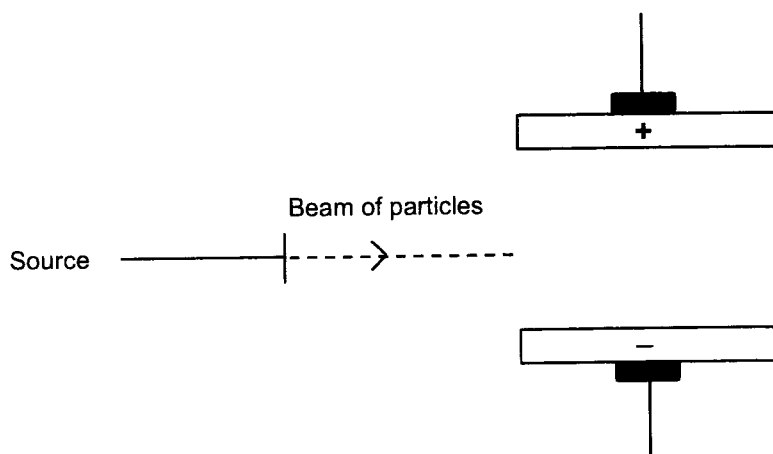


2

- 1 In two separate experiments, a beam of protons and electrons, travelling at the same velocity is passed through an electric field as shown.



Which statement is correct?

- A The proton beam is deflected in a parabolic path to a larger extent than the electron beam.
- B The proton beam travels in a straight path towards the negatively charged plate.
- C The electron beam travels in a straight path towards the negatively charged plate.
- D The proton beam is deflected in a parabolic path towards the negatively charged plate.
- 2 *Use of the Data Booklet is relevant to this question.*

The table below shows the fifth, sixth, seventh, eighth and ninth ionisation energies of an element **D** ($Z \leq 20$) in the Periodic Table.

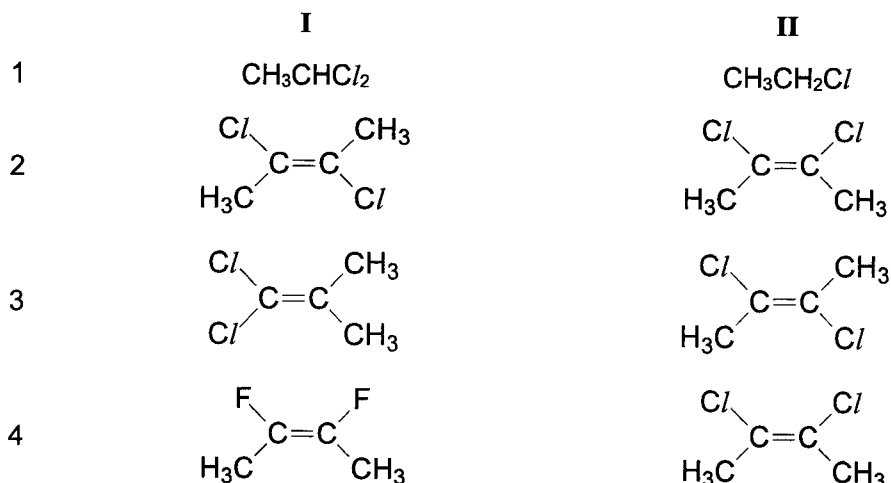
	5th	6th	7th	8th	9th
ionisation energy / kJ mol^{-1}	6530	9353	11 019	33 606	38 676

What can be inferred about the element from the above data?

- A It is in the second period of the Periodic Table.
- B It has a valence electronic configuration of ns^2np^4 .
- C Its 5th and 6th electrons are removed from different subshells.
- D It is likely to form an ionic compound Mg_3D_2 with magnesium.

3

- 3 Which pair of molecules have a greater permanent dipole in molecule I than in molecule II?



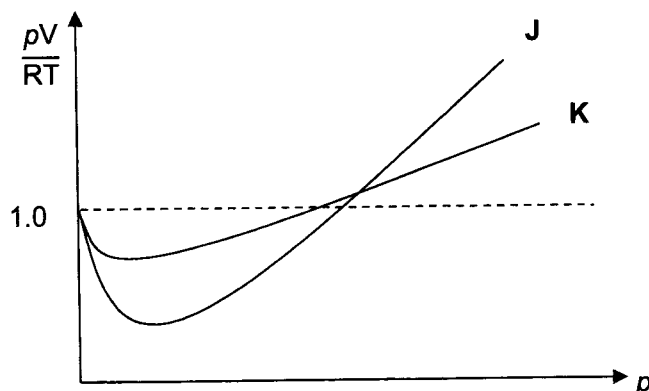
- A 1 and 2 only
 B 3 and 4 only
 C 2, 3 and 4 only
 D 1, 3 and 4 only
- 4 Four substances have the physical properties as shown.

Compound	Melting point/ $^{\circ}\text{C}$	Electrical conductivity of solid	Electrical conductivity of molten substance
E	-72	poor	poor
F	801	poor	good
G	842	good	good
H	1710	poor	poor

Which of the following shows the correct type of structures for each compound?

	E	F	G	H
A	simple molecular structure	giant ionic structure	giant metallic structure	giant molecular structure
B	giant molecular structure	giant metallic structure	giant ionic structure	giant molecular structure
C	giant molecular structure	simple molecular structure	giant metallic structure	giant ionic structure
D	simple molecular structure	giant ionic structure	giant molecular structure	giant metallic structure

- 5 The value of $\frac{pV}{RT}$ is plotted against p for one mole of each of the two gases, **J** and **K**, where p is the pressure, V is the volume and T is the temperature of the gas.



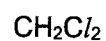
Which of the following statements is true about gases **J** and **K**?

- A** Gas **J** is N_2 and gas **K** is O_2 because there is stronger instantaneous dipole-induced dipole interactions between N_2 molecules than O_2 .
- B** Gas **J** is HBr and gas **K** is HI because there is stronger instantaneous dipole-induced dipole interactions between HI molecules than HBr .
- C** Gas **J** is HBr and gas **K** is H_2O because there is stronger permanent dipole-permanent dipole interactions between HBr molecules than the weaker instantaneous dipole-induced dipole interactions between H_2O molecules.
- D** Gas **J** is HBr and gas **K** is F_2 because there is stronger permanent dipole-permanent dipole interactions between HBr molecules than the weaker instantaneous dipole-induced dipole interactions between F_2 molecules.

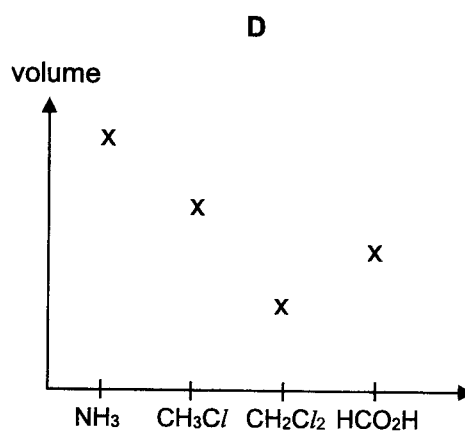
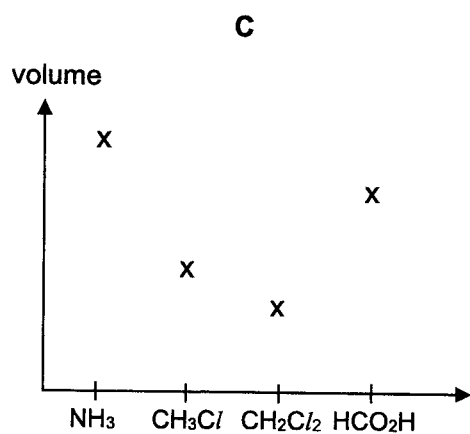
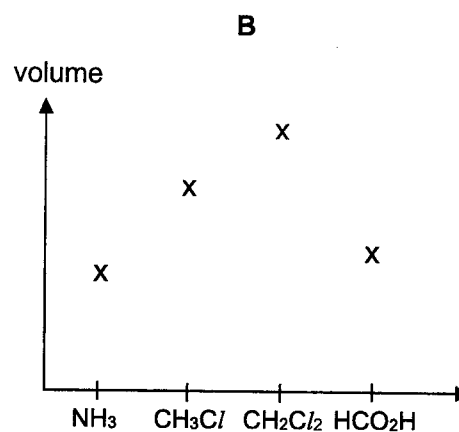
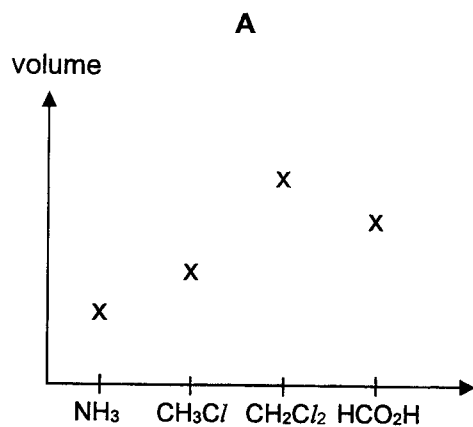
5

- 6 Use of Data Booklet is relevant to this question.

At 800 K, the following compounds all behave as ideal gases.



Which of the following diagram is correct for a given mass of each of these gases at constant pressure?



- 7 Use of Data Booklet is relevant to this question.

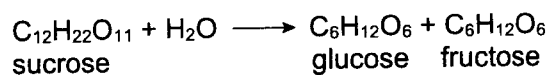
What is the correct order of the lattice energies of magnesium oxide, magnesium chloride and sodium chloride, starting with the highest numerical value?

- A $\text{MgO} > \text{NaCl} > \text{MgCl}_2$
 B $\text{MgO} > \text{MgCl}_2 > \text{NaCl}$
 C $\text{MgCl}_2 > \text{MgO} > \text{NaCl}$
 D $\text{MgCl}_2 > \text{NaCl} > \text{MgO}$

6

- 8 Which quantity would best indicate the relative strengths of the intermolecular forces of attraction between the molecules in liquid hydrogen halides?
- A Bond dissociation energies
 B Enthalpy changes of vapourisation
 C Enthalpy changes of formation
 D Enthalpy changes of atomisation

- 9 Sucrose undergoes an acid-catalysed hydrolysis according to the following equation.



The following results were obtained using hydrochloric acid as the catalyst.

experiment	initial [HCl] / mol dm ⁻³	initial [sucrose] / mol dm ⁻³	initial rate / mol dm ⁻³ s ⁻¹
I	0.10	0.10	0.024
II	0.10	0.15	0.036
III	0.30	0.10	0.072

The half-life of sucrose in experiment I was 3.0 s.

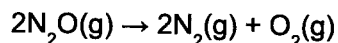
What is the half-life of sucrose in experiment II and in experiment III?

	experiment II	experiment III
A	3.0	3.0
B	3.0	1.0
C	2.0	1.0
D	2.0	3.0

- 10 Which suggested mechanism is consistent with the experimentally obtained rate equation?

	rate equation	suggested mechanism
1	$\text{rate} = k_1 [\text{H}_2\text{O}_2] [\text{I}^-]$	$\text{H}_2\text{O}_2 + \text{I}^- \xrightarrow{\text{slow}} \text{H}_2\text{O} + \text{OI}^-$ $\text{OI}^- + \text{H}^+ \xrightarrow{\text{fast}} \text{HOI}$ $\text{HOI} + \text{H}^+ + \text{I}^- \xrightarrow{\text{fast}} \text{I}_2 + \text{H}_2\text{O}$
2	$\text{rate} = k_2 [\text{H}_2] [\text{I}_2]$	$\text{H}_2 \xrightarrow{\text{slow}} 2\text{H}$ $2\text{H} + \text{I}_2 \xrightarrow{\text{fast}} 2\text{HI}$
3	$\text{rate} = k_3 [\text{HBr}]^2 [\text{O}_2]^{1/2}$	$2\text{HBr} + \text{O}_2 \xrightarrow{\text{fast}} 2\text{HBrO}$ $\text{HBrO} + \text{HBr} \xrightarrow{\text{slow}} \text{H}_2\text{O} + \text{Br}_2$

- A 1 and 2 only
 B 1 only
 C 1 and 3 only
 D 2 and 3 only
- 11 In the presence of gold wire as a catalyst, 25.0 kPa of dinitrogen oxide, N_2O , decomposes in a closed container according to the equation below.

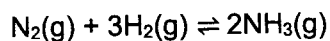


The units of the rate constant was found to be s^{-1} .

Which of the following remains constant during the experiment?

- A The rate of the reaction.
 B The total pressure of the reaction mixture.
 C The value of rate constant in the absence of gold.
 D The time taken for the pressure of N_2O to drop by half.

- 12 The rates of the reversible reaction to produce ammonia in a closed vessel can be affected by changing the pressure of reactants or adding a catalyst.



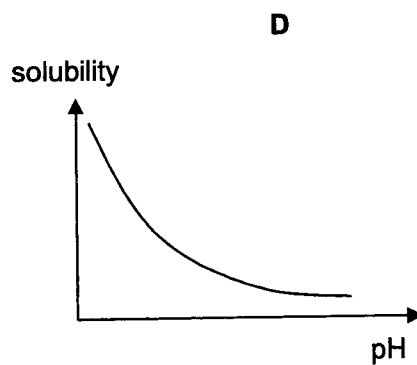
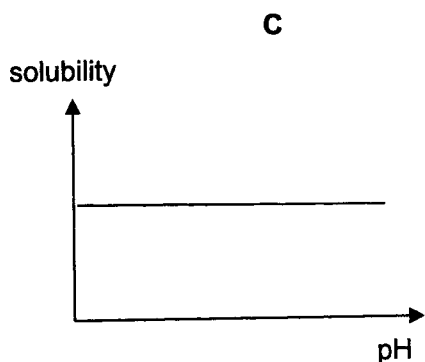
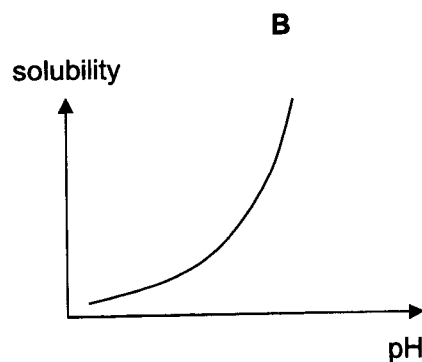
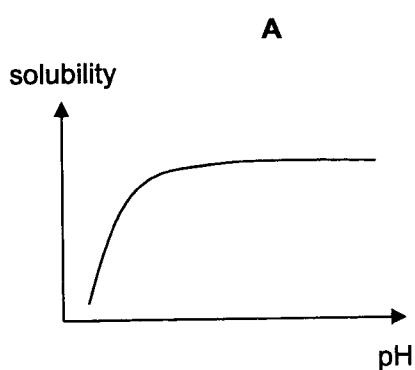
Which of the following statements about the system are correct?

