain why.

The volume of air in the lungs increases greatly when he surfaces (from 6 to 15 dm³, hence he must exhale or the pressure increase results in lung damage).
(in their own words)

- (iii) A scuba diver uses Nitrox for a dive. Calculate the total pressure of the Nitrox mixture that corresponds to oxygen at a partial pressure of 1.3 atm. Hence, determine the maximum depth the diver can descend to safely. [2]

Partial pressure of oxygen = 1.3 atm

$$\text{Total pressure} = 1/0.32 \times 1.3 = 4.0625 \text{ atm}$$

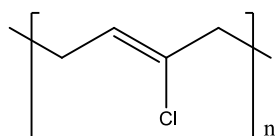
$$\text{Maximum depth} = (4.0625 - 1) \times 10 = 30.6 \text{ m}$$

- (iv) State an assumption that you have made in your calculations for (b)(i) and (b)(iii). [1]

Temperature remains constant.

Or These gases behave as ideal gases.

- (c) Diving suits are commonly made of neoprene, a synthetic polymer that is waterproof and a good insulator.



neoprene

Neoprene can be synthesised from 1,3-butadiene by the following route shown in Fig. 3.2.

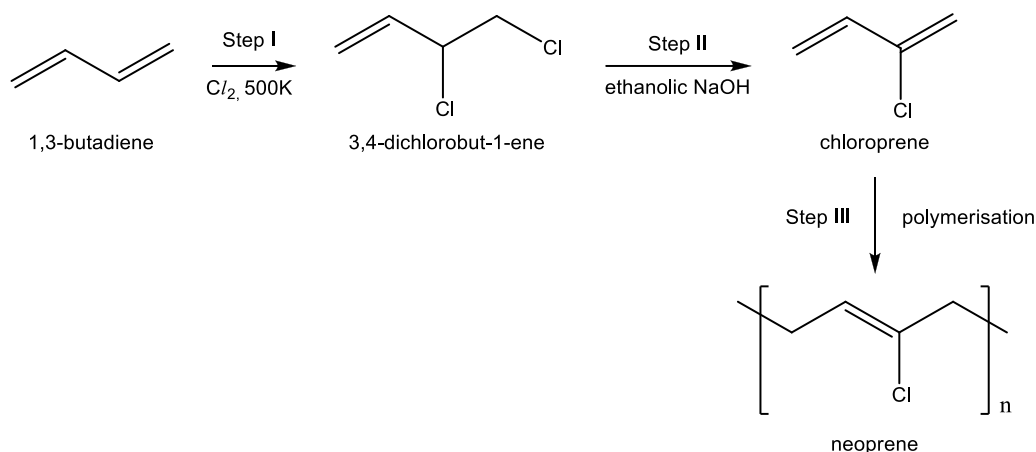
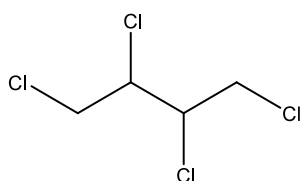


Fig. 3.2

- (i) Draw the structure of a possible side product formed in Step I. [1]



- (ii) Suggest how to minimise formation of this side product in (c)(i). [1]

Use **limited chlorine** / **excess 1,3-butadiene**

- (iii) Name the type of reaction occurring in Step II. [1]

Elimination

- (d) The polymerisation of chloroprene proceeds via a free radical mechanism. A common class of free radical polymerisation initiators are peroxide compounds, ROOR.

Explain what is meant by the term *free radical* and explain how the bond in ROOR breaks to form $\text{RO}\bullet$ free radicals. You may use a diagram in your answer. [2]

- (i) Free radical is an atom or group of atoms/species having an unpaired electron.

The homolytic fission of the O–O bond within peroxide compounds forms $\text{RO}\bullet$ free radicals.

OR



- (ii) Suggest why only a trace amount of ROOR is required in the polymerisation of chloroprene. [1]

Since the only function of the radical initiator, ROOR, is the generation of the first RO• involved in the chain reaction in the system, it is used in trace amounts.