- 1 Increasing partial pressure of nitrogen increases the rate of the forward reaction.
- 2 Decreasing the partial pressure of nitrogen increases the rate of the reverse reaction.
- 3 Adding a catalyst does not affect the value of the rate constant, k .
- 4 Adding a catalyst reduces the activation energies for both the forward and reverse reaction.

- A** 1, 2 and 4
B 2, 3 and 4
C 2 and 3
D 1 and 4 only

- 13 Aqueous HF is a weak acid. Magnesium fluoride is sparingly soluble.

Which graph below shows how the solubility of MgF_2 in water will vary with pH at constant temperature?



- 14 The variation of the ionic product of water, K_w , with temperature is given in the table.

Temperature/ °C	$K_w / \text{mol}^2 \text{dm}^{-6}$
25	1.00×10^{-14}
50	5.50×10^{-14}
62	1.00×10^{-13}

What can be deduced from this information?

- A The ionisation of water is an exothermic process.
 B $[\text{H}^+]$ is more than $[\text{OH}^-]$ as temperature increases.
 C pH of water at 10 °C is higher than at 25 °C.
 D The equilibrium position lies furthest to the right at 25 °C.
- 15 Aqueous ethanenitrile, CH_3CN , has no effect on litmus but aqueous ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$, turns litmus blue.

Which statements below can be used to explain this observation?

- 1 Delocalisation of the lone pair of electrons on the nitrogen atom of CH_3CN over the $\text{C}\equiv\text{N}$ group strengthens the C-N bond.
- 2 Lone pair of electrons on the nitrogen atom of $\text{C}\equiv\text{N}$ are in an sp hybridised orbital which is closer to the nucleus than the lone pair of electrons on the sp^3 hybridised nitrogen atom of the NH_2 group.
- 3 The ethyl group in ethylamine is a stronger electron donating group than the methyl group in ethanenitrile as it has one more carbon atom.

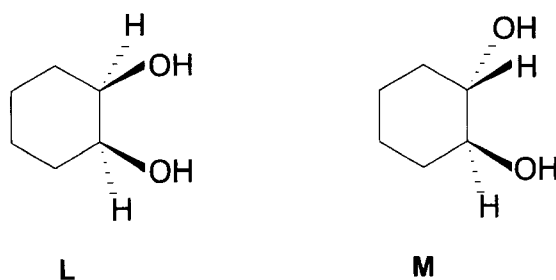
- A 1, 2 and 3 B 1 only C 2 and 3 D 2 only
- 16 1 mol each of an aliphatic alkane and an alkene with the same number of carbon atoms per molecule, are separately burned.

Which statement about the complete combustion of these hydrocarbons is always correct?

- A The volume of gas produced at 298 K is the same for both reactions.
 B The volume of oxygen required for combustion of the alkane is twice that required for the alkene.
 C The volume of steam produced from the alkene is twice the volume of carbon dioxide at 400 K.
 D The volume of oxygen required for the alkane is directly proportional to the number of carbon atoms present in the molecule.

10

17 Two isomers, **L** and **M**, of cyclohexane-1,2-diol are shown below.

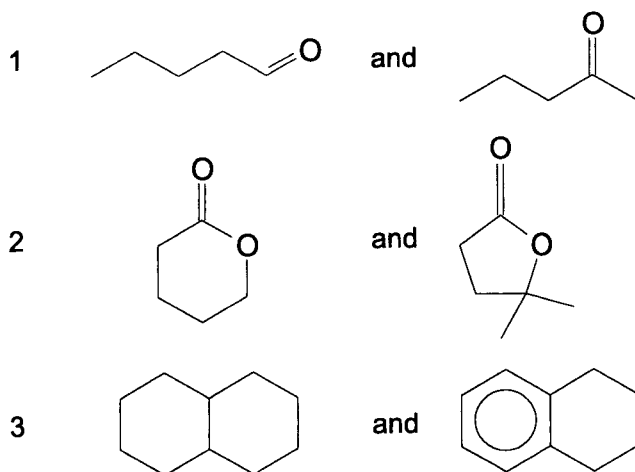


Which statements are correct?

- 1 **L** and **M** are a pair of cis-trans isomers.
- 2 Both isomers **L** and **M** rotate plane-polarised light.
- 3 An equimolar mixture of **L** and **M** forms a racemic mixture.

A 1, 2 and 3 **B** 2 and 3 **C** 1 only **D** 3 only

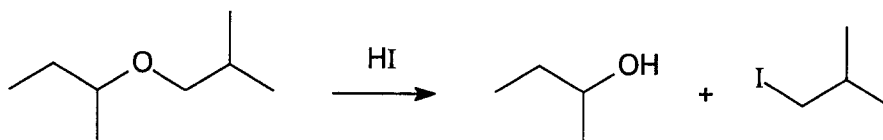
18 Which of the following pairs of compounds can be distinguished from each other when heated with aqueous acidified KMnO_4 ?



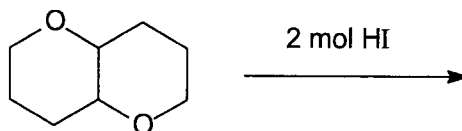
A 1, 2 and 3 **B** 1 and 3 **C** 2 and 3 **D** 1 only

11

19 Ethers are cleaved by HI via an S_N2 mechanism.



Which of the following is the most likely product for the following reaction?

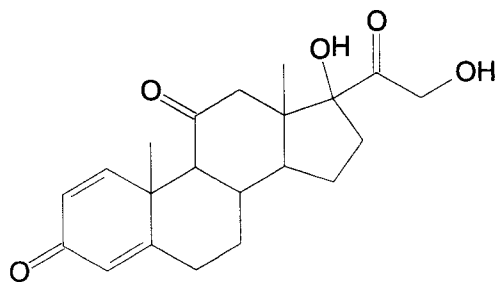


- A
- B
- C
- D

12

20 Compound **P** is a steroid medication used to reduce inflammation and treat certain allergies.

P can be reduced to compound **Q** by NaBH_4 in ethanol.



compound **P**

How many chiral centres exist for **P** and for **Q**?

	P	Q
A	6	7
B	6	9
C	7	8
D	7	10

21 Equal amounts of two organic compounds, **Y** and **Z**, were added to water and the pH values of both solutions were determined. It was found that the pH of the aqueous solution of **Y** is higher.

Which pairs of compounds could be **Y** and **Z**?

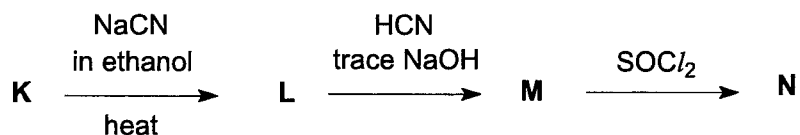
	Y	Z
1	$(\text{CH}_3)_2\text{NH}$	CH_3NH_2
2	$\text{CH}_3\text{COCH}_2\text{NH}_2$	$\text{CH}_3\text{CH}_2\text{CONH}_2$
3	$\text{C}_6\text{H}_5\text{O}^-\text{Na}^+$	$\text{C}_6\text{H}_5\text{CO}_2^-\text{Na}^+$

A 1, 2 and 3 **B** 1 and 2 **C** 2 and 3 **D** 1 only

13

22 **K**, C_2H_3OCl , produces a grey-black solid with Tollens' reagent.

K can be converted into **N** as shown.

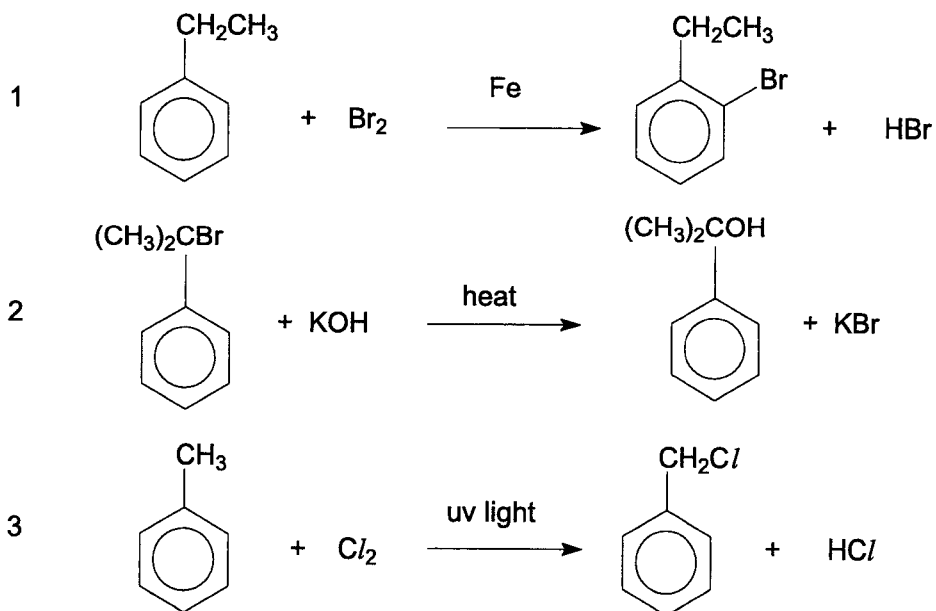


What could be the structure of **N**?



23 In some organic reactions, the reactive carbon atom is tetrahedral in the reactant molecule but **not** tetrahedral in the organic intermediate.

To which of the following reactions does this statement apply?



A 1, 2 and 3

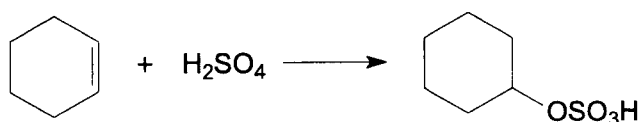
B 2 and 3

C 1 only

D 3 only

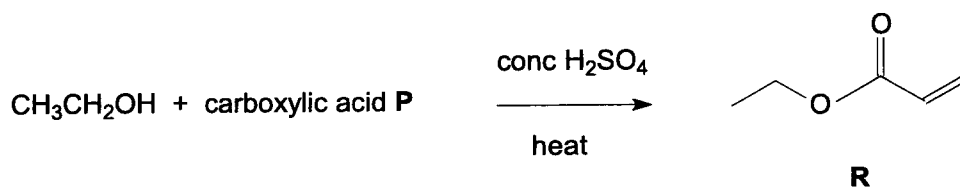
14

- 24 Cyclohexene reacts with cold, concentrated sulfuric acid in an addition reaction to produce alkyl hydrogensulfate.



Which of the following statements best explain why benzene does **not** react in a similar way?

- A** The π electron cloud of the benzene repels the HSO_4^- ion.
B Steric hindrance by benzene prevents SO_3H^+ from reacting with it.
C The concentrations of the ions produced from the dissociation of concentrated H_2SO_4 are too low.
D Reacting with sulfuric acid in an addition reaction prevents the continuous overlap of the p orbitals of all the six carbon atoms in the benzene ring.
- 25 **R** can be synthesized in the laboratory by heating ethanol and carboxylic acid **P** in the presence of concentrated sulfuric acid as shown.



What could be **P** and a by-product of this reaction?

	P	by-product
1	$\text{CH}_3\text{CH}_2\text{COOH}$	
2	$\text{HOCH}_2\text{CH}_2\text{COOH}$	
3	$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	

A 1 and 3**B** 1 only**C** 2 and 3**D** 3 only

- 26 Element Z is a solid with a very low electrical conductivity at room temperature. It forms only one chloride, which is a liquid at room temperature and is a non-conductor of electricity. The chloride hydrolyses in water forming a white solid and a strongly acidic solution.

Which of the following could be Z?

- A Aluminium
- B Magnesium
- C Phosphorus
- D Silicon

- 27 Prussian blue is a deep blue insoluble pigment that is used as a dye for paper and ink.

It is made up of Fe^{3+} cations and octahedral $[\text{Fe}(\text{CN})_6]^{4-}$ complex anions, with the chemical formula $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

It can be prepared in two methods.

Method 1: mixing aqueous solutions of FeCl_3 and $\text{K}_4\text{Fe}(\text{CN})_6$

Method 2: mixing aqueous solutions of FeCl_2 and $\text{K}_3\text{Fe}(\text{CN})_6$

Which of these statements are correct?

- 1 Method 1 involves a redox reaction.
- 2 Method 2 involves a ligand exchange reaction.
- 3 Both methods will produce blue ppt and a colourless solution.

- A 1, 2 and 3
- B 1 and 2
- C 2 and 3
- D 2 only

- 28 Which statement explains why an aqueous solution of silver(I) nitrate is colourless?

- A Silver is a transition element.
- B There is no d-orbital splitting in silver(I) ion.
- C The 4d subshell of silver(I) ion is fully filled.
- D The size of the energy gap between the non-degenerate d-orbitals is too big.

16

29 Use of the Data Booklet is relevant to this question.

A voltaic cell is made up of Mg^{2+}/Mg half-cell and $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell.

Which one of the following statements is correct?

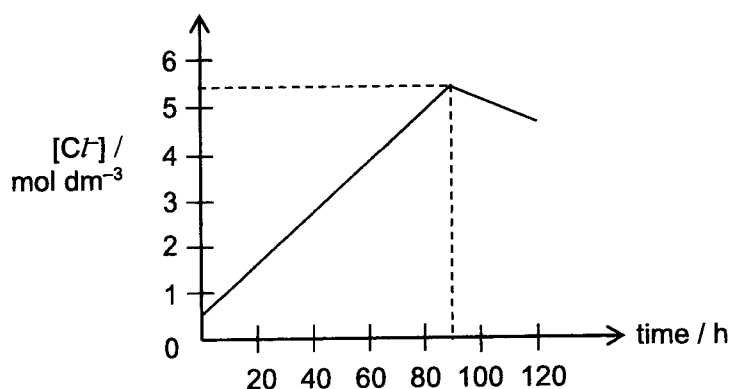
- A The Mg^{2+}/Mg half-cell is the positive electrode.
- B Increasing the size of Mg electrode has no effect on the e.m.f. of the cell.
- C Addition of water to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell decreases the e.m.f. of the cell.
- D Decreasing the pressure of the voltaic cell would increase the e.m.f. of the cell.