OR

Radicals are (re)generated in the propagation step

OR

Mechanism is a chain reaction

- (e) (i) Complete Fig. 3.3 to suggest the mechanism for the chain growth. Show the structure of the 2 unit intermediate and the movement of electrons in steps 1 and 2 by using curly arrows.

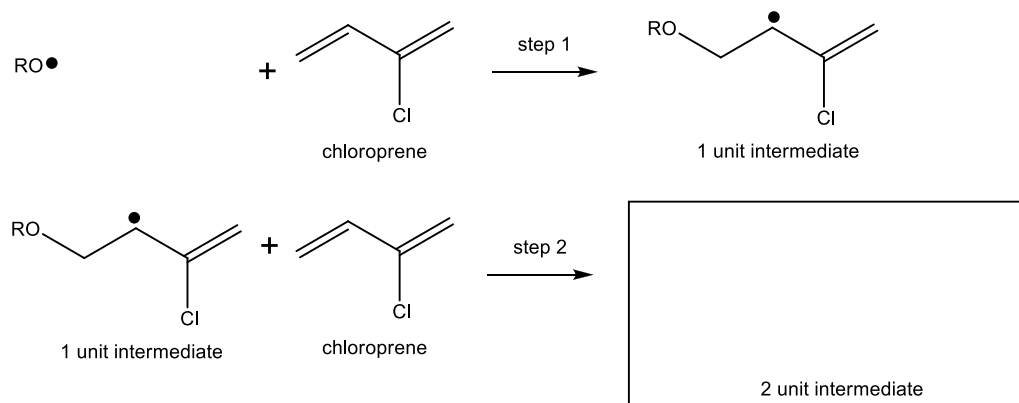
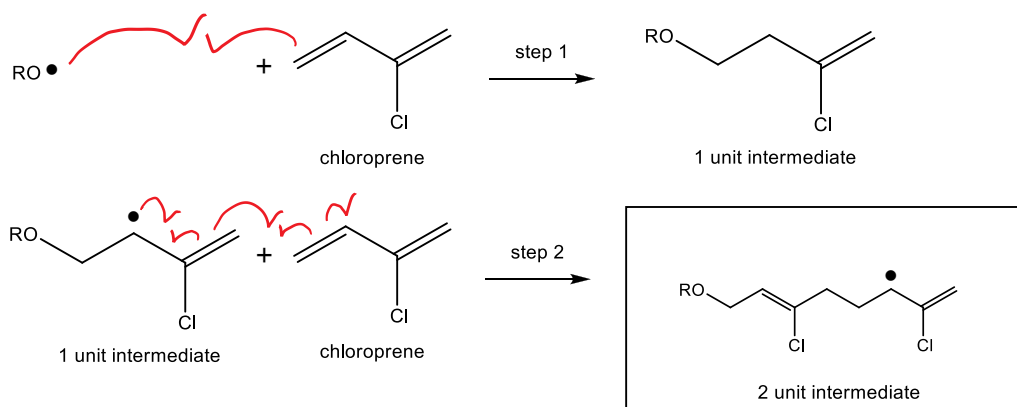
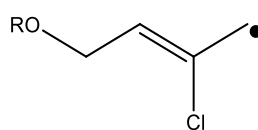


Fig. 3.3

[3]



- (ii) Explain the preferential production of the 1 unit intermediate over isomer **E** in step 1.



Isomer **E**

[1]

E is a primary radical, which is less stable than the actual secondary radical formed due to the presence of fewer electron donating alkyl groups.

- (f) (i) Besides diving suits, neoprene can be used to make alkali resistant rubber gloves. Suggest a reason why neoprene is not susceptible to reaction with alkali such as aqueous NaOH.

[1]

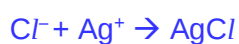
- Electron rich double / C=C bond repels incoming OH⁻ nucleophile.
- OR
- Lone pair of electrons in p orbital of Cl overlap with C=C pi bond, resulting in partial double bond character

- (ii) Under suitable conditions, NaOH can be used to distinguish between 3,4-dichlorobut-1-ene and chloroprene.

Describe the simple chemical test involving NaOH to distinguish between the two compounds. Write relevant balanced equations for the reactions that occurred.

[2]

Heat with aq NaOH, cool, and acidify with HNO₃, followed by aq AgNO₃



[Total: 24 marks]

4 (a) Gallium is an element in Group 13.

A sample of gallium contains two isotopes, ^{69}Ga and ^{71}Ga . The relative atomic mass of the gallium in this sample is 69.8.

(i) Explain what is meant by the term *relative atomic mass*. [1]

The relative atomic mass (A_r) of an element is defined as the ratio of the average mass of one atom of the element to $\frac{1}{12}$ the mass of a ^{12}C atom.

Or
$$A_r = \frac{\text{Average mass of 1 atom of the element}}{\frac{1}{12} \times \text{mass of 1 atom of } ^{12}\text{C}}$$

(ii) Calculate the percentage abundance of each of these isotopes. Show your working. [2]

Let % abundance of $^{69}\text{Ga} = x$

$$(x/100 \times 69) + ((1-x)/100 \times 71) = 69.8$$

% abundance of ^{69}Ga , $x = 60.0$

% abundance of $^{71}\text{Ga} = 40.0$

(iii) Complete the table which describes a gaseous atom of gallium. [2]

Isotope	Number of neutrons	Type of orbital contains electron in highest energy level	Total number of electrons in this highest occupied orbital
^{69}Ga	38	(4)p	1

(b) Gallium and its compounds show similar properties to aluminium and its compounds. Gallium reacts with excess chlorine to form gallium trichloride.

In their gaseous form, equimolar amounts of PH_3 and GaCl_3 combine to form a solid product PH_3GaCl_3 at 120°C in a closed reaction vessel.



The equilibrium constant was determined to be $550 \text{ mol}^{-2} \text{ dm}^6$.

(i) The reaction between PH_3 and GaCl_3 is similar to that between NH_3 and AlCl_3 . [2]

Suggest the role of GaCl_3 in this reaction. Explain your answer.

GaCl_3 functions as a Lewis acid as it has energetically accessible empty orbitals on Ga to accept lone pair of electrons from P in PH_3 .

- (ii) Write the expression for the equilibrium constant, K_c , for equilibrium 1. Hence, [2]
show that the concentration of PH_3 in the closed vessel was $0.0426 \text{ mol dm}^{-3}$
after some solid PH_3GaCl_3 was formed at equilibrium.

Let x be the equilibrium concentration of the reacting gases, PH_3 and GaCl_3 .

$$K_c = \frac{1}{[\text{PH}_3][\text{GaCl}_3]} = \frac{1}{x^2} = 550$$

$$x = 0.04264 = \underline{0.0426 \text{ mol dm}^{-3}}$$

- (iii) Suggest what happens to the concentration of PH_3 when some of the solid [1]
 PH_3GaCl_3 is removed.

If some solid PH_3GaCl_3 is removed, the position of equilibrium remains unchanged and hence the concentration of PH_3 (and GaCl_3) remains unchanged.

- (iv) Predict the effect on the equilibrium constant, K_c , when the reaction vessel is [2]
heated. Explain your answer.

In the formation of PH_3GaCl_3 , a dative bond exists within the molecule of PH_3GaCl_3 .

Thus the forward reaction is exothermic due to the formation of bond.

An increase in temperature would increase the rate constant of backward reaction to a greater extent than that of the forward reaction / rate of backward reaction increase more than rate of forward reaction.

Since $K_c = \frac{k_f}{k_b}$, K_c will decrease.

- (v) The value of K_c does not change when a catalyst is added. Explain why this is [2]
the case.

A catalyst provides an alternate reaction pathway with a lower activation energy for both the reaction hence the rate increase. The forward and backward reaction rate constants / rate increases by the same extent.

$K_c = \frac{k_f}{k_b}$ does not change.

- (c) Gallium is a silver-grey solid. Aluminium and gallium share many similar chemical properties.

Write the equation for the reaction between Ga_2O_3 and dilute hydrochloric acid. [1]



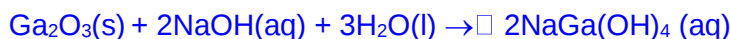
- (d) Gallium objects have a thin insoluble oxide layer on their surfaces. This oxide layer can be removed by adding aqueous sodium hydroxide to the gallium object.