30 Use of the Data Booklet is relevant to this question.

The primary source of oxygen gas in modern submarines comes from the electrolysis of seawater. Typically, seawater contains less than 1 mol of sodium chloride in 1 dm^3 of seawater.

In an experiment, a sample of seawater was electrolysed over a period of 120 hours, and no additional seawater was introduced during this period.

A graph was plotted to show how the concentration of chloride ions changes as the reaction proceeds.



Which of these statements is **incorrect**?

- A At 90 h, Cl^- is preferentially oxidised to Cl_2 gas.
- B Concentration of Cl^- increases linearly as the H_2O is reacted away.
- C At 60 h, the volume of gas collected at cathode and anode is the same.
- D Purple litmus solution added at 20 h would turn red and blue at the anode and the cathode respectively.



ANDERSON SERANGOON JUNIOR COLLEGE

2022 JC 2 PRELIMINARY EXAMINATION

NAME: _____ () CLASS: 22 / _____

CHEMISTRY

Paper 2 Structured Questions

9729/02

14 September 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register 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.

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

A Data Booklet is provided.

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

For Examiner's Use		
Paper 2	1	/ 10
	2	/ 12
	3	/ 15
	4	/ 10
	5	/ 18
	6	/ 10
s.f./units		
Total		/ 75

This document consists of **21** printed pages and **3** blank pages.

Answer **all** the questions.

- 1 (a) Calcium, magnesium, and zinc are three minerals that are vital to several bodily processes. Though they occur naturally in a variety of food, many people take supplements that contain these minerals usually found in the +2 oxidation state.

- (i) State and explain how the second ionisation energy of calcium compares with that of magnesium.

.....

[2]

- (ii) By quoting relevant data from the *Data Booklet*, suggest how the thermal stability of ZnCO_3 compares with that of MgCO_3 and CaCO_3 . Explain your answer.

.....

[2]

- (b) Beryllium exhibits physical and chemical properties that are anomalous to the rest of the Group 2 alkaline earth metals. Due to the similarities in electronegativity, beryllium shares many physical and chemical properties with aluminium in Group 13 instead.

- (i) Beryllium forms a complex ion in aqueous solutions with the following structure, $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$.

Suggest an equation to show the hydrolysis of beryllium ions in water.

.....[1]

- (ii) Beryllium oxide is amphoteric.

Write two chemical equations, with state symbols, showing its reaction with aqueous NaOH and dilute HCl respectively.

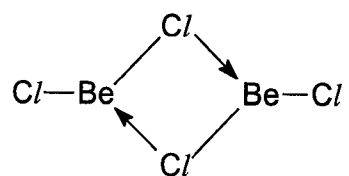
.....
[2]

- (iii) Explain why beryllium chloride is not ionic.

.....
[1]

3

(iv) When beryllium chloride is heated, it sublimes and forms gaseous Be_2Cl_4 dimers.



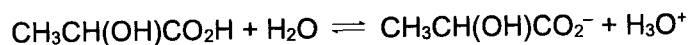
By considering the numbers and type of electron pairs, explain the change in shape and bond angle about the Be atom during the dimerisation of beryllium chloride.

.....
.....
.....
.....[2]

[Total: 10]

- 2 (a) Both lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$, and ethanoic acid are colourless liquids at 298 K.

Lactic acid dissociates in water to form its conjugate base, lactate ion $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2^-$.



An intramolecular hydrogen bond can be formed in the lactate ion.

- (i) Draw the structure of the lactate ion showing the intramolecular hydrogen bond formed.

[1]

- (ii) Hence, suggest how the K_a of lactic acid would differ from that of ethanoic acid. Explain your answer.

.....
[1]

- (b) Nicotinamide adenine dinucleotide (NAD^+) is a coenzyme responsible for carrying electrons from one reaction to another in living cells.

The electrode potential for the reduction of NAD^+ in a biological system, $E(\text{pH } 7)$, in which the conditions are at 1 mol dm^{-3} , 25°C and $\text{pH } 7$, is as shown. The reduced form of NAD^+ is represented as NADH .



The Nernst equation can be used to calculate the electrode potential of the above system when $[\text{NAD}^+]$ and $[\text{NADH}]$ change.

$$E = E(\text{pH } 7) - \left(\frac{0.0592}{n} \right) \log_{10} \frac{[\text{NADH}]}{[\text{NAD}^+]}$$

where n is the number of moles of electrons transferred in the system.

- (i) Using the Nernst equation given, determine the ratio $\frac{[\text{NADH}]}{[\text{NAD}^]}$ when $E = -0.350 \text{ V}$.

[1]

5

- (ii) Hence, calculate the percentage of NAD^+ in the NAD^+ - NADH mixture when $E = -0.350 \text{ V}$.

[1]

During intense exercise where there is insufficient supply of oxygen, pyruvic acid, $\text{CH}_3\text{COCO}_2\text{H}$, is converted to lactic acid.

This process involves the conjugate bases of the two acids and the conversion of coenzyme NADH to NAD^+ , as shown below. The standard cell potential of this reaction is measured at 25°C and $\text{pH } 7$.



- (iii) Write the half-equation for the reduction of pyruvate to lactate in an acidic condition and calculate its standard electrode potential at 25°C and $\text{pH } 7$.

.....

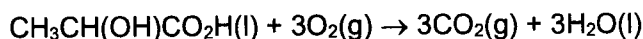
[2]

- (iv) Calculate ΔG for the anaerobic metabolism of pyruvate at $\text{pH } 7$.

[1]

6

- (c) The standard enthalpy change of combustion of lactic acid can be represented as shown.



- (i) What do you understand by the term *standard enthalpy change of combustion of lactic acid*?

.....

[1]

- (ii) Using the data in Table 2.1, calculate standard enthalpy change of combustion, ΔH_c^\ominus , of lactic acid.

Table 2.1

Species	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}(\text{l})$	-483.2
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{l})$	-285.8

[1]

- (iii) Use the bond energies given in the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of lactic acid.

[2]

- (iv) Apart from average bond energy values found in the *Data Booklet*, suggest one other reason for the difference in your answers in (c)(ii) and (c)(iii).

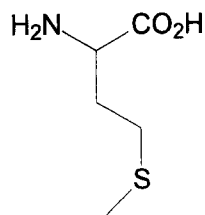
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[1]

[Total: 12]

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8

- 3 (a) Methionine is an essential amino acid in humans. It plays a critical role in the metabolism and health of humans because it is the precursor of other amino acids such as cysteine and taurine.



Methionine

The pK_a values associated with methionine are 2.28 and 9.21.

- (i) Calculate the pH of 0.15 mol dm^{-3} solution of methionine, ignoring the effect of the second pK_a value.

[1]

- (ii) Draw the structure of the zwitterionic form of methionine.

[1]

- (iii) Write two equations to describe how a solution containing the zwitterionic form of methionine can act as a buffer.

[2]

9

- (iv) When 10 cm^3 of 0.15 mol dm^{-3} of **protonated** methionine was titrated against aqueous sodium hydroxide, the first equivalence point was reached when 15 cm^3 of the 0.10 mol dm^{-3} NaOH was added.

At the first equivalence point, only the zwitterionic form of methionine exists.

With the use of relevant equilibrium constant values, explain if the pH of the solution at the first equivalence point is less than, equal to or more than 7.

.....

[2]

- (v) Using the value and information from (a)(i) and (a)(iv), as well as the pK_a values provided, sketch the pH–volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.15 mol dm^{-3} **protonated** methionine.

[2]

- (vi) Suggest a suitable indicator for the first equivalence point in the above titration.

.....
[1]

10

- (b) Fig. 3.1 shows the four-step synthesis of an amino acid from an aldehyde, via an intermediate **G**.

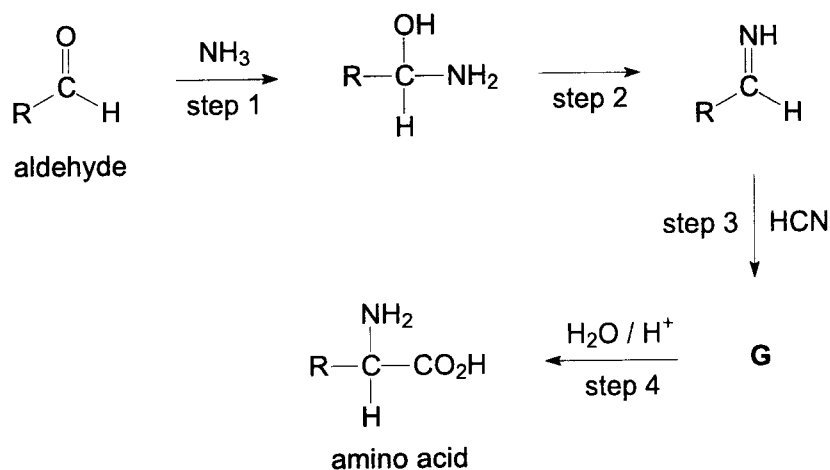


Fig. 3.1

- (i) State the types of reaction that occur during each of the steps 1 and 2.

.....
[2]

- (ii) Suggest the structure of compound **G**.

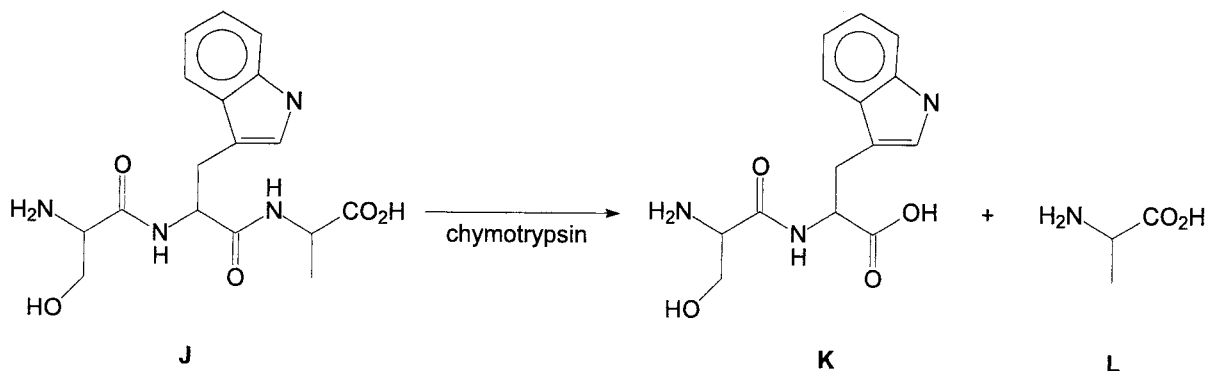
[1]

- (iii) Draw the displayed formula of a suitable starting aldehyde that can be used to synthesise methionine.

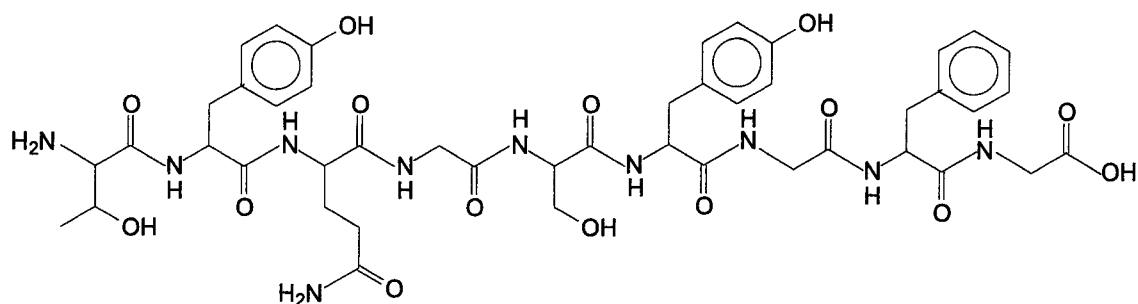
[1]

11

- (c) Chymotrypsin is an enzyme that hydrolyses proteins into smaller peptides and amino acids. It specifically hydrolyses the peptide bond on the carboxyl side of a residue that contains an aromatic ring. For example, the tripeptide **J** produces two compounds **K** and **L** as shown.



The following shows part of a short amino acid sequence found in human protein.



Draw the two dipeptides formed when the above amino acid sequence is hydrolysed by chymotrypsin.

[2]

[Total: 15]

- 4 (a) Table 4.1 shows the pK_a values for some chlorine-containing organic acids.

Table 4.1

acid	pK_a
$\text{CH}_3\text{CHClCO}_2\text{H}$	2.80
$\text{CH}_3\text{CCl}_2\text{CO}_2\text{H}$	1.74
$\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$	x

- (i) Explain the relative pK_a values of $\text{CH}_3\text{CHClCO}_2\text{H}$ and $\text{CH}_3\text{CCl}_2\text{CO}_2\text{H}$.

.....

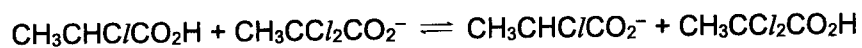
[2]

- (ii) Suggest a value for x and explain your answer.

.....

[1]

- (iii) An equilibrium is set up between $\text{CH}_3\text{CHClCO}_2\text{H}$ and $\text{CH}_3\text{CCl}_2\text{CO}_2\text{H}$ in the aqueous medium.



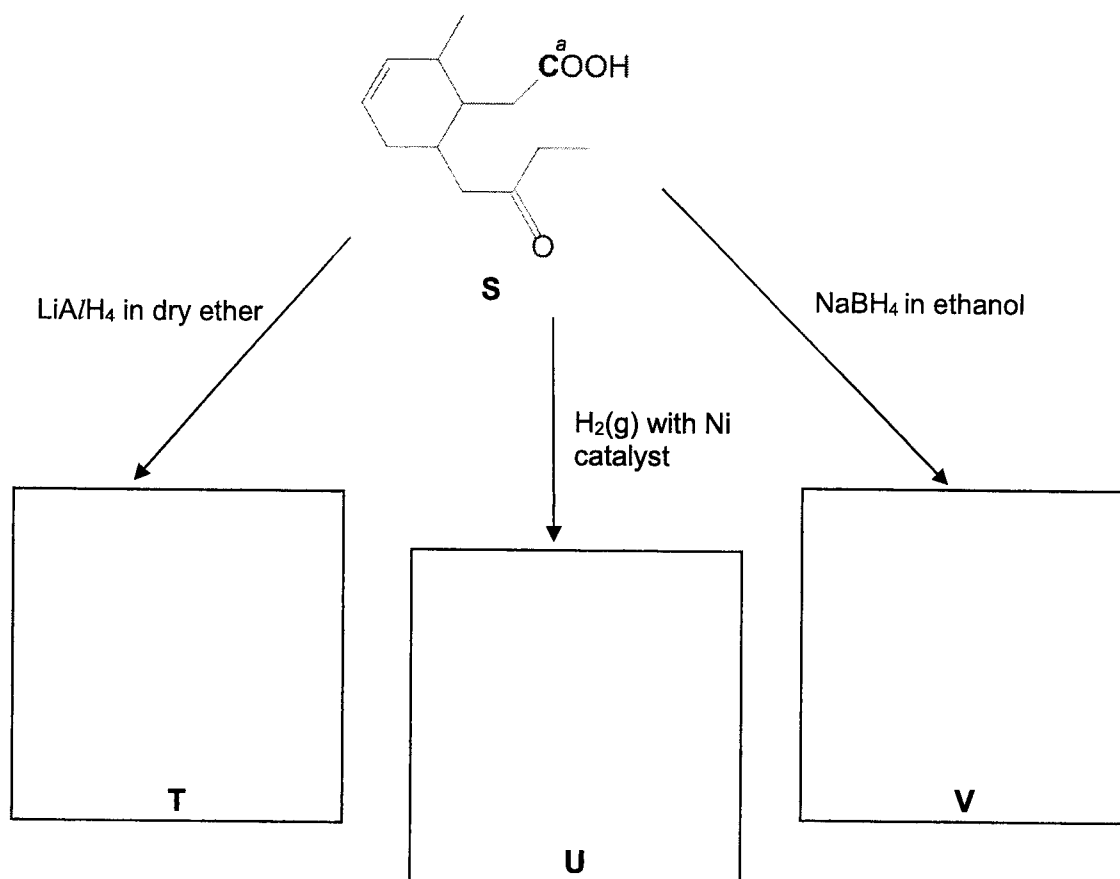
Using the data in Table 4.1, calculate K_c for the above equilibrium.

[2]

13

- (b) (i) The following reagents are added to separate samples of compound **S**.

Draw the structure of each of the organic products, **T**, **U** and **V**.



[3]

- (ii) LiAlH₄ is a source of H⁻ and widely used as a reducing agent in organic chemistry.

Identify the functional group, other than alkane, in compound **S** that is not reduced by LiAlH₄. Suggest why.

.....
[1]

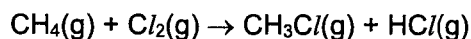
- (iii) Determine the change in oxidation number of C^a when compound **S** is reduced to **T**.

.....[1]

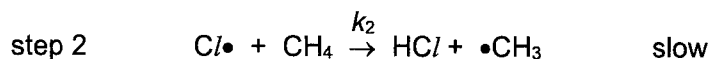
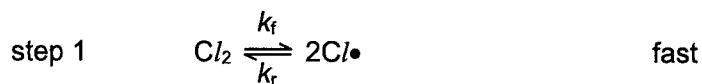
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- 5 (a) The kinetics of the chlorination of methane is studied.



The first two steps of the mechanism of the reaction are shown below.



- (i) The rate equation for the reverse of step 1 is $\text{rate} = k_r[\text{Cl}\bullet]^2$.

At equilibrium, the rates of the forward and reverse reactions in step 1 are equal.

Write the rate equation for the forward reaction of step 1 and hence write an expression for the concentration of the intermediate $\text{Cl}\bullet$ radicals.

.....
[2]

- (ii) Write the rate equation for the forward reaction of step 2.

.....[1]

- (iii) Use your answer to (a)(i) and the rate equation for step 2 to write the overall rate equation for the chlorination of methane.

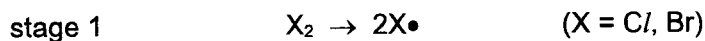
Hence, deduce the orders of reaction with respect to the concentration of the species in the overall rate equation and the overall order of the reaction.

.....

[2]

16

- (b) When chlorine and bromine react with methane, light of different energy and wavelength is required for stage 1 of the reaction.



Light of longer wavelength is lower in energy than light of shorter wavelength.

This relationship between the energy and wavelength of light is shown in the equation below.

$$E = \frac{hc}{\lambda}$$

Where: E is the energy of the light of certain wavelength in Joule (J)
 h is Planck constant = 6.63×10^{-34} J s
 c is the speed of light = 3.00×10^8 m s⁻¹
 λ is the wavelength of light in metre (m)

- (i) Bond energy is the energy required to break **one mole** of a covalent bond in the gaseous state.

Using the *Data Booklet* and the equation $E = \frac{hc}{\lambda}$, determine the wavelength of light required to break **one Cl-Cl** bond.

Leave your answer in nanometres (nm). One nm is equivalent to 10^{-9} m.

[2]

17

- (ii) Using Table 5.1, identify the colour of light that provides the minimum energy for the reaction between chlorine and methane.

Table 5.1

Colour	Wavelength / nm
Violet	380 – 450
Blue	450 – 495
Green	495 – 570
Yellow	570 – 590
Orange	590 – 620
Red	620 – 750

.....[1]

- (iii) Hence, explain why the bromination of methane can be carried out with yellow light. (Calculation is not required)

.....
.....[1]

18

- (c) Fig. 5.1 shows four possible monohalogenoalkanes that can be formed from the reaction of 2-methylbutane with chlorine or bromine. ($X = Cl$ or Br)

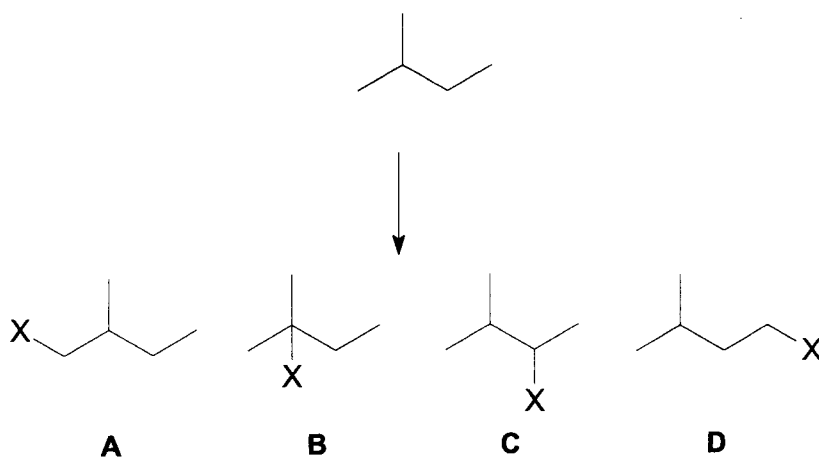


Fig. 5.1

- (i) State the expected ratio of products **A**, **B**, **C** and **D** in the mixture, assuming equal rate of substitution of all the H atoms.

.....[1]

- (ii) The ratio of the isomeric products is more accurately determined if the relative rates of substitution of different H atoms by different halogen atoms are taken into account.

The types of hydrogen atoms in alkanes, together with their relative rates of substitution by Cl and Br atom, are shown in Table 5.2.

Table 5.2

Types of H atoms	Structure	Relative rate of substitution by Cl atom	Relative rate of substitution by Br atom
Primary	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	1	1
Secondary	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{H} \\ \\ \text{R}' \end{array}$	3	80
Tertiary	$\begin{array}{c} \text{R}'' \\ \\ \text{R}-\text{C}-\text{H} \\ \\ \text{R}' \end{array}$	5	1600

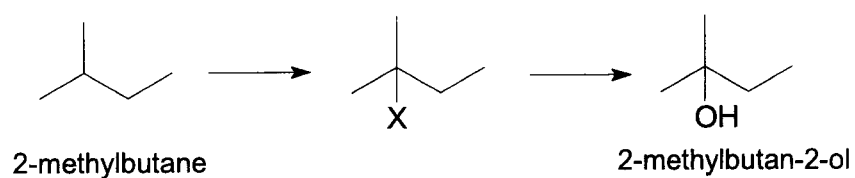
By taking into account the relative rates of substitution of H atoms given above, show that:

- the monochlorinated forms of products **A**, **B**, **C** and **D** are formed in the ratio of 6:5:6:3.
- the monobrominated forms of products **A**, **B**, **C** and **D** are formed in the ratio of 6:1600:160:3.

[2]

20

- (iii) 2-methylbutan-2-ol may be synthesised from 2-methylbutane by using the reaction scheme as shown.



Using the ratios given in (c)(ii), explain if chlorine or bromine is a better choice of reagent in this synthesis.

.....
.....[1]

21

- (d) One of the possible termination steps in the free radical substitution reaction is the reaction between two alkyl radicals to form an alkane.

The equation shows the collision of two propyl radicals in the termination step of a reaction between propane and chlorine.



- (i) Use the data in Table 5.3 to calculate the enthalpy change for this termination step at 298 K.

Table 5.3

species	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\bullet\text{C}_3\text{H}_7(\text{g})$	+103
$\text{C}_6\text{H}_{14}(\text{g})$	-167

[1]

- (ii) Explain how the values of ΔH^\ominus and ΔS^\ominus relate to the changes that occur at the molecular level for this termination step.

.....

[2]

- (iii) Calculate ΔG^\ominus for this termination step at 298 K and explain the effect on the spontaneity of this reaction of increasing the temperature above 298 K.

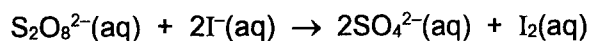
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[2]

[Total: 18]

22

- 6 (a) Iron(II) ions catalyse the reaction between iodide ions and peroxodisulfate ions ($\text{S}_2\text{O}_8^{2-}$) in aqueous solution.



- (i) With reference to relevant E^\ominus values from the *Data Booklet*, show that the uncatalysed reaction between iodide ions and peroxodisulfate ions ($\text{S}_2\text{O}_8^{2-}$) would occur.

[1]

- (ii) Explain why the uncatalysed reaction between iodide ions and peroxodisulfate ions ($\text{S}_2\text{O}_8^{2-}$) is kinetically slow.

.....
[1]

- (iii) With the aid of a sketch of the Boltzmann distribution, explain why the addition of iron(II) ions speeds up this reaction.

.....

[3]

23

- (iv) Explain why iron(II) ion is able to act as homogeneous catalyst while Ca^{2+} is unable to do so.

.....

[2]

- (b) Many iron-containing complexes are coloured. **X** and **Y** are two examples of such complexes.

The colour of a compound is due to the absorption of light at specific wavelengths. The colour observed is the complement of the colour absorbed.

Table 6.1 shows the colours absorbed for these two iron-containing complexes.

Table 6.1

iron complex	colour absorbed
X	red
Y	yellow

- (i) Suggest the observed colours of **X** and **Y**.

X: **Y**: [1]

- (ii) Using the information provided in Table 5.1 on page 17, deduce the relative size of d-orbital splitting in the two iron complexes in Table 6.1.

.....

[2]

[Total: 10]

24
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ANDERSON SERANGOON JUNIOR COLLEGE

2022 JC 2 PRELIMINARY EXAMINATION

NAME: _____ ()

CLASS: 22 / _____

CHEMISTRY

Paper 3 Free Response Questions

9729/03

16 September 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Write in dark blue or black pen.

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

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

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

Section A

Answer **all** questions

Section B

Answer **one** question

A Data Booklet is provided.

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

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

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

For Examiner's Use				
Paper 3	A1	/ 18	Paper 1 (15%)	/ 30
	A2	/ 19	Paper 2 (30%)	/ 75
	A3	/ 23	Paper 3 (35%)	/ 80
	B4*	/ 20	Paper 4 (20%)	/ 55
	B5*	/ 20	Percentage	
	*Circle the question you have attempted			Grade

This document consists of 32 printed pages.

2

Section A

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

1 NO₂ has been identified as a pollutant with strong evidence for public health concern. Exposure to NO₂ can irritate airways and aggravate respiratory diseases.

(a) (i) Draw a dot-and-cross diagram to show the bonding in a molecule of NO₂. [1]

(ii) The 2s and 2p orbitals of nitrogen atoms can hybridise in the same way as the 2s and 2p orbitals of carbon atoms.

State the shape with respect to the nitrogen atom in NO₂. Hence, suggest the hybridisation state of nitrogen in NO₂. [1]

Table 1.1 shows the bond lengths of two nitrogen–oxygen bonds.

Table 1.1

Bond	N–O	N=O
Bond length (pm)	136	115

The observed bond length of each nitrogen–oxygen bond in the NO₂ is 119 pm.

(iii) What do you understand by the term *bond length*? [1]

(iv) With reference to your answers to (a)(i) and (a)(ii), explain the observed bond length in NO₂. [2]

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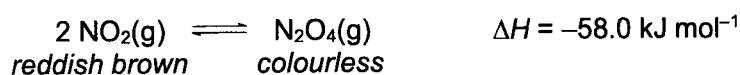
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- (b) At room temperature, reddish brown nitrogen dioxide, NO_2 , dimerises into colourless nitrogen tetroxide, N_2O_4 . The two gases are in dynamic equilibrium as shown.



- (i) Using your answer in (a)(i), explain why the dimerisation of NO_2 to form N_2O_4 is an exothermic process. [1]

The graph in Fig. 1.1 shows the pressure-temperature (p - T) relationship of two separate gaseous samples in an enclosed volume.

At 273 K, the first sample contains 1 mole of helium gas and the second sample contains 1 mole of gaseous N_2O_4 . As temperature increases, it is observed that the second sample behaves differently from the helium gas in the first sample.