An initial reaction occurs during which no observations are made. After a short time, bubbles of hydrogen gas are produced. When these bubbles appear, the object is removed from the aqueous sodium hydroxide and rinsed.

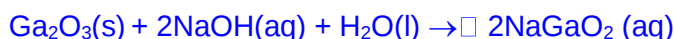
- (i) Explain why Ga_2O_3 is insoluble in water. [1]

Energy released in the ion-dipole attractions is not sufficient to overcome the strong ionic bonds in Ga_2O_3 and hydrogen bonds between water molecules.

- (ii) Write an equation, with state symbols, which describes the initial reaction occurring when $\text{NaOH}(\text{aq})$ is first added to the object, before the bubbles are seen. [2]



Or



- (iii) Explain, with the aid of a relevant equation, the reaction that resulted in the formation of H_2 gas. [2]

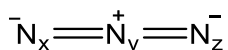


Once the Ga_2O_3 layer is removed by the $\text{NaOH}(\text{aq})$, Ga can react with water to form hydrogen gas.

[Total: 20 marks]

- 5 One important class of chemicals in everyday life are the azides, compounds which contain the azide anion N_3^- .

- (a) Given the structure of the azide ion, deduce the hybridisation of the nitrogen atom labelled N_y, and state the number of σ and π bonds present in the ion.



Azide ion

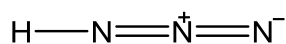
[2]

Hybridisation: sp

Number of σ bonds: 2

Number of π bonds: 2

- (b) The azide ion can be obtained from gaseous hydrazoic acid, HN₃, which has the following structure.



Hydrazoic acid

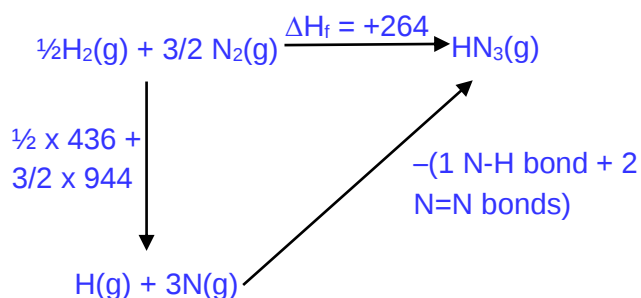
- (i) The enthalpy change of formation of gaseous hydrazoic acid is +264 kJ mol⁻¹. Using the relevant bond energy values from Table 5.1, calculate the average bond energy of the N=N double bond in hydrazoic acid.

You can assume that the bond energy in hydrazoic acid is not affected by the charges on the N atoms.

Bond	Bond energy / kJ mol ⁻¹
H-H	436
N≡N	944
N-H	390

Table 5.1

[3]



OR

ΔH_f = energy of bonds broken – energy of bonds formed

$$+264 = (\frac{1}{2} \times 436 + \frac{3}{2} \times 944) - (1 \times 390 + 2 \times \text{N=N bond})$$

$$\text{N=N bond energy} = +490 \text{ kJ mol}^{-1}$$

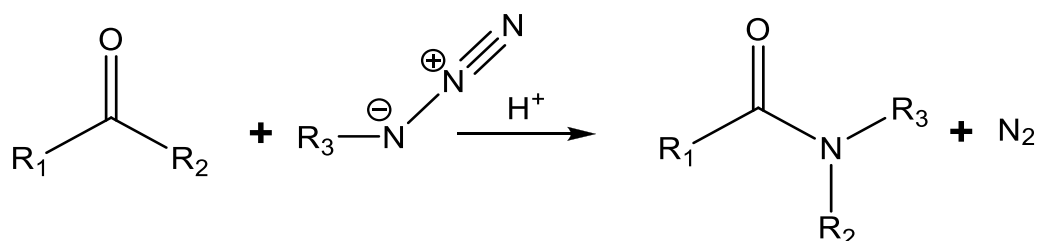
- (ii) Suggest why the value calculated in (b)(i) is different from the value stated in the *Data Booklet*.

[1]

The value from the Data Booklet is only an average value.