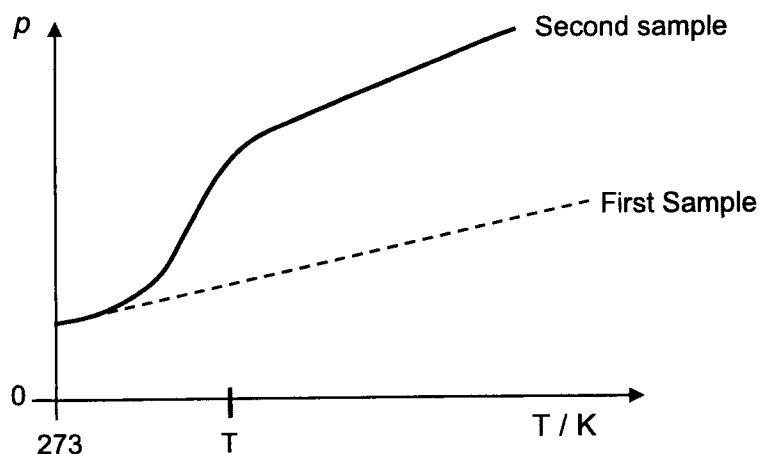


Fig. 1.1

- (ii) Explain the shape of p - T graph for the second sample in Fig. 1.1.
- The steeper slope as temperature increases from 273 K to T K.
 - The gentler slope as temperature increases after temperature T K. [3]
- (iii) State the visible observation that would be made for the second sample as the temperature increases. [1]

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As NO_2 has detrimental impacts on human health, it is important to monitor the level of ambient NO_2 in the atmosphere. One method to detect and measure ambient NO_2 involves the use of open tube diffusion sampler to collect air samples and measure the concentration of NO_2 in the air.

The process of determination of NO_2 can take place in three main stages:

(c) Stage 1: Collection of gas sample using a diffusion tube

Fig. 1.2 shows a typical diffusion tube used for sample collection. It has a length (L) of 7.1 cm and cross-sectional area (A) of 0.91 cm^2 .

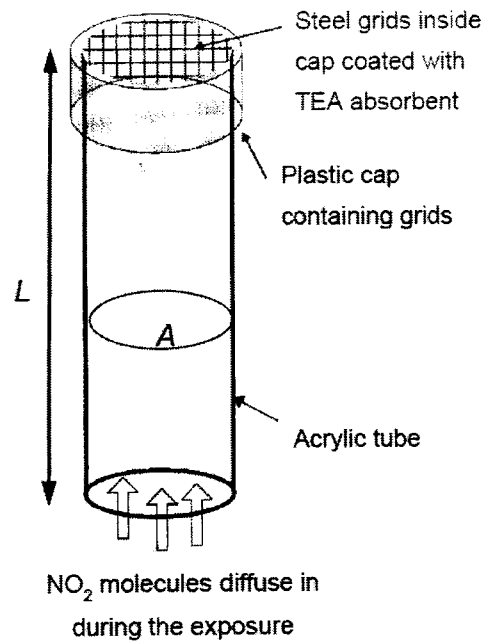
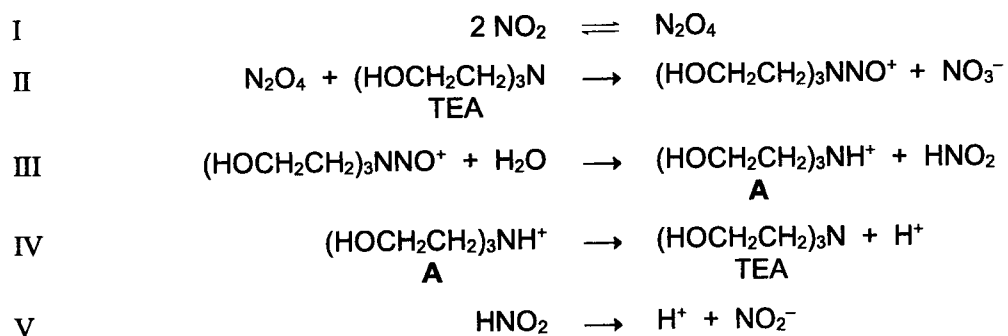


Fig. 1.2

The air sample to be analysed diffuses into the tube through an opening at the bottom. Triethanolamine (TEA), $(\text{HOCH}_2\text{CH}_2)_3\text{N}$, which is coated on the steel mesh grid, absorbs and converts NO_2 to produce nitrite NO_2^- in Stage 2.

Stage 2: Conversion of NO_2 to NO_2^-

The following mechanism, consisting of steps I to V, has been proposed for the conversion of NO_2 to NO_2^- by TEA.



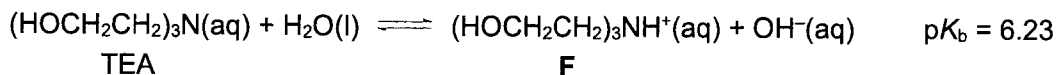
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(i) Write an overall equation for the reaction between NO₂ and TEA. Hence, state the type of reaction that has taken place. [2]

(ii) The species in the reaction mechanism have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason for each case, the roles of TEA and species A. [2]

(iii) TEA dissociates in water forming its conjugate acid F as shown.



Calculate the pH of an aqueous solution containing $6.00 \times 10^{-2} \text{ mol dm}^{-3}$ of species F. [2]

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(d) Stage 3: Analysis and determination of the concentration of NO₂

The NO₂⁻ produced is treated with suitable reagents to form a purple-coloured azo dye before it is placed in a colorimeter. The absorbance of light by the dye, measured at fixed wavelength, is proportional to the concentration of NO₂⁻.

The average concentration of nitrogen dioxide in the air, [NO₂]_{av}, in µg m⁻³, can be determined using the expression given below.

$$[\text{NO}_2]_{\text{av}} = \frac{QL}{ADt}$$

- where Q is the amount of NO₂⁻ (µg),
- L is the length of the diffusion tube (m),
- A is the cross-sectional area of the diffusion tube (m²),
- D is the diffusion coefficient for NO₂ in the air at room temperature = 1.56 × 10⁻⁵ m² s⁻¹,
- t is the duration of exposure (s).

The World Health Organisation (WHO) guideline states that ambient air quality is good when the concentration of NO₂ is below 25 µg m⁻³ (24-hour mean).

To monitor the quality of ambient air in a school compound, a diffusion tube with dimensions as shown in Fig. 1.2 was installed in the classroom for 10 days. The amount of NO₂⁻ was found to be 4.13 × 10⁻³ µg.

Hence, determine the average concentration of NO₂, in µg m⁻³, in the ambient air of the school compound and use this to comment on the quality of air in terms of NO₂ level, during the 10-day monitoring.

(1 µg = 10⁻⁶ g)

[2]

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[Total: 18]

2 Iodine is found naturally in compounds in many different oxidation numbers and is essential in the synthesis of thyroid hormones in the human body.

- (a) (i) Draw a fully labelled diagram to show how the standard electrode potential of the $I_2(aq)/I^-(aq)$ system can be measured.

You are to also include the labelling of

- the direction of electron flow
- the cathode and anode
- polarity of the electrodes

[3]

- (ii) Describe and explain the effect of the addition of a few drops of aqueous silver nitrate into the $I_2(aq)/I^-(aq)$ half-cell on the cell potential of the electrochemical cell described in (a)(i). [2]

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- (b) When sodium iodide is added to concentrated sulfuric acid, it is first converted to hydrogen iodide.

Hydrogen iodide, HI, formed undergoes further reaction with excess concentrated sulfuric acid present to form I_2 , H_2O and H_2S as products. State the changes in oxidation number during the reaction of hydrogen iodide with concentrated sulfuric acid and use them to construct the balanced equation for the reaction. [2]

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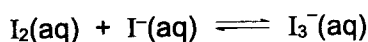
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- (c) Molecular iodine is not very soluble in water but dissolves readily in aqueous solutions containing iodide ions. This is due to the formation of the complex triiodide ions, I_3^- , which exist in equilibrium with the iodine molecules, I_2 and iodide ions, I^- .



Due to the difference in solubility of molecular iodine in water and organic solvent, iodine can be extracted from water when shaken with an organic solvent in a separating funnel as shown in Fig. 2.1.

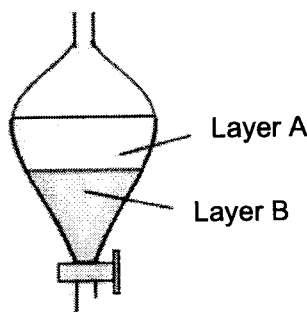
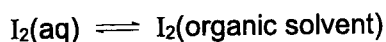


Fig. 2.1

An equilibrium is established when the mixture is left to stand.

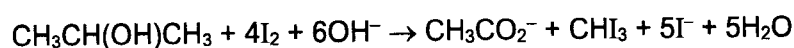


The partition coefficient (K_{pc}) of iodine is the ratio of the concentrations of iodine in the two different immiscible solvents in contact with each other when equilibrium has been established at a particular temperature.

$$K_{pc} = \frac{[I_2(\text{organic solvent})]}{[I_2(aq)]}$$

- (i) An experiment was carried out to investigate the equilibria represented above. 15 cm³ of cyclohexane is added to a separating funnel with 50 cm³ of an aqueous solution of I_2 in aqueous KI. The mixture is shaken and left to stand till no further change is observed.

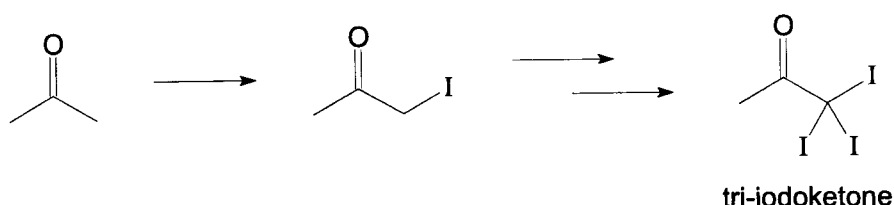
- (d) Iodine is used in a chemical test to confirm the identity of an unknown organic compound such as propan-2-ol, through the formation of tri-iodomethane as a by-product.



The mechanism for the formation of tri-iodomethane and ethanoate ions from propan-2-ol takes place in four stages:

Stage 1: Alkaline aqueous I_2 oxidises propan-2-ol to propanone and itself is reduced to iodide ions.

Stage 2: The propanone formed reacts with I_2 in a series of substitution reaction to produce a tri-iodoketone as shown below.



Stage 3: The hydroxide nucleophile reacts with the tri-iodoketone via a **two-step** nucleophilic acyl substitution mechanism.

- In the first step, the nucleophile attacks the carbonyl carbon to form an alkoxide intermediate.
- In the second step, the intermediate reforms the $\text{C}=\text{O}$ bond and breaks a $\text{C}-\text{C}$ bond to form ethanoic acid and CI_3^- .

Stage 4: Ethanoic acid and CI_3^- then react to form the organic products shown in the above balanced equation.

- (i) State the oxidation number of the carbon atom which is directly bonded to the hydroxyl group in propan-2-ol. [1]
- (ii) Construct a chemical equation for the reaction in Stage 1 between iodine and propan-2-ol. [1]
- (iii) Suggest the nucleophilic acyl substitution mechanism in Stage 3. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]
- (iv) State the type of reaction taking place in stage 4. [1]
- (v) The tri-iodomethane chemical test can be used to test positively for CH_3COCH_3 but not $\text{CH}_3\text{COC}l$. Suggest why $\text{CH}_3\text{COC}l$ does not have a positive tri-iodomethane test. [1]

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- 3 (a) Describe how the halogenoethanes, C_2H_5Cl , C_2H_5Br and C_2H_5I could be distinguished using aqueous sodium hydroxide with other suitable reagents. State the observations for each of the halogenoethanes. [2]

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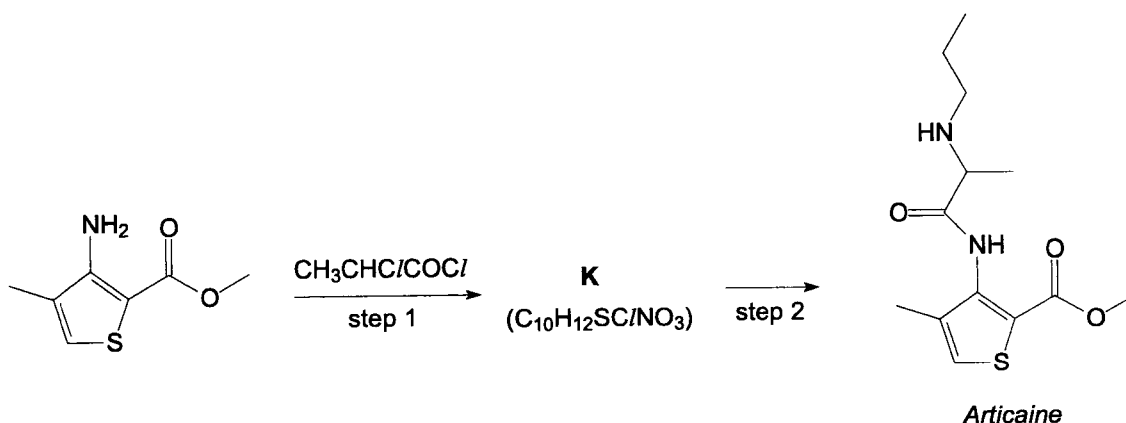
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Organohalogeno-compounds is a versatile group of polar organic compounds where the reactivities of carbon-halogen bond can be exploited by changing the reaction conditions.

- (b) The reaction scheme in Fig. 3.1 outlines the synthesis of *Articaine*, a local anaesthetic used in dentistry. Step 1 of the synthesis involves the use of a dichloro-compound, CH_3CHCl_2COCl .

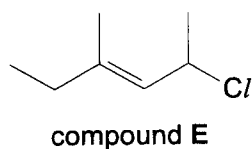


- (i) Deduce the structure for the organic compound **K** and state the reagent required for step 2. [2]
- (ii) Explain the difference in the reactivities of the two chlorine atoms in CH_3CHCl_2COCl . [1]
- (iii) *Articaine* is a safer anaesthetic than other similar amide-containing local anaesthetic as its structure contains an additional ester group which is rapidly hydrolysed by enzymes in the blood and tissues.

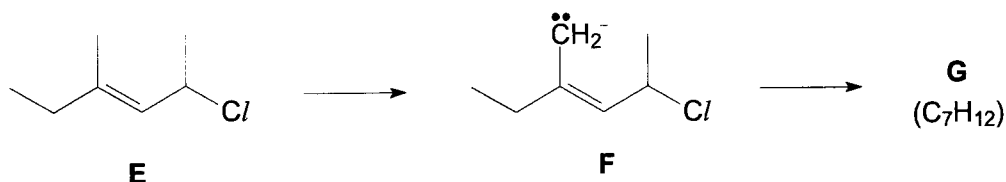
Suggest why an ester group is more rapidly hydrolysed than an amide group. [1]

16

- (c) In the presence of different bases, compound **E** undergoes nucleophilic substitution reactions to form different products.