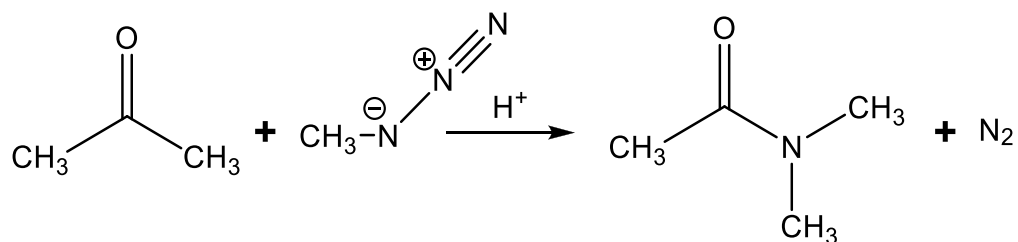
- (c) Azides are also a functional group in organic chemistry with the structure $R-N_3$, where R is an alkyl group. These are known as alkyl azides.

In the Schmidt/Boyer reaction, alkyl azides react with carbonyl compounds under acidic conditions to form amides.



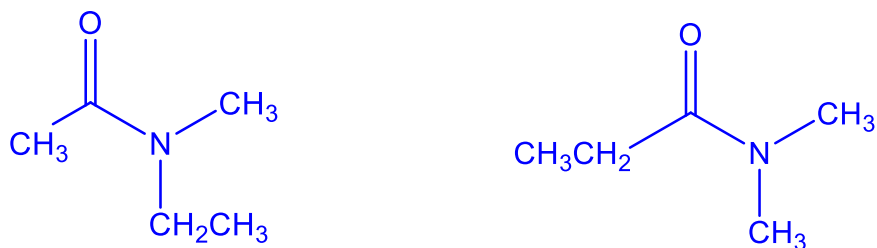
Where R₁/R₂ are H or alkyl groups.

For example, propanone reacts with methyl azide to form an amide.



- (i) When butanone reacts with methyl azide, two products are formed. Draw the structure of both organic products.

[2]



One mark for each product

- (ii) The Schmidt/Boyer reaction is very useful in synthesising β -lactams, four-member cyclic amides, a structure found in many antibiotics.

[2]

Compound **R** is an example of a simple β -lactam. Compound **R** can be prepared by a sequence of reactions, starting from 3-chloro-2-methylpropanal as shown in Fig. 5.1.

Suggest the type of reaction for Reaction **1**, and suggest the structure of compound **Q**, which has an aldehyde and an azide group.

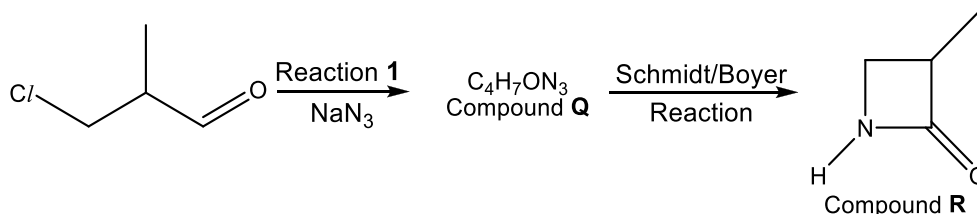
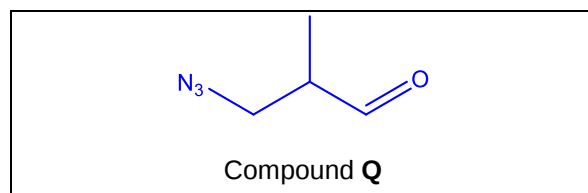


Fig 5.1

Reaction **1**: Nucleophilic substitution



- (iii) Compound **R** is not basic. Explain. [1]

The lone pair of electrons on the N atom are delocalised over the N-C-O group and hence not available for donation.

- (iv) Using VSEPR theory **only**, state the *expected* bond angle of the C-N-C bond in compound **R**. [1]

3 bond pairs, 1 lone pair

Expected bond angle: 107°

- (v) The C-N-C bond in compound **R** has been experimentally found to be 90° . Using this information and your answer in (c)(iv), suggest why compound **R** undergoes hydrolysis more readily than ethanamide. [1]

There is ring strain present, hence the C-N bond is weak and easily broken.

[Total: 13 marks]