In the presence of a strong base, such as NaNH_2 in liquid ammonia, the nucleophilic substitution reaction occurs via a negatively-charged organic intermediate, **F**, to form a cyclic product **G**, C_7H_{12} .



- (i) Suggest the structure of the cyclic product **G**. [1]
- (ii) The stability of alkyl carbocations can affect the rate of $\text{S}_{\text{N}}1$ reactions.

The allylic carbocation, where the positively charged carbon is adjacent to a $\text{C}=\text{C}$, is unusually stable. The stability of an allylic carbocation is due to resonance. An example of the two resonance forms of the allylic carbocation is shown in Fig. 3.2.

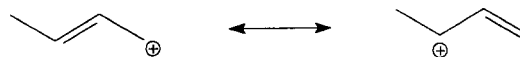


Fig. 3.2

Draw curly arrow on Fig. 3.2 to show how the resonance forms are converted into each other. [1]

When a single enantiomer of compound **E** reacts with another base, aqueous NaOH , the stereochemical outcome depends on whether the reaction goes via the $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism.

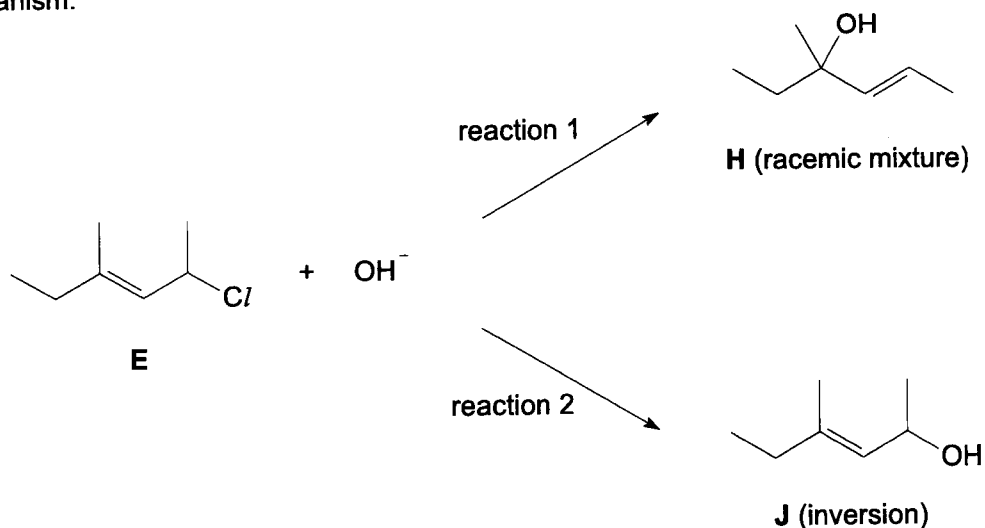


Fig. 3.3

(iii) Based on the information given in Fig. 3.3, state whether reaction 1 proceed via the S_N1 or the S_N2 mechanism.

[1]

(iv) With reference to information in (c)(ii) and your answers in (c)(iii), suggest the mechanism for reaction 1.

Where appropriate, indicate curly arrows, lone pairs of electrons and dipoles in your mechanism.

[3]

(v) Based on the mechanism for reaction 2 in Fig. 3.3, explain why **J** has an inversion of configuration.

[1]

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(d) Organohalogen-compounds are important in the production of quaternary ammonium compounds, QACs. The general structure of a QAC is R_4N^+ , where R can be the same or different alkyl or aryl group.

(i) A quaternary ammonium compound can be produced when excess C_2H_5Br is heated with NH_3 in ethanol. With reference to the mechanism of the reaction, explain why the QAC can be formed. [1]

An attempt to prepare QACs was made by reacting ethylamine with a 1:1 molar mixture of 1-chlorobutane and benzyl chloride, $C_6H_5CH_2Cl$.

(ii) Predict the number of different possible QACs that could be prepared. [1]

(iii) Draw the **skeletal** structure of the QAC which contains only one benzyl group. [2]

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Section B

Answer **one** question from this section

- 4 (a)** When potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$, is dissolved in 6 mol dm^{-3} of hydrobromic acid, HBr , and cooled, orange crystals of a potassium salt **A** are precipitated.

A has a formula mass of 219.0 and the following composition by mass: K, 17.9%; Cr, 23.7%; Br, 36.5% O, 21.9% and the oxidation state of the chromium in salt **A** is the same as that of $\text{K}_2\text{Cr}_2\text{O}_7$.

When aqueous silver nitrate was added to a solution of **A**, an acidic solution is produced and a cream-coloured precipitate **B** is formed. An initial yellow solution **C** is also observed which rapidly turns to an orange solution, **D**.

On addition of sulfur dioxide to solution **D**, a green solution **E** is obtained.

- (i) Show that the formula of **A** is KCrBrO_3 and hence write a balanced equation showing its formation from potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$. [2]
- (ii) Identify species **B**, **C**, **D** and **E**.

Hence, state the type of reaction for the formation of solution **E** from solution **D**, giving a balanced equation for the reaction. [4]

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- (b) Cis–trans isomers of transition metal complexes differ from each other in the arrangement of the ligands around the central metal ion or atom.

Cis isomers have two of the same ligands 90° apart from one another in relation to the central metal ion or atom, whereas trans isomers have two of the same ligands 180° apart.

Propose the structures of the cis and trans isomers of tetraaquadichlorochromium(III) ion, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$. Label your structures clearly. [2]

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- (c) Compound **K** can be synthesised using the following reaction scheme shown in Fig. 4.1.

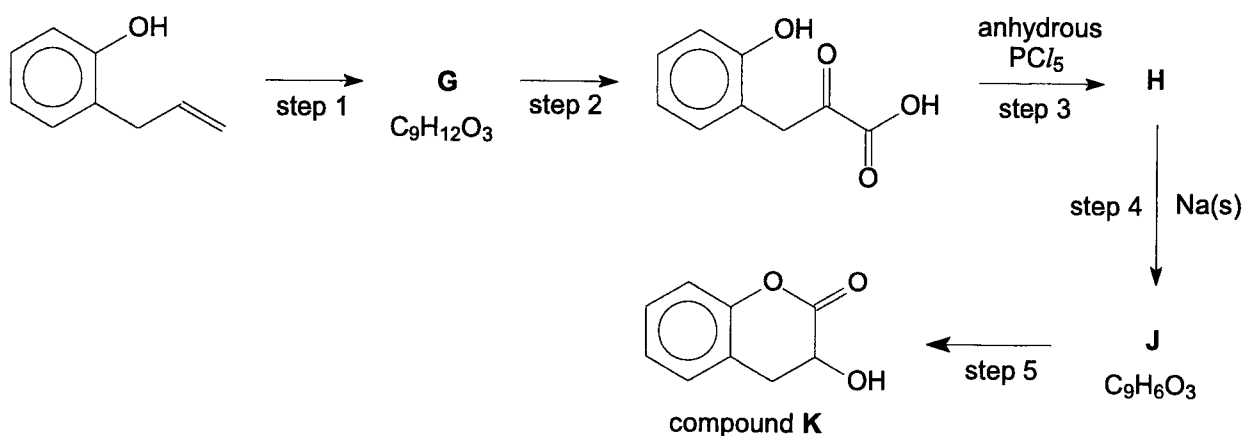


Fig. 4.1

- (i) Suggest structures for the compounds **G**, **H** and **J**. [3]
- (ii) Suggest reagents and conditions for each of the steps 1, 2 and 5. [3]

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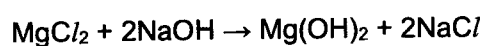
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- (d) Magnesium chloride gives a weakly acidic solution when dissolved. It can be titrated with a strong base to give a rapid pH change upon complete reaction at the equivalence volume.



In an experiment, 50.0 cm³ of aqueous magnesium chloride was titrated with 1.00 mol dm⁻³ sodium hydroxide. The pH of the solution changed as shown in Fig 4.2.

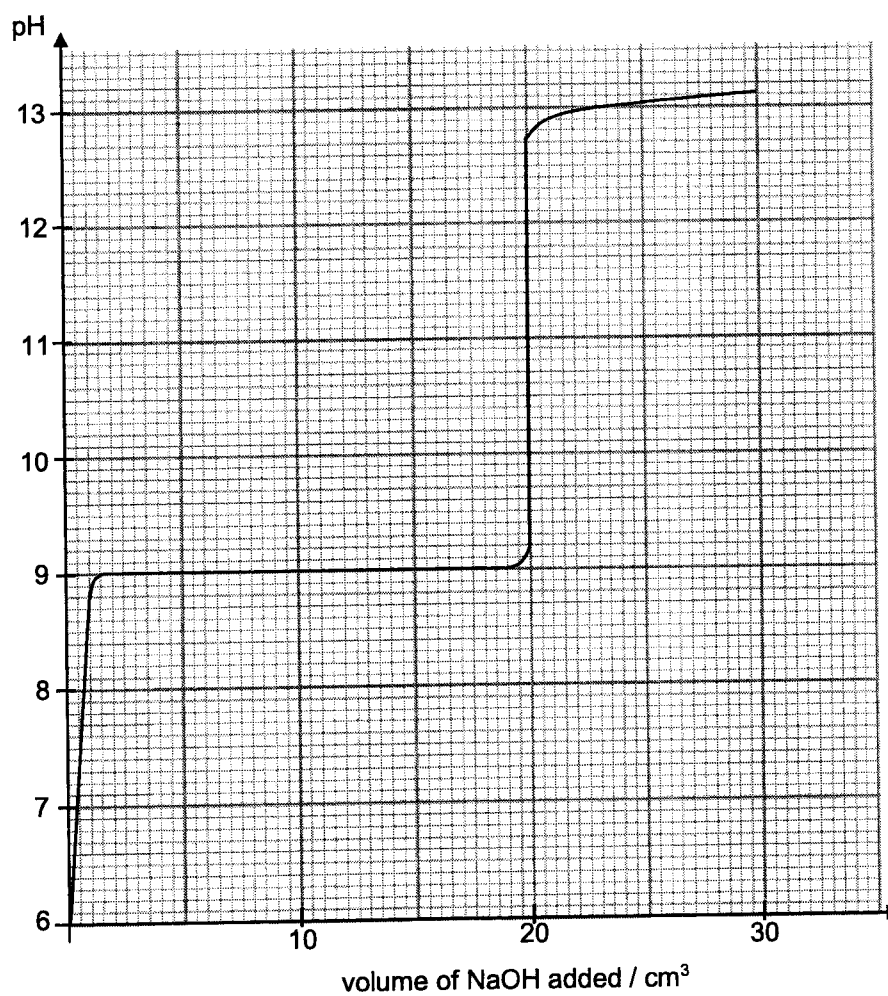


Fig. 4.2

- 5 (a) Describe the reaction, if any, of the chlorides of sodium and silicon with water, stating the approximate pH of any solution formed. Include equations where appropriate. [3]

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- (b) Ethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, can act as a ligand for transition metal ions.

(i) A student proposed to synthesise ethylenediamine from cyanogen, $(\text{CN})_2$. Deduce the number of σ bonds and π bonds in one molecule of cyanogen. [1]

(ii) The proposed synthesis in (b)(i) did not yield the desired product. Instead, ethylenediamine can be synthesised from ethene in two steps. Suggest reagents and conditions for each step. Draw the structure of the intermediate compound. [3]

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(c) Nickel(II) chloride reacts with ethylenediamine (en) to form an octahedral complex with the formula, $[\text{Ni}(\text{en})_3]^{2+}$.

(i) Each molecule of ethylenediamine can form two coordinate bonds to a transition metal ion.

Draw the structure of ethylenediamine and on this structure circle the two atoms that could form these coordinate bonds. [1]

(ii) Complete the diagram in Fig. 5.1 to suggest the structure of the complex formed, showing the 3-dimensional arrangement around the Ni(II) ion. Indicate the overall charge on this complex. [1]

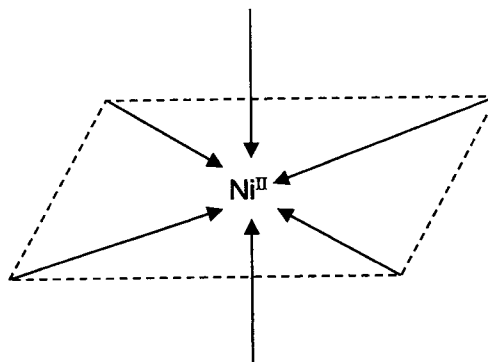


Fig. 5.1

(iii) The $[\text{Ni}(\text{en})_3]^{2+}$ complex that you have drawn in (c)(ii) can exist as a pair of stereoisomers with different effects on plane-polarised light.

State the type of isomerism present and draw the structure of its stereoisomer. [2]

The colour of a given transition metal ion in a complex depends on its oxidation state, shape and the ligands that it is bonded to. Cu(I) compounds are usually white or colourless while Cu(II) compounds are usually coloured.

(iv) Copper(I) chloride, CuCl , is insoluble in water but dissolves in concentrated aqueous sodium chloride to give a colourless solution. The complex anion **Q** in the colourless solution has a linear shape and contains copper and chlorine only.

CuCl reacts with an aqueous solution of ethylenediamine ($\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) to form a blue solution, **R** and a pink-coloured solid, **S**. The complex in solution **R** contains only the ethylenediamine ligand and has a square planar shape.

With aqueous silver nitrate, the blue solution **R** gives a white precipitate, **T**, which is soluble in dilute aqueous ammonia.

Identify species **Q**, **R**, **S** and **T** and write equations for all reactions. [5]

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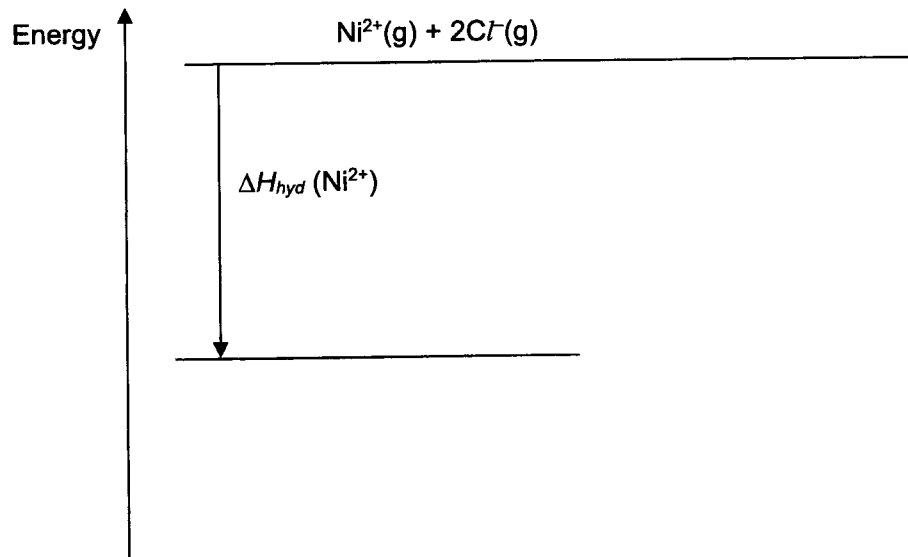
- (d) (i) Define what is meant by the term enthalpy change of solution. [1]
- (ii) Use the following data to determine the enthalpy change of solution, ΔH_{soln} of nickel(II) chloride.

	kJ mol^{-1}
Enthalpy change of hydration of Cl^-	-381
Enthalpy change of hydration of Ni^{2+}	-2096
Lattice energy of nickel(II) chloride	-2753

[1]

- (iii) On the energy level diagram below, draw arrows to show the enthalpy change of solution, ΔH_{soln} of nickel(II) chloride and each of the enthalpy changes you have used in the calculation above.

Label each level with the appropriate formulae.



[2]

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[Total: 20]

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ANDERSON SERANGOON JUNIOR COLLEGE

2022 JC 2 PRELIMINARY EXAMINATION

NAME: _____ ()

CLASS: 22 / _____

CHEMISTRY

Paper 4 Practical

9729/04

25 August 2022

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number on all the work you hand in.
 Give details of the practical shift and laboratory where appropriate, in the boxes provided.
 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.
 You may lose marks if you do not show your working or if you do not use appropriate units.
 Quantitative Analysis Notes are printed on pages 23 and 24.

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.

Shift
Laboratory

For Examiner's Use	
1	/ 14
2	/ 21
3	/ 9
4	/ 11
Total	/ 55

This document consists of **22** printed pages and **2** blank pages.

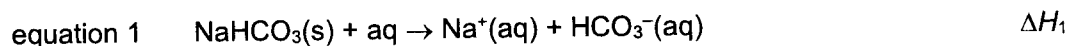
Answer **all** the questions in the spaces provided.

1 Determination of a value for an enthalpy change of solution by an indirect method

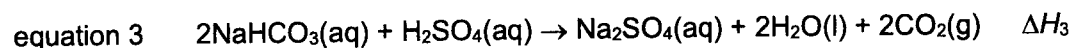
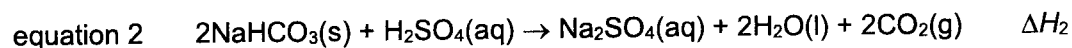
FA 1 is solid sodium hydrogencarbonate, NaHCO_3 .

FA 2 is 1.50 mol dm^{-3} sulfuric acid, H_2SO_4 .

Sodium hydrogencarbonate dissolves in water according to equation 1.



Both solid and aqueous sodium hydrogencarbonate react with sulfuric acid.



In this question, you will perform an experiment to determine a value for ΔH_2 . You will use data provided to calculate ΔH_3 and hence a value for ΔH_1 .

(a) Determination of the molar enthalpy change of reaction, ΔH_2

In this experiment, you will determine the maximum temperature change when a known mass of solid sodium hydrogencarbonate, **FA 1**, reacts with dilute sulfuric acid, **FA 2**.

In an appropriate format in the space provided on page 3, prepare tables in which to record for your experiment:

- all weighings to an appropriate level of precision,
- all values of temperature, T , to an appropriate level of precision.

Procedure

1. Weigh the capped bottle containing **FA 1**. Record this mass.
2. Place one polystyrene cup inside another polystyrene cup and place both in a glass beaker.
3. Use a 25 cm^3 measuring cylinder to transfer 25 cm^3 of **FA 2** into the polystyrene cup.
4. Stir the **FA 2** in the polystyrene cup with the thermometer. Read and record its initial temperature, T_i .
5. Slip the thermometer through the lid. Carefully transfer all the solid **FA 1** in the bottle to the **FA 2** in the polystyrene cup, in small portions, to avoid too much frothing. Secure the lid onto the cup.
6. Use the thermometer to stir the mixture. Observe the temperature until it shows the maximum change from the initial temperature. Record this temperature, T_m .
7. Reweigh the empty capped bottle. Record this mass.

Determine the maximum temperature change, ΔT , and the mass of **FA 1** used.

Results

[5]

(b) In the following calculations, you should assume that the specific heat capacity of the solution is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$, and the density of the solution is 1.00 g cm^{-3} .

(i) Use your results from 1(a) to calculate the heat change for your experiment.

heat change = [1]

(ii) Hence, determine a value for ΔH_2 . The sulfuric acid is in excess.

Include the sign of ΔH_2 in your answer.

[A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]

$\Delta H_2 = \dots\dots\dots$ [1]

The results of an experiment where a solution of $0.690 \text{ mol dm}^{-3}$ aqueous sodium hydrogencarbonate, $\text{NaHCO}_3(\text{aq})$ was reacted completely with an excess of dilute sulfuric acid, **FA 2**, are shown in Table 1.1.

Table 1.1

volume of $\text{NaHCO}_3(\text{aq})$ used / cm^3	50.0
initial temperature of $\text{NaHCO}_3(\text{aq})$ / $^\circ\text{C}$	27.6
volume of FA 2 used / cm^3	25.0
initial temperature of FA 2 / $^\circ\text{C}$	31.2
minimum temperature / $^\circ\text{C}$	28.4

- (iii) Use the results given in Table 1.1 and the formula below to calculate the weighted average initial temperature, T_{av} , of the reaction mixture.

The formula for T_{av} is given as

$$T_{\text{av}} = \frac{(\text{vol. of FA 2} \times \text{initial temp. of FA 2}) + (\text{vol. of NaHCO}_3 \times \text{initial temp. of NaHCO}_3)}{\text{total volume of reaction mixture}}$$

$$T_{\text{av}} = \dots\dots\dots [1]$$

- (iv) Hence, calculate a value for ΔH_3 .

$$\Delta H_3 = \dots\dots\dots [4]$$

- (c) Use your answers from **1(b)(ii)** and **1(b)(iv)** to calculate a value for ΔH_1 for the reaction shown in equation 1.

If you are not able to determine a value for **1(b)(ii)** and/or **1(b)(iv)**, you may use x and y to represent the respective enthalpy changes and proceed with this part of the question.

$\Delta H_1 = \dots\dots\dots$ [2]

[Total: 14]

2 To determine the order of reaction with respect to the concentration of iodine in the iodination of propanone reaction

FA 3 is 1.00 mol dm⁻³ sulfuric acid, H₂SO₄.

FA 4 is 1.00 mol dm⁻³ propanone, CH₃COCH₃.

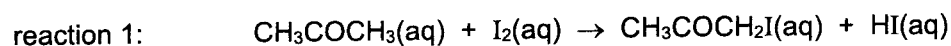
FA 5 is an aqueous solution of iodine, I₂.

FA 6 is 0.0100 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃.

FA 7 is 0.50 mol dm⁻³ sodium hydrogencarbonate, NaHCO₃.

You are also provided with a starch indicator.

The equation in reaction 1 represents the reaction between CH₃COCH₃ and I₂.



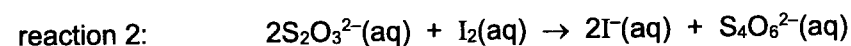
This reaction is first order with respect to both CH₃COCH₃ and H⁺ ions.

You are to investigate the order of reaction with respect to I₂.

A reaction mixture containing an acidified solution of CH₃COCH₃ and I₂ is first prepared. At timed intervals, aliquots (portions) of this reaction mixture will be removed and quenched using excess NaHCO₃.

It is **not** essential that you complete the titration of one aliquot before extracting the next one from the reaction mixture. However, you **must** ensure that each aliquot is mixed **immediately** with NaHCO₃.

The remaining amount of I₂ at different times can then be determined by titration against Na₂S₂O₃. Na₂S₂O₃ reacts with I₂ as shown in the equation in reaction 2.



The required order of reaction can be obtained by graphical analysis of your results.

(a) Preparing and titration of the reaction mixture

Notes:

You will perform each titration **once** only. Great care must be taken that you do not exceed the end-point.

Once you have started the stopwatch, it must continue running for the duration of the experiment. You must **not** stop the stopwatch until you have finished this experiment.

You should aim to transfer your first aliquot approximately four minutes after starting the reaction.

You should aim **not** to exceed a maximum reaction time of 20 minutes for this experiment.

In an appropriate format in the space provided on page 8, prepare a table in which to record for each aliquot

- the time of transfer, *t*, in minutes and seconds,
- the decimal time, *t_d*, in minutes, to 0.1 min, for example, if *t* = 4 min 33 s then *t_d* = 4 min + 33/60 min = 4.6 min,
- the burette readings and the volume of **FA 6** added.

Question 2 continues on the next page.

Safety:

Propanone is flammable. Transfer your titrated solutions into the **waste** bottle for later disposal. Keep this bottle stoppered when not in use.

Keep the conical flask labelled **reaction mixture** stoppered except when removing aliquots.

1. Fill a burette with **FA 6**.
2. Using a 25 cm³ measuring cylinder, add the following to a 100 cm³ beaker.
 - 25.0 cm³ of **FA 3**
 - 25.0 cm³ of **FA 4**
3. Using a 100 cm³ measuring cylinder, transfer 50.0 cm³ of **FA 5** into the 250 cm³ conical flask, labelled **reaction mixture**.
4. Pour the contents of the 100 cm³ beaker into this 250 cm³ conical flask. Start the stopwatch, **insert the stopper** and swirl the mixture thoroughly to mix its contents.
5. Using a 10 cm³ measuring cylinder, measure 10.0 cm³ of **FA 7** into a second conical flask.
6. At approximately 4 minutes, using a 10.0 cm³ pipette, remove a 10.0 cm³ aliquot of the reaction mixture. **Immediately** transfer this aliquot into the second conical flask containing **FA 7** and swirl the mixture thoroughly.

Note the time of transfer, *t*, to the nearest second, when half of the reaction mixture has been dispensed from the pipette. Replace the stopper in the reaction flask.
7. Titrate the iodine in the second conical flask with **FA 6**. When the colour of the solution turns pale yellow, add about 1 cm³ of starch indicator. The solution will turn blue-black. The end-point is reached when the blue-black colour just disappears. Record your results.
8. Empty the contents of this conical flask into the waste bottle. Wash this conical flask thoroughly with water.
9. Repeat steps 5 to 8 until a total of **five** aliquots have been titrated and their results recorded.

Results

[3]

- (b) (i) On the grid in Fig. 2.1, plot a graph of the volume of **FA 6** added, on the y -axis, against decimal time, t_d , on the x -axis.

Draw the most appropriate best-fit line taking into account all of your plotted points. Extrapolate (extend) this line to $t_d = 0.0$ min.

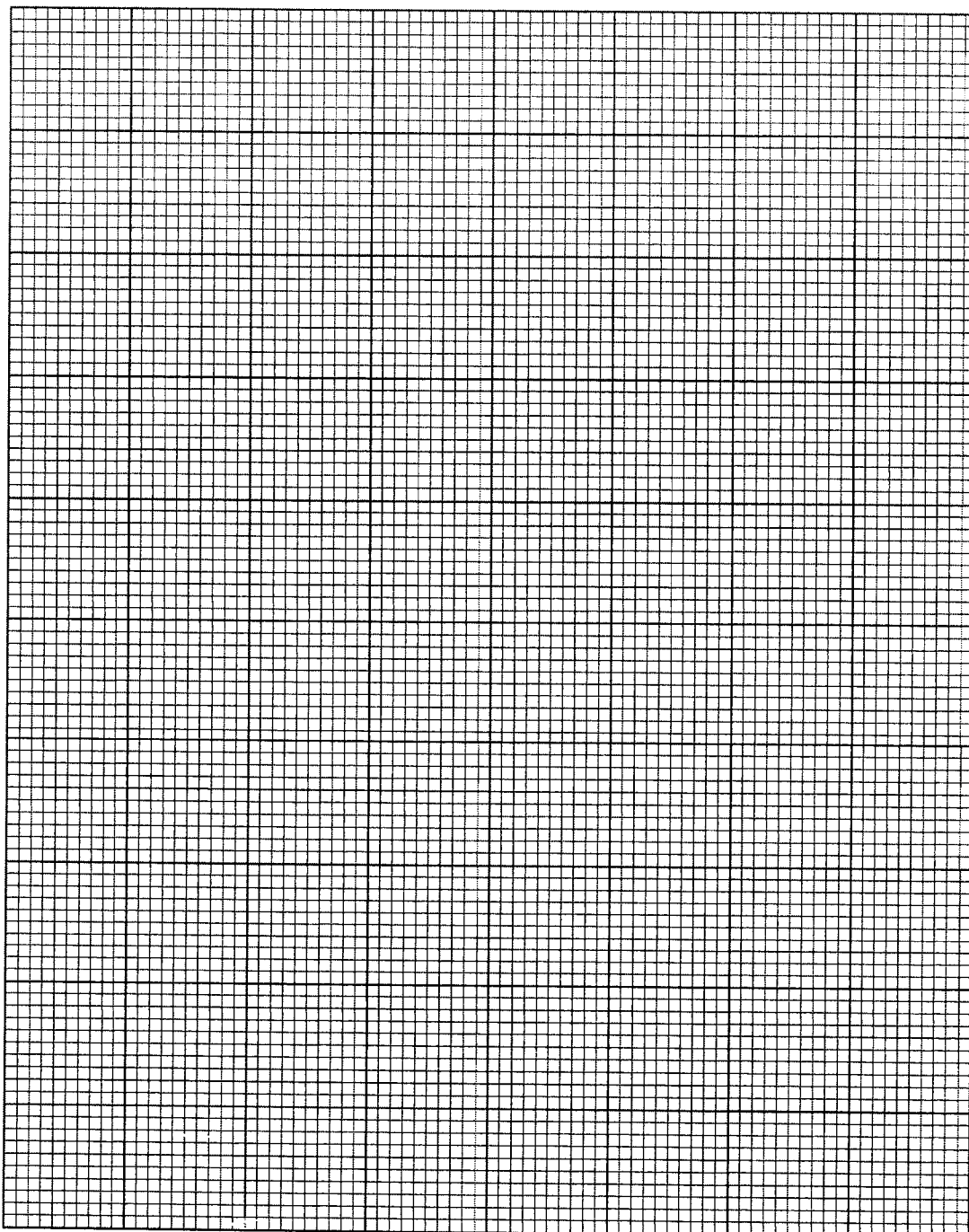


Fig. 2.1

[4]

- (ii) Deduce the order of reaction with respect to the $[I_2]$ in reaction 1. Explain your answer.

order.....

explanation.....

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..... [1]

- (iii) Calculate the gradient of the line, showing your working clearly on the graph.

gradient = $\text{cm}^3 \text{min}^{-1}$ [2]

- (iv) The y-intercept of your line gives the volume of sodium thiosulfate required to completely react with the iodine present if an aliquot is taken at $t_d = 0.0$ min.

Read from your graph and record this volume of **FA 6**, V_{max} . Use this value to calculate the concentration of iodine in **FA 5**.

volume of **FA 6**, $V_{\text{max}} = \text{.....cm}^3$

concentration of iodine in **FA 5** = mol dm^{-3} [3]

- (v) Use your answer to part **2(b)(iii)** together with your value for V_{max} to estimate t_{max} , the time at which all the iodine in your reaction mixture would have reacted completely.

$t_{\text{max}} = \text{.....min}$ [1]

- (c) Use the information provided on page 6 and your answer to **2(b)(ii)**, write an expression for the rate equation for reaction 1. Include the units for rate in your answer.

Rate = [1]

- (d) A student performed a modified experiment of the one that you performed in **2(a)**. Instead of using 25.0 cm³ of **FA 4**, the student used a 25.0 cm³ solution prepared from equal volumes of **FA 4** and water.

On the axes in Fig. 2.2, sketch the graph you have obtained in **2(b)(i)** and the graph you would expect to obtain from the modified experiment conducted by the student. Label both graphs clearly.

Explain your answer.

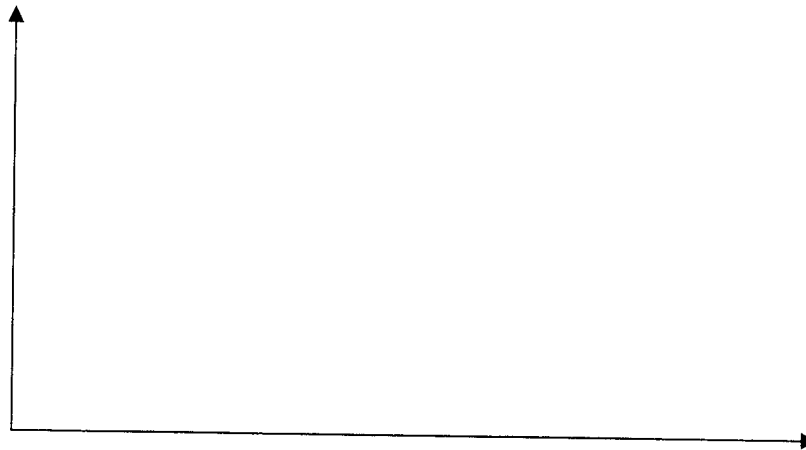


Fig. 2.2

explanation

 [2]

- (e) In step 6 of the experimental procedure, the aliquot is transferred into the second conical flask containing **FA 7**.

- (i) Explain why it is necessary to add **FA 7**, and how the titre values will be affected with the omission of **FA 7**.

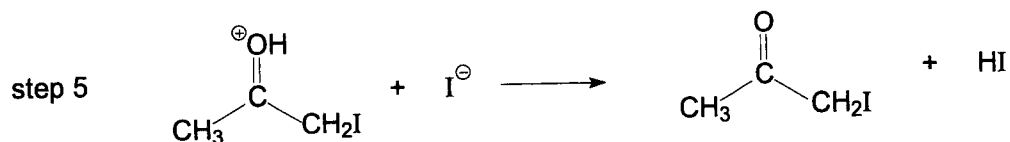
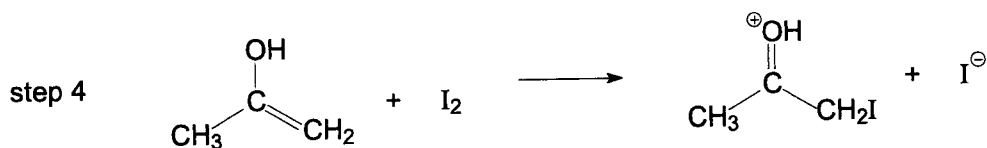
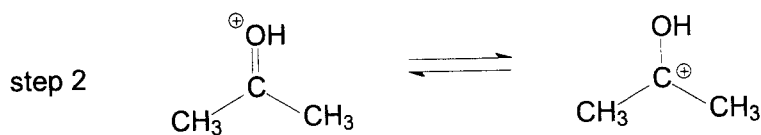
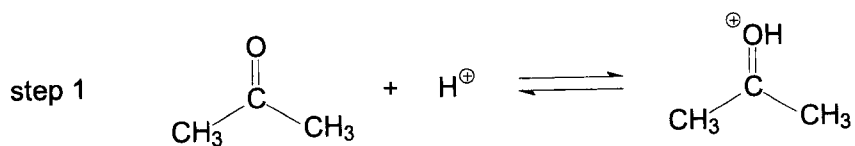
.....
 [1]

- (ii) A small temperature change is observed upon the transfer of the aliquot into the second conical flask.

Suggest, with a reason, how the temperature would change.

.....
 [1]

(f) The following steps represent a possible mechanism for reaction 1.



(i) Deduce the role of H^+ ions in the mechanism for reaction 1. Explain your answer.

.....

[1]

(ii) Based on your answer to 2(c), identify the rate-determining step in this mechanism.

.....[1]

[Total: 21]

3 Investigation of the chemistry of some vanadium ions

FA 8 contains vanadate(V) ions, VO_3^- , of concentration 0.50 mol dm^{-3} .

FA 9 is a metal.

FA 10 is a solution made by reacting solid **FA 9** with dilute sulfuric acid.

You are also provided with **FA 3**, 1.00 mol dm^{-3} of sulfuric acid, H_2SO_4 used in **Q2**.

Ammonium vanadate(V), NH_4VO_3 , is a crystalline solid that is slightly yellow in colour. It has a relatively low solubility in water at room temperature.

You are provided with a solution, **FA 8**, produced by warming solid NH_4VO_3 with aqueous sodium hydroxide. In this reaction, a more soluble salt is formed and the anion is unchanged.

- (a) Write an equation for the reaction between ammonium vanadate(V) and sodium hydroxide to produce **FA 8**.

Describe a simple test that can be performed to confirm the presence of one of the products of the reaction between ammonium vanadate(V) and sodium hydroxide.

equation

test

.....

.....

[2]

- (b) When **FA 8** is acidified and reacted with **FA 9**, a series of colour changes can be observed during the reaction.

You will carry out tests to study the reactions of acidified **FA 8** with **FA 9**. Record your observations in Table 3.1.

In these reactions, you do **not** need to test for any gas that is evolved.

Table 3.1

	tests	observations
(i)	<p>Using a 50 cm³ measuring cylinder, measure about 10 cm³ of FA 8 into a 250 cm³ beaker.</p> <p>Using the same measuring cylinder, measure about 40 cm³ of FA 3 to the same beaker.</p> <p>The resulting solution obtained is solution W, which will be used in 3(b)(ii) and 3(c).</p>	
(ii)	<p>Transfer about 30 cm³ of solution W into a 100 cm³ conical flask, using the same measuring cylinder used in 3(b)(i).</p> <p>Using a spatula, slowly add all the FA 9 provided, a small spatula measure each time, into the conical flask. Swirl after each addition.</p> <p>You may then leave the mixture to stand, swirling the flask from time to time and observe the solution until no further changes are seen.</p>	
<p>While you are waiting, continue with the test in 3(c).</p>		

[2]

- (c) Reaction of solution **W** with tin powder gives different observations from those observed with **FA 9**. Record your observations in Table 3.2.

Table 3.2

test	observations
<p>Transfer about 10 cm³ of solution W into a boiling tube using the same measuring cylinder used in 3(b)(i).</p> <p>Add all the tin powder in the weighing bottle into the boiling tube and shake the mixture.</p> <p>Gently warm the boiling tube. You should not allow the mixture in the boiling tube to boil or heat to dryness.</p> <p>To view the colour of the solution clearly, you may find it necessary, from time to time, to allow the tin to settle.</p> <p>Observe the mixture until no further changes are seen.</p>	

[1]

- (d) (i) You will perform tests to identify the metal cation present in **FA 10** and hence the identity of **FA 9**.

Carry out the following tests. Record your observations in Table 3.3.

Table 3.3

tests		observations
1	To about 1 cm depth of FA 10 in a test-tube, add aqueous sodium hydroxide until no further changes are observed.	
2	To about 1 cm depth of FA 10 in a test-tube, add aqueous ammonia until no further changes are observed.	

[2]

- (ii) Identity of **FA 9**:

[1]

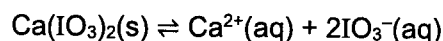
- (iii) Write equations to explain the recorded observations for test **2** in Table 3.3.

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[1]

[Total: 9]

4 Planning

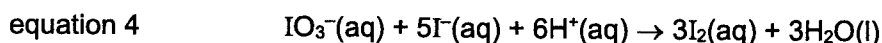
Calcium iodate(V), $\text{Ca}(\text{IO}_3)_2$, has low solubility of $6.2 \times 10^{-3} \text{ mol dm}^{-3}$ in water at 20°C . When calcium iodate (V) is added to water, the following equilibrium is established.



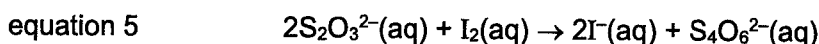
You are to plan an experiment to determine the solubility product, K_{sp} , of $\text{Ca}(\text{IO}_3)_2(\text{s})$ by first preparing a saturated solution of $\text{Ca}(\text{IO}_3)_2$. A saturated solution is one in which no more solid can dissolve at a particular temperature. In a saturated solution with undissolved $\text{Ca}(\text{IO}_3)_2(\text{s})$, the above equilibrium is established after about one hour.

The mixture is then filtered and the amount of iodate(V) ions, IO_3^{-} , in the filtrate is determined as described below.

10 cm^3 of potassium iodide (in excess) and 10 cm^3 of sulfuric acid are added to 25 cm^3 of the filtrate containing IO_3^{-} ions. Iodine is liberated, as shown in equation 4.



The liberated iodine is then titrated with a standard solution of sodium thiosulfate, as shown in equation 5.



- (a) Calculate the minimum mass of $\text{Ca}(\text{IO}_3)_2(\text{s})$ that is required to prepare a saturated solution of $\text{Ca}(\text{IO}_3)_2$ in 100 cm^3 of deionised water at 20°C .

[molar mass of $\text{Ca}(\text{IO}_3)_2 = 389.9 \text{ g mol}^{-1}$]

[1]

(b) Plan a procedure to prepare a saturated solution of $\text{Ca}(\text{IO}_3)_2$ in 100 cm^3 of deionised water and an investigation to determine the solubility product of the salt at 20°C .

You may assume that you are provided with:

- deionised water
- solid calcium iodate(V), $\text{Ca}(\text{IO}_3)_2$
- $0.100 \text{ mol dm}^{-3}$ sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$
- aqueous potassium iodide, KI
- 1.00 mol dm^{-3} dilute sulfuric acid, H_2SO_4
- starch indicator
- filter funnel and filter paper
- the apparatus and equipment normally found in a school or college laboratory.

In your plan you should include brief details of:

- the apparatus you would use
- the quantities you would use
- the procedure you would follow
- the measurements you would make
- how you would ensure that an **accurate** and **reliable** value of K_{sp} is obtained.

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- (c) (i) Write an expression for the K_{sp} of $\text{Ca}(\text{IO}_3)_2$.

.....[1]

- (ii) Outline how you would use your titration results to calculate the K_{sp} of $\text{Ca}(\text{IO}_3)_2$.
You may wish to use $V \text{ dm}^3$ as your average titre volume.

[3]

[Total: 11]

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Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	NH₃(aq)
aluminium, Al ³⁺ (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH ₄ ⁺ (aq)	ammonia produced on heating	–
barium, Ba ²⁺ (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca ²⁺ (aq)	white ppt. with high [Ca ²⁺ (aq)]	no ppt.
chromium(III), Cr ³⁺ (aq)	grey–green ppt. soluble in excess giving dark green solution	grey–green ppt. insoluble in excess
copper(II), Cu ²⁺ (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe ²⁺ (aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe ³⁺ (aq)	red–brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg ²⁺ (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn ²⁺ (aq)	off–white ppt., rapidly turning brown on contact with air insoluble in excess	off–white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn ²⁺ (aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $\text{Cl}^-(\text{aq})$	gives white ppt. with $\text{Ag}^+(\text{aq})$ (soluble in $\text{NH}_3(\text{aq})$)
bromide, $\text{Br}^-(\text{aq})$	gives pale cream ppt. with $\text{Ag}^+(\text{aq})$ (partially soluble in $\text{NH}_3(\text{aq})$)
iodide, $\text{I}^-(\text{aq})$	gives yellow ppt. with $\text{Ag}^+(\text{aq})$ (insoluble in $\text{NH}_3(\text{aq})$)
nitrate, $\text{NO}_3^-(\text{aq})$	NH_3 liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil
nitrite, $\text{NO}_2^-(\text{aq})$	NH_3 liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil NO liberated by dilute acids (colourless $\text{NO} \rightarrow$ (pale) brown NO_2 in air)
sulfate, $\text{SO}_4^{2-}(\text{aq})$	gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}(\text{aq})$	SO_2 liberated on warming with dilute acids; gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (soluble in dilute strong acids)

(c) Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple