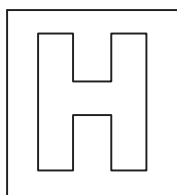


Candidate Name: _____

Class	Adm No



2017 Preliminary Examinations II

Pre-University 3

H2 CHEMISTRY

Paper 1 Multiple Choice

9647/01

20 Sept 2017

1 hour

Additional materials: Multiple Choice Answer Sheet

Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Write in soft pencil.

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

Write your name, class and admission number in the spaces provided at the top of this page and on the Multiple Choice Answer Sheet provided.

There are **forty** questions on this paper. Answer **ALL** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the Multiple Choice Answer Sheet provided.

Read the instructions on the Multiple Choice Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this question paper.

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

This question paper consists of **16** printed pages and **2** blank pages.

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

- 1 Dolomite is a carbonate-containing mineral with formula $\text{MgZ}(\text{CO}_3)_2$ where **Z** is a metal ion. It is insoluble in water but reacts with acids.

When 2.00 g of dolomite was completely dissolved in an excess of hydrochloric acid, 0.759 g of carbon dioxide was given off. What is the identity of the metal **Z**?

- A** Ba **B** Ca **C** Ra **D** Sr

- 2 Sulfur dioxide gas is an irritant to the eyes and respiratory system. The maximum safe toleration level of sulfur dioxide in air is 0.014 mg dm^{-3} .

How many molecules of sulfur dioxide gas are present in 1 dm^3 of air at this toleration level?

- A** $\frac{0.014}{6.02 \times 10^{23}} \times 64.1$ **B** $\frac{0.014}{1000} \times \frac{1}{64.1} \times 6.02 \times 10^{23}$
C $\frac{0.014}{64.1} \times 6.02 \times 10^{23}$ **D** $\frac{0.014}{1000} \times 64.1 \times 6.02 \times 10^{23}$

- 3 The element technetium, Tc (mass number 99; atomic number 43), was discovered in 1937 by two Italian scientists, Segre and Perrier.

Under suitable conditions, technetium reacts with fluorine to form TcF_6 .

Which of the following options shows the correct number of protons, neutrons and electrons in Tc^{6+} ?

	number of protons	number of neutrons	number of electrons
A	43	43	56
B	43	56	37
C	49	43	37
D	43	56	49

4 Which of the following atoms has three unpaired electrons?

- A Br B Co C Ga D Sc

5 Under standard conditions, water exists in the liquid state but hydrogen sulfide exists in the gaseous state.

Which of the following best explains this phenomenon?

- A Water has a higher relative molecular mass than hydrogen sulfide.
B The O-H covalent bond in water is stronger than the S-H covalent bond in hydrogen sulfide.
C The hydrogen bonds between water molecules are stronger than the Van der Waals' forces between hydrogen sulfide molecules.
D Hydrogen sulfide has a more spherical structure compared to water.

6 Antimony, Sb, is in Group V of the Periodic Table. It was proposed that antimony is able to form SbF_4^{n-} anion, the structure of which is of square planar shape.

Which of the following shows the correct value of n and the oxidation number of Sb in this anion?

	value of n	oxidation number of Sb
A	1	+3
B	1	+5
C	3	+1
D	3	+3

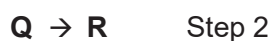
[Turn over

- 7 **X** and **Y** are ideal gases that do not react with one another. The molar mass of **X** is twice that of **Y**.

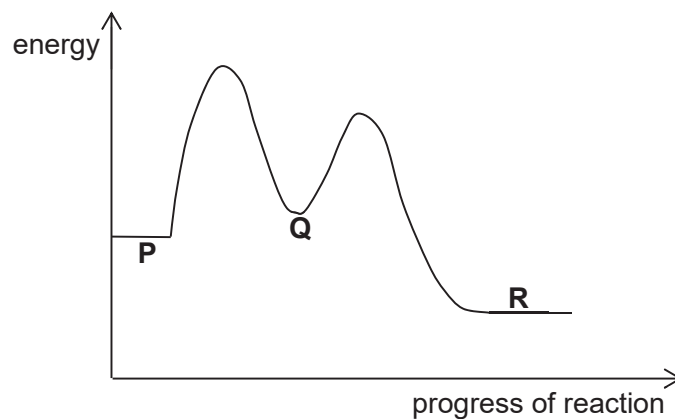
If all measurements are taken at room temperature and pressure, which statement correctly describes **X** and **Y**?

- A The volume occupied by 2 g of **X** is half that occupied by 2 g of **Y**.
- B The mass of 5 dm³ of **X** is half that of 5 dm³ of **Y**.
- C The volume occupied by 2.5 g of **X** is equal to the volume occupied by 5 g of **Y**.
- D On mixing 1 dm³ of **X** with 1 dm³ of **Y**, the partial pressure of **X** is twice that of **Y**.

- 8 The two steps in the conversion of compound **P** to compound **R** are shown below.



The energy profile of the reaction is shown below.



Which of the following statements about the reaction can be deduced from the information given?

- A The enthalpy change for the reaction is endothermic.
- B **Q** acts as a catalyst in the reaction.
- C Step 1 is the rate determining step.
- D **R** is thermodynamically less stable than **P**.

- 9 When liquid SOCl_2 is added to $\text{Ba}(\text{OH})_2$, a vigorous reaction occurs and the temperature decreases from $25\text{ }^\circ\text{C}$ to $5\text{ }^\circ\text{C}$.

What are the correct signs of ΔH , ΔS and ΔG for this reaction?

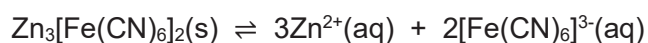
	ΔH	ΔS	ΔG
A	+	+	-
B	+	-	+
C	-	+	-
D	-	-	+

- 10 A sample of finely ground copper was contaminated with zinc powder. Treatment of the sample with an excess of hydrochloric acid produced 120 cm^3 of hydrogen gas, measured at room temperature and pressure. The remaining copper was then reacted with acidified potassium manganate(VII). It was found that 0.00424 mol of potassium manganate(VII) was required for complete oxidation of copper to copper(II) ions.

What is the percentage by mass of copper in the sample?

- A** 45.2% **B** 65.8% **C** 67.3% **D** 90.4%

- 11 Zinc(II) reacts with the complex anion hexacyanoferrate(III), $[\text{Fe}(\text{CN})_6]^{3-}$, to give a sparingly soluble salt which dissociates in water according to the following equilibrium.



If the solubility product, K_{sp} , of $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ is X , what is the concentration of $\text{Zn}^{2+}(\text{aq})$ at equilibrium?

- A** $\left(\frac{3X}{2}\right)^{\frac{1}{3}}$ **B** $\left(\frac{3X}{2}\right)^{\frac{1}{5}}$ **C** $\left(\frac{9X}{4}\right)^{\frac{1}{3}}$ **D** $\left(\frac{9X}{4}\right)^{\frac{1}{5}}$

[Turn over

- 12 Which of the following statements about the rate constant, k , of chemical reactions is **not** true?
- A The rate constant increases when temperature increases.
 - B The rate constant increases when the concentration of the reactant increases.
 - C The rate constant decreases when the activation energy increases.
 - D The units of the rate constant depends on the overall order of reaction.
- 13 A Period 3 element forms an oxide that is soluble in both water and aqueous sodium hydroxide. Which of the following could be the identity of this element?
- A aluminium B silicon C sodium D sulfur
- 14 In which of the following pairs is the radius of the first species greater than that of the second species?
- A Mg, Al B Ca, Ba C Mg^{2+} , Na^+ D K^+ , Ar
- 15 Which of the following properties of the Group II elements and their compounds decreases down the group?
- A Ease of oxidation of the elements
 - B Electronegativity of the elements
 - C Reactivity of elements with chlorine
 - D Thermal stability of nitrates
- 16 With reference to the chemistry of Group VII elements and their compounds, which of the following would be a correct prediction for astatine?
- A Astatine reacts vigorously with hydrogen at room temperature.
 - B Astatine exists as a gas at room temperature.
 - C Astatine reacts with cold aqueous hydroxide to form AtO^- and At^- .
 - D Molten At/At_3 can conduct electricity.

17 Which of the following products is **least** likely to act as a ligand?

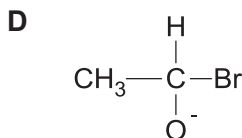
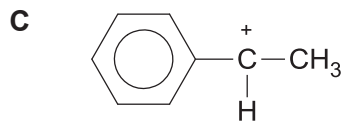
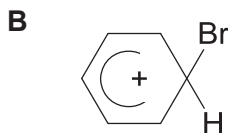
- A AlH_3 B CO C $\text{C}_2\text{H}_5\text{OH}$ D CH_3NH_2

18 The use of *Data Booklet* is relevant to this question.

An element **G** has an atomic number of 23. Which of the following compounds of **G** is **not** likely to exist?

- A KGO_3 B G_2O_5 C K_2GO_4 D GOCl_2

19 Which of the following species could be an intermediate in an electrophilic addition reaction?



20 How many structural isomers with the molecular formula $\text{C}_5\text{H}_{10}\text{O}$ gives an orange precipitate with Brady's reagent and a yellow precipitate with alkaline aqueous iodine?

- A 1 B 2 C 3 D 4

[Turn over

- 21 In an experiment, it was found that during the free radical substitution of alkanes, primary, secondary and tertiary hydrogen atoms were replaced by bromine atoms at different rates, as shown in the table below.

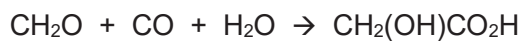
Reaction	Relative Rate
Primary : $\text{RCH}_3 \rightarrow \text{RCH}_2\text{Br}$	1
Secondary : $\text{R}_2\text{CH}_2 \rightarrow \text{R}_2\text{CHBr}$	8
Tertiary : $\text{R}_3\text{CH} \rightarrow \text{R}_3\text{CBr}$	20

With reference to the information given, which of the following shows the 2 products obtained from the reaction of 2,3-dimethylbutane with bromine gas under UV light and their relative ratio?

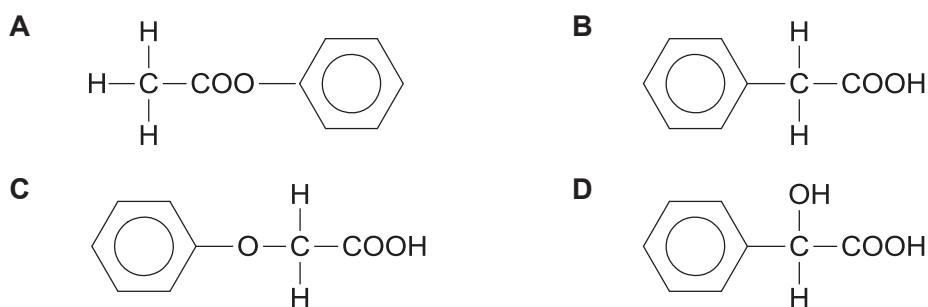
- A $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{CH}_2\text{Br} : (\text{CH}_3)_2\text{CBrCH}(\text{CH}_3)_2 = 3 : 10$
- B $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{CH}_2\text{Br} : (\text{CH}_3)_2\text{CBrCH}(\text{CH}_3)_2 = 1 : 20$
- C $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{Br} : (\text{CH}_3)_3\text{CCHBrCH}_3 = 3 : 8$
- D $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{Br} : (\text{CH}_3)_3\text{CCHBrCH}_3 = 3 : 20$
- 22 Concentrated ammonia was heated in a sealed tube with excess bromoethane. Which of the following products will **not** be formed?
- A $\text{C}_2\text{H}_7\text{N}$ B $\text{C}_3\text{H}_9\text{N}$ C $\text{C}_4\text{H}_{11}\text{N}$ D $\text{C}_8\text{H}_{20}\text{NBr}$
- 23 Which of the following statements about phenol is **incorrect**?

- A Acidic hydrolysis of phenylethanoate will give ethanoic acid and phenol.
- B Phenol reacts with ethanoic acid to give phenylethanoate.
- C Phenol gives violet colouration with neutral FeCl_3 .
- D Phenol gives a white precipitate with aqueous bromine.

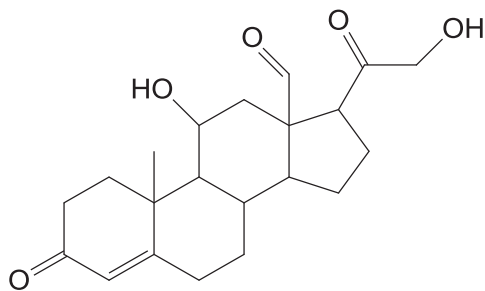
- 24 Several reactions that involve the 'insertion' of carbon monoxide into organic molecules are of industrial importance. One of such reactions is the synthesis of hydroxyethanoic acid from methanal.



Which of the following shows the product formed when benzaldehyde undergoes a similar reaction with carbon monoxide in the presence of water?



- 25 Aldosterone is a hormone essential for sodium conservation in the kidney, salivary glands and colon.



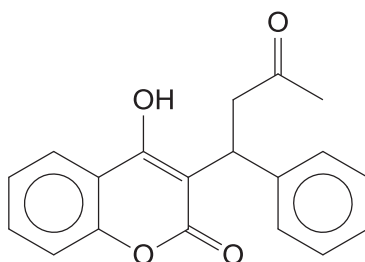
aldosterone

How many chiral carbons are there in the product of the reaction between aldosterone and LiAlH_4 in dry ether?

- A** 7 **B** 8 **C** 9 **D** 10

[Turn over

- 26 Warfarin is a drug used as an anticoagulant to prevent stroke in people who have heart disease.

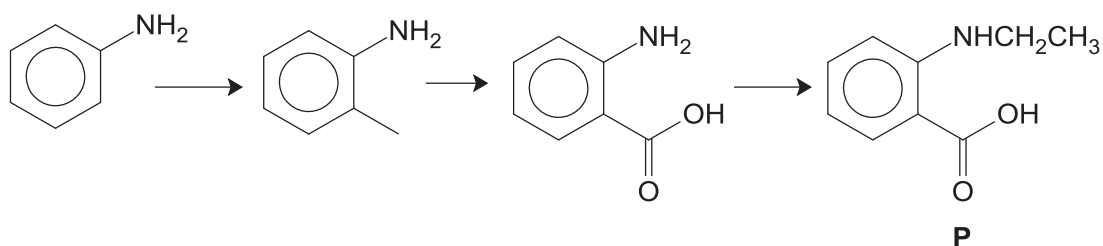


warfarin

Which of the following statements is true about warfarin?

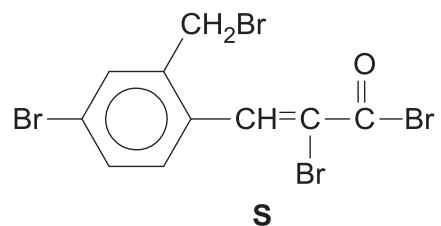
- A 1 mole of warfarin reacts with 2 moles of 2,4-dinitrophenylhydrazine.
 B Warfarin can undergo substitution reaction with SOCl_2 .
 C Warfarin reacts with I_2 and dilute NaOH to give a colourless solution.
 D There are 16 sp^2 hybridised carbon atoms in 1 molecule of warfarin.
- 27 Which of the following amino acids is **not** involved in the formation of proteins in the body?
- A $\text{H}_2\text{NCH}(\text{COOH})\text{CH}(\text{CH}_3)_2$ B $\text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2\text{COOH}$
 C $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{COOH}$ D $\text{H}_2\text{NCH}(\text{CH}_2\text{C}_6\text{H}_5)\text{COOH}$
- 28 Why are amides less basic than amines?
- A Amides form a zwitterion, causing its nitrogen atom to carry a positive charge.
 B The amide carbonyl group withdraws lone pair of electrons from nitrogen atom, releasing the H atom on NH_2 as proton.
 C The C-N bond in amides is stronger than that in amines.
 D The resonance structure of amides causes the movement of a pair of electrons from the nitrogen atom to the oxygen atom.

- 29 The reaction scheme below shows the synthesis of compound **P** from phenylamine.



Which of the following types of reaction is **not** involved in the reaction scheme shown?

- | | |
|-------------------------------------|--------------------------------|
| A electrophilic substitution | B nucleophilic addition |
| C nucleophilic substitution | D oxidation |
- 30 The structure of compound **S** is shown below.



0.01 mol of **S** is reacted with excess hot ethanolic silver nitrate. What is the mass of the silver bromide formed from the reaction?

- | | | | |
|------------------|------------------|------------------|------------------|
| A 1.878 g | B 3.758 g | C 5.634 g | D 7.512 g |
|------------------|------------------|------------------|------------------|

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

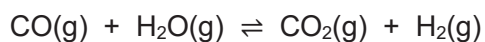
No other combination of statements is used as a correct response.

- 31** Which of the following types of bonding are present in $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]\text{Cl}_2$?
- 1 covalent bonding
 - 2 dative bonding
 - 3 ionic bonding
- 32** Which of the following are **incorrect** assumptions made in the kinetic theory about an ideal gas?
- 1 The gaseous particles are in constant random motion.
 - 2 The gaseous particles have constant interactions with one another.
 - 3 The volume of the container is negligible.

- 33 When 290 C of electricity are passed through a molten compound of a metal, 0.001 mol of atoms of the metal is deposited at the cathode.

What could the metal be?

- 1 aluminium
 - 2 copper
 - 3 silver
- 34 The following reaction between carbon monoxide and steam occurs in the presence of a suitable catalyst.



The standard enthalpy changes of formation of the compounds involved in the reaction are given below.

Compound	Standard enthalpy change of formation / kJ mol ⁻¹
CO(g)	-111
H ₂ O(g)	-242
CO ₂ (g)	-394

Which of the following changes would increase the yield of H₂(g) in the reaction above?

- 1 decrease in temperature
- 2 adding sodium hydroxide into the system
- 3 adding more catalyst into the system

[Turn over

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

35 Which of the following statements are true for the hydrogen halides HCl, HBr and HI?

- 1 Hydrogen iodide is the strongest acid.
- 2 Hydrogen iodide has the lowest thermal stability.
- 3 Hydrogen chloride has the lowest boiling point.

36 Which of the following properties of copper and calcium are likely to differ?

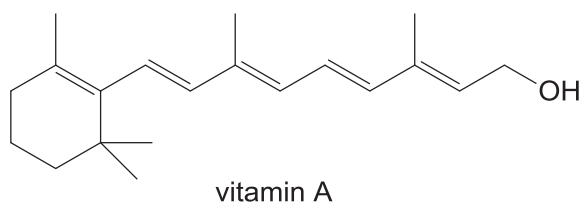
- 1 density
- 2 ability to display variable oxidation states
- 3 reactivity with acid

37 In the catalytic converter in the exhaust system of a car, harmful gases are converted to less harmful ones.

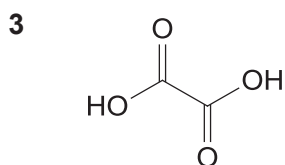
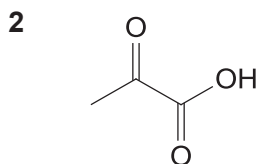
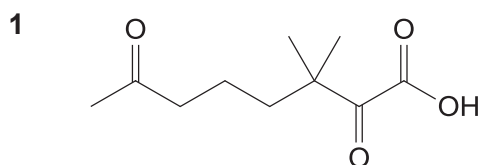
Which of the following processes take place in the catalytic converter?

- 1 hydrocarbons + oxides of nitrogen → carbon dioxide + water + nitrogen
- 2 carbon monoxide + oxides of nitrogen → carbon dioxide + nitrogen
- 3 carbon dioxide + oxides of nitrogen → carbon + nitrogen + water

38 The structure of vitamin A is shown below.



Which of the following are possible products of the reaction of vitamin A with excess hot acidified potassium manganate(VII)?



39 Which compounds reacts with an excess of sodium metal to give one mole of $\text{H}_2(\text{g})$ per mole of the compound?

- 1 $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COOH}$
- 2 $\text{CH}_3\text{CH}_2\text{COCH}(\text{OH})\text{COOH}$
- 3 $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$

[Turn over

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 40** Hippuric acid can be produced by adding benzoyl chloride to aminoethanoic acid. Which changes in bonding occur during this synthesis?



hippuric acid

- 1** A carbon-chlorine bond is broken.
- 2** A carbon-nitrogen bond is formed.
- 3** A hydrogen-chlorine bond is formed.

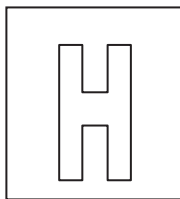
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Candidate Name: _____

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2017 Preliminary Examination II

Pre-University 3

H2 CHEMISTRY**9647/02**

Paper 2 Structured Questions

12th Sept 2017**2 hours**

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST**Do not turn over this question paper until you are told to do so**

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

Write in dark blue or black pen.

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

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

Answer **all** questions.

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

A Data Booklet is provided.

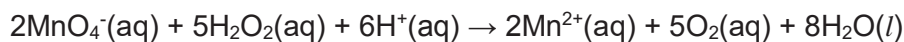
At the end of the examination, fasten all your work securely together.

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

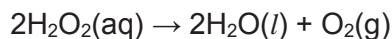
Question	1	2	3	4	5	Total
Marks	12	14	15	11	20	72

1 Planning (P)

Hydrogen peroxide undergoes a redox reaction with acidified KMnO_4 as follows:



By itself, hydrogen peroxide decomposes slowly in accordance to the following equation:



It is found that the decomposition reaction is first order with respect to H_2O_2 . The reaction can be accelerated by using solid manganese(IV) oxide as the catalyst.

(a) Write the rate equation for the decomposition of hydrogen peroxide.

..... [1]

(b) Using the information given, you are required to write a plan to determine the rate constant for the decomposition of hydrogen peroxide using the continuous titration method.

You may also assume that you are provided with:

- 250 cm³ of 0.0100 mol dm⁻³ acidified KMnO_4 ;
- 250 cm³ of 0.0250 mol dm⁻³ H_2O_2 solution;
- Solid manganese(IV) oxide;
- 25.0 cm³ pipette;
- Stopwatch;
- the apparatus normally found in a school or college laboratory.

Your plan should include:

- practical details of how you would
 - determine if dilution of the reaction mixture is needed for titration against H_2O_2 ;
 - ensure the reaction is complete;
 - carry out the titration;
- a sketch of the graph you would expect to obtain;
- brief, but specific, details of how the results would then be used to obtain
 - the initial rate of reaction of decomposition in mol dm⁻³ min⁻¹.
 - the rate constant for the reaction

- 2 Hydrogen iodide can undergo decomposition to give a mixture of hydrogen gas and iodine gas.



- (a) State Le Chatelier's Principle.

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

- (b) Predict and explain the effect of the following changes on the position of the above equilibrium, if any.

- (i) Increasing the temperature

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

- (ii) Reducing the pressure

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

- (iii) Addition of catalyst

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

- (c) When 1.4 mol of hydrogen iodide is heated in a closed vessel at 550 K, the total pressure at equilibrium was 6 atm.

Given that the mole ratio of hydrogen iodide to iodine gas at equilibrium is 9:4, calculate the equilibrium constant, K_p , at 550 K.

[3]

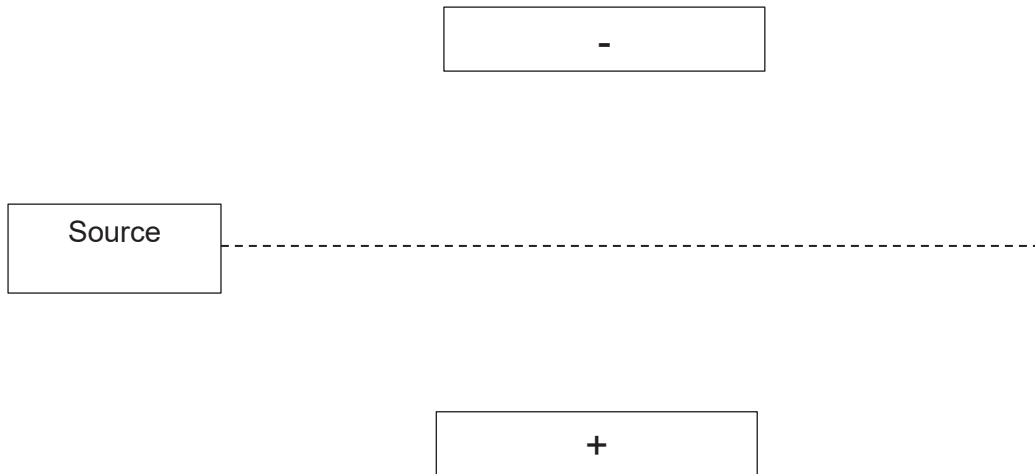
- (d) Hydrogen chloride and hydrogen bromide also undergoes a similar decomposition to give hydrogen gas and its respective halogens.

Describe the trend in the volatility and colours of the halogens.

.....
.....
.....
.....[3]

(e) It was observed that a beam of protons gives an angle of 27° in the following electric field.

Indicate on the diagram below how a beam of protons, $^{127}\text{I}^-$ and $^{23}\text{Na}^+$ ions, travelling at the same speed, behave in the same electric field. Calculate the respective angles of deflection.

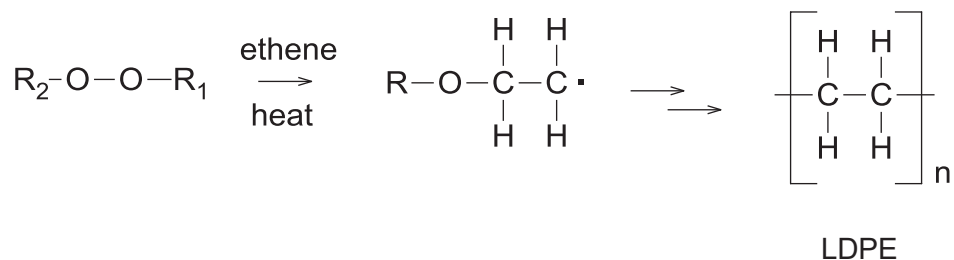


Working:

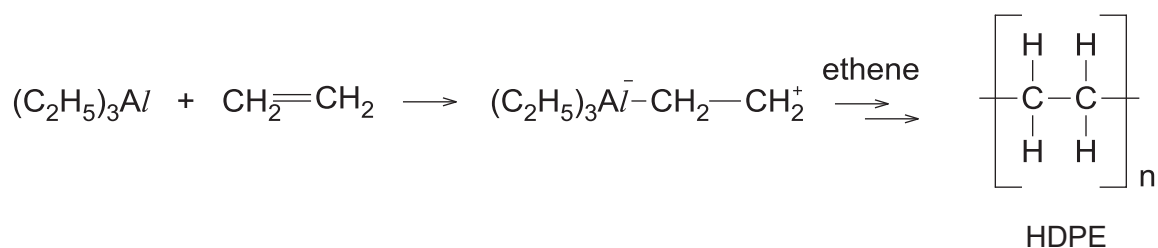
[3]

[Total: 14]

- 3 In 1933, chemists in Britain discovered that when ethene was subjected to high pressures in the presence of a trace amount of oxygen or organic peroxide, it produced low-density poly(ethene) (LDPE). The radical mechanism using organic peroxides is shown below.



Using triethylaluminium, also known as Ziegler-Natta catalyst, developed by Karl Ziegler and Giulio Natta in 1953, ethene can be polymerised at much lower pressures to produce high-density poly(ethene) (HDPE). In the first step, triethylaluminium can accept the pair of π electrons of ethene to form a carbocation which is very similar to that found in the usual electrophilic addition reactions. This carbocation then undergoes an addition reaction with another ethene molecule. Eventually, long chains of ethene units form.



The major differences between the structures of LDPE and HDPE are that

- the average chain length of LDPE is much shorter than that of HDPE
- the chains of LDPE are branched, while the chains of HDPE are unbranched.

The table below compares the physical properties of LDPE and HDPE.

Property	Polymer	
	LDPE	HDPE
Density	Low	High
Melting Point	Approximately 130 °C	Approximately 160 °C
Tensile strength	Low	High
Flexibility	Very flexible	Much more rigid

- (a) (i) Using structure and bonding, explain the difference in melting point between LDPE and HDPE.

.....

 [2]

- (ii) Suggest why LDPE has a lower density than HDPE.

.....

 [1]

- (b) (i) Write an equation to represent the first step in the radical mechanism.

..... [1]

- (ii) With reference to the mechanism given, explain why the production of LDPE only starts upon heating.

.....
 [1]

(iii) Suggest why the chains of LDPE are branched.

.....
 [1]

(c) (i) State the role of triethylaluminium in the reaction using Ziegler-Natta catalysts.

..... [1]

(ii) Similar to ethene, propene can be polymerised using the Ziegler-Natta catalysts. Show the structure of the carbocation intermediate formed in the first step.

[1]

(d) **Use the table of characteristics values for the infra-red absorption in the Data Booklet to answer this question.**

Infra-red absorptions can be used to identify functional groups in organic compounds. For example, ethanol shows absorptions at $1000-1300\text{ cm}^{-1}$ and $3230-3550\text{ cm}^{-1}$.

Use the table to identify the infra-red absorption range that will be shown by

(i) Ethene but not by poly(ethene)

..... cm^{-1}

(ii) Propyl ethanoate but not by propene

..... cm^{-1}

[3]

(e) The four methods used to dispose polymers are incineration, recycling, depolymerisation and bacterial fermentation.

(i) Combustion of the polymers during incineration can lead to the formation of pollutants such as carbon monoxide which is toxic to humans, if the conditions are not carefully controlled.

In terms of the bonding involved, explain how carbon monoxide prevents oxygen from being transported around the body.

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

(ii) State two advantages of recycling.

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

[Total: 15]

4 Iron is a transition element in Period 4 of the Periodic Table.

(a) Explain what is meant by a transition element.

..... [1]

(b) Most iron oxide samples have a mole ratio of iron to oxygen in a range between 0.84 : 1 to 0.96 : 1. Suggest why these samples have variable compositions.

.....
 [1]

(c) The reaction between peroxodisulfate ions, $\text{S}_2\text{O}_8^{2-}$ and iodide ions is very slow at room conditions, while addition of iron(III) ions can speed up the reaction rate.

(i) Suggest why the reaction between $\text{S}_2\text{O}_8^{2-}$ and iodide ions is very slow.

.....
 [1]

(ii) Construct ionic equations to outline the catalytic role of iron(III) ions in the reaction.

.....
 [2]

(iii) State another iron species that can also act as a catalyst for the reaction.

..... [1]

(d) When thiocyanate ligand, SCN^- , is added to the yellow solution of FeCl_3 , a deep red solution **H** is obtained.

(i) Suggest the formula of the complex responsible for the deep red solution **H**.

..... [1]

(ii) State the type of reaction when FeCl_3 forms **H**.

..... [1]

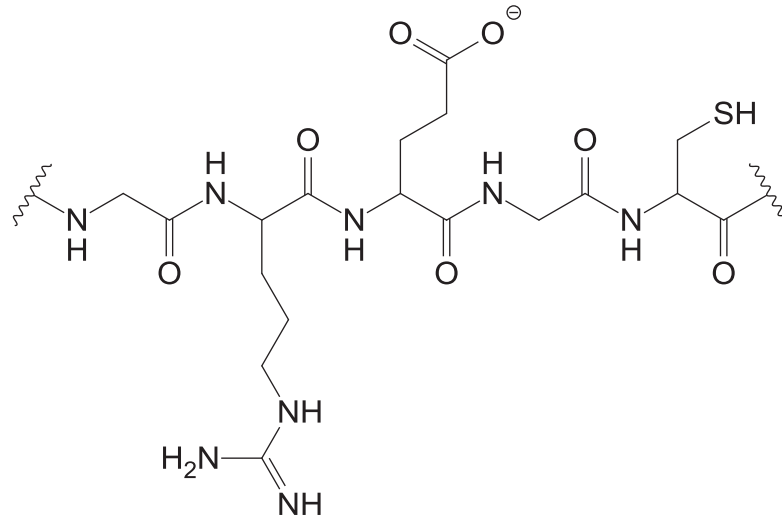
(iii) Explain why aqueous Fe^{3+} solutions are coloured.

.....
.....
.....
..... [3]

[Total: 11]

- 5 The pancreas produces the protein insulin that regulates the metabolism of carbohydrates, fats and proteins.

The structure of a portion of the insulin molecule is shown below. This portion contains a number of amino acids.



- (a) Describe the tertiary structure of insulin.

.....

 [2]

- (b) (i) What is meant by the term *denaturation*?

.....
 [1]

- (ii) Suggest a brief outline of one method by which insulin may be denatured.

.....

 [2]

- (iii) State the reagent and conditions required for complete hydrolysis of protein in the laboratory.

..... [1]

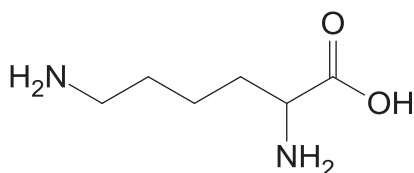
- (iv) One of these amino acid residues are present more than once in the above portion of the insulin molecule. Draw a displayed formula for this amino acid residue.

[1]

- (v) Explain, with the aid of equations, how the zwitterionic form of the amino acid in (b)(iv) act as a buffer.

..... [2]

- (c) Lysine is a α -amino acid that is used in the biosynthesis of proteins.



- (i) Explain what is meant by the term pK_a as applied to a weak acid HA.

.....

..... [1]

- (ii) State the functional groups present in lysine.

..... [1]

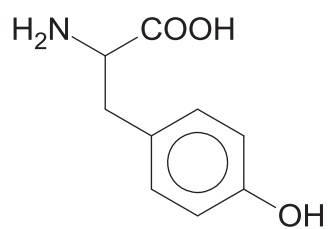
(iii) There are three pK_a values associated with lysine: 2.1, 8.9 and 10.5.

Make use of these pK_a values to suggest the major species present in the solutions of the amino acid with the following pH values.

pH 1	pH 4
pH 9	pH 12

[4]

- (d) Tyrosine is another amino acid present in insulin.



Draw the organic products when tyrosine undergoes reaction with

- (i) $\text{Br}_2(\text{aq})$

[1]

- (ii) $\text{NaOH}(\text{aq})$

[1]

- (iii) excess $\text{CH}_3\text{CH}_2\text{COCl}$

[1]

- (e) State the type of reactions for **reaction with**.

$\text{Br}_2(\text{aq})$

$\text{NaOH}(\text{aq})$

[2]

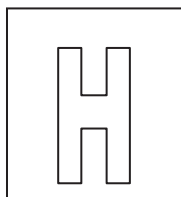
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2017 Preliminary Examination II

Pre-University 3

H2 CHEMISTRY**9647/03**

Paper 3 Free Response

15th Sept 2017**2 hours**

Candidates answer on separate paper.

Additional materials: Answer Paper

Data Booklet

READ THESE INSTRUCTIONS FIRST**Do not turn over this question paper until you are told to do so**

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

Write in dark blue or black pen.

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

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

Answer any **four** questions.

A Data Booklet is provided.

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

You are reminded of the need for good English and clear presentation in your answers.

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

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

Question	1	2	3	4	5	Total
Marks	20	20	20	20	20	80

1 (a) Graphite is a naturally-occurring form of crystalline carbon and is found in metamorphic and igneous rocks. Graphite is extremely soft and cleaves with very light pressure yet it is extremely resistant to heat and nearly inert in contact with almost any other material. These extreme properties give it a wide range of uses in metallurgy and manufacturing.

(i) With reference to the structure, account for the following properties of graphite.

- Soft
- Heat resistant and inert

[3]

(ii) The following table shows some thermochemistry data.

Reaction	$\Delta H / \text{kJ mol}^{-1}$
Standard enthalpy change of atomisation of carbon	+715
Enthalpy change of $4\text{H}(\text{g}) + \text{O}(\text{g}) + \text{C}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$	-2069

With the use of relevant data from the *Data Booklet* and the above information, calculate the enthalpy change of formation of methanol.

[3]

(b) A butane burner is used to heat the air in a hot air balloon. The hot air balloon has a volume of 2.1 m^3 and its volume does not change when the enclosed air is heated.

(i) Using the ideal gas equation, calculate the amount of gas molecules the balloon contains at temperature 800 K and a pressure of $1.0 \times 10^6 \text{ Pa}$.

[1]

(ii) Hence calculate the mass of air it contains, assuming an average relative molecular mass of 29.

[1]

(iii) The standard enthalpy change of combustion of butane is $-2877.5 \text{ kJ mol}^{-1}$. It requires 1.0 J of energy to raise the temperature of 1.0 g of air by 1.0 K.

Using your answer in (b)(ii), calculate the mass of butane that needs to be burnt to raise the temperature of the air in the balloon by 20 K. Assume that the hot air balloon is a closed system.

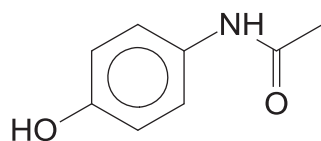
[2]

(iv) The actual mass of butane that needs to be burnt to raise the temperature of the air in the balloon by 20 K was found to be 3.81 g.

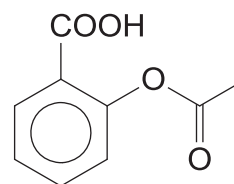
Suggest why this differs from your answer in (b)(iii).

[1]

- (c) Paracetamol and aspirin are effective at pain and fever relief due to their ability to dissolve quickly in the blood stream and are soluble in fatty compounds found in cell membrane.

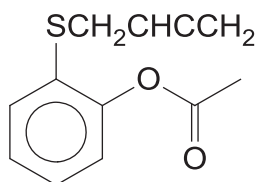


Paracetamol

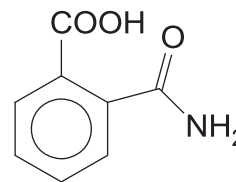


Aspirin

- (i) Account for these properties based on the structure and bonding of aspirin. [2]
- (ii) One of the pain relievers cause more stomach irritation than the other. With reference to the functional groups present, suggest and explain the pain reliever that you will recommend to someone who suffers from gastric bleeding. [2]
- (iii) Write the structural formula of the organic product(s) formed when paracetamol tablet is refluxed with sodium hydroxide. [2]
- (iv) Extensive research has been made to improve the effectiveness of the pain-relievers. Two proposals were made to modify aspirin.



Drug A



Drug B

Given that the melting points of drugs **A** and **B** are 179 °C and 154 °C respectively, account for the melting point in terms of structure and bonding. [2]

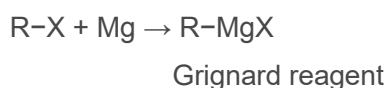
- (v) State the relative solubility of drugs **A** and **B** in water. [1]

[Total: 20]

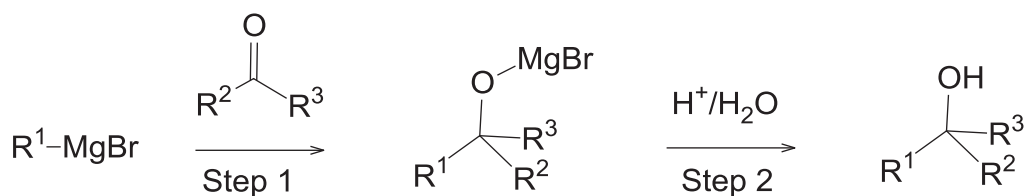
2 Halogens and their compounds can be toxic but some are essential for the human body's functioning and are used in daily products. The oxidising power of chlorine allows it to act as a good disinfectant.

(a) With the use of *Data Booklet*, explain why FeCl_3 exists but FeI_3 does not. [4]

(b) Grignard reaction is an important reaction which helps in lengthening the carbon chain. A Grignard reagent has a general formula of R-MgX where R is an alkyl or aryl group and is formed via the reaction of an alkyl or alkyl halide with magnesium powder.



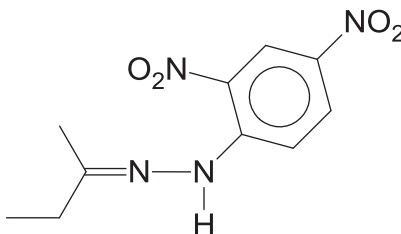
Carbonyl compounds react with Grignard reagent to increase the carbon chain.



- (i) In the formation of Grignard reagent, it is important to carry out the reaction in a dry environment. Suggest a reason. [1]
- (ii) It was observed that the reaction to form the Grignard reagent is very slow at the start when magnesium powder is added to the alkyl halide in diethyl ether solvent. Suggest a reason. [1]
- (iii) The addition of the Grignard reagent to the carbonyl typically proceeds through a six-membered ring transition state. For the reaction of each molecule of carbonyl compound, two molecules of Grignard reagents are involved in the formation of the transition state.

Suggest the transition state of Step 1 for the reaction between propanone and CH_3MgBr shown above. [1]

- (iv) Suggest a four-step synthesis of compound **Q** from a carbonyl compound. State the reagents and conditions for each stage and draw structures of the intermediate organic products. The first two steps should involve the use of Grignard reaction between CH_3MgBr and a relevant carbonyl compound.



Compound Q

[5]

- (c) (i) Describe what is observed when NaCl and NaBr reacts with concentrated sulfuric acid respectively. In each case, suggest the products of the reaction and write equations where appropriate. [2]
- (ii) Explain any difference in their reactions with concentrated sulfuric acid. [1]
- (d) When cold aqueous sodium hydroxide is added to a yellowish-green solution of chlorine in trichloromethane and shaken together, two immiscible colourless layers (aqueous layer and organic layer) were observed.
- (i) State the type of reaction and give an equation, including state symbols, for this reaction. [2]
- (ii) Assuming that the starting reagents were added in stoichiometric ratio, suggest the chemical species found in the two immiscible colourless layers respectively. [2]
- (e) One of the compounds that may be formed between chlorine and iodine is iodine tetrachloride, ICl_4^- . Construct a 'dot-and-cross diagram' to show the arrangement of electrons in ICl_4^- . [1]

[Total: 20]

- 3 (a) Hunsdiecker reaction is the organic reaction of silver salts of carboxylic acids with halogens to give organic halides.

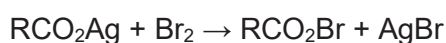
The overall reaction is:



The reaction mechanism of the Hunsdiecker reaction is believed to involve organic radical intermediates.

The steps involved in the reaction mechanism are as follows:

1. The silver salt of the carboxylic acid quickly reacts with bromine to form the acyl hypohalite intermediate, RCO_2Br .



2. The initiation step involves the formation of two radicals from the acyl hypohalite intermediate. One of which is bromine radical.
3. The first step of propagation involves the removal of CO_2 from the radical formed in step 2, forming $\text{R}\bullet$ and CO_2 .
4. $\text{R}\bullet$ recombines with the acyl hypohalite intermediate to form the desired organic halide.

- (i) Write equations to illustrate the reaction mechanism of Hunsdiecker reaction. [3]
- (ii) Draw the structure of the organic product formed when $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{COOAg}$ reacts with Br_2 . [1]
- (iii) The product in (a)(ii) displays optical isomerism as it has a chiral centre. Explain the term *chiral centre* and label the chiral centre in (a)(ii) with an asterix(*) sign. [2]
- (iv) Chlorine and iodine can be used in place of bromine to react with silver salts of carboxylic acids.

A student wanted to compare the rate of reaction of iodine reacting with silver salts of carboxylic acids with that of bromine. However, he did not label the apparatus and ended up not able to tell which apparatus has the iodine-containing and bromine-containing organic products.

Describe a chemical test which can allow the student to derive correctly the apparatus with the iodine-containing and bromine-containing organic products respectively. Include the observations, if any. [4]

(b) Write the equations and state the observations of the following reactions, where appropriate.

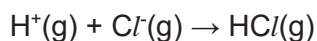
- Reaction between sodium and oxygen
- Reaction between sulfur and oxygen

[4]

(c) (i) The following table shows some thermochemistry data.

Reaction	$\Delta H / \text{kJ mol}^{-1}$
enthalpy change of formation of $\text{HCl}(\text{g})$	-92
first electron affinity of $\text{Cl}(\text{g})$	-364

Using the following data, and relevant data from the *Data Booklet*, construct an energy level diagram to calculate the standard enthalpy change for the following reaction.

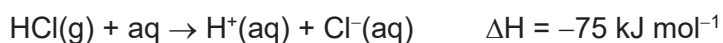


[4]

(ii) The following reaction is expected to be an endothermic reaction.



However, the following reaction is an exothermic reaction.



Explain the above observations.

[2]

[Total: 20]

- 4 (a) (i) Heating compound **P**, $C_{10}H_{12}O_3$, with dilute sulfuric acid yields compound **Q**, $C_9H_{12}O_2$, and methanoic acid.

On treatment with dilute nitric acid, compound **Q** forms compound **R** with the formula $C_9H_{11}NO_4$. Compound **Q** also reacts with aqueous bromine to form compound **S**, $C_9H_9O_2Br_3$.

Heating compound **R** with tin in concentrated hydrochloric acid, followed by adding excess aqueous sodium hydroxide to the product gives compound **T**, $C_9H_{12}NO_2Na$.

Compound **T** turns hot acidified potassium dichromate solution green and forms compound **U**, $C_9H_{12}NO_3$. 1 mole of compound **U** reacts with 3 moles of aqueous sodium hydroxide. Compound **T** reacts with hot acidified potassium manganate(VII) and forms compound **V**, $C_8H_8NO_5$.

Suggest structures for compounds **P–V** and give an account of the chemistry involved.

[14]

- (ii) Write the equation for the reaction of compound **P** being heated with dilute sulfuric acid. [1]

- (b) Ester is an organic molecule which has many uses. Esters with low molecular masses are commonly used as fragrances and are found in essential oils. Phosphoesters form the backbone of DNA molecules.

- (i) Given that methyl methanoate and ethyl methanoate are the simplest esters available, suggest a chemical test which can distinguish the two compounds. [3]

- (ii) Acyl chlorides and esters are both derivatives of carboxylic acids. Compare and account for the acidity of methyl methanoate and ethanoyl chloride. [2]

[Total: 20]

- 5 Vehicle frames are usually made from aluminium as it is lightweight and strong. However, the aluminium frames have to be made more resistant to corrosion as certain parts could be exposed to rainwater and acidic gases in vehicle exhaust.

The industrial process for the anodising of aluminium uses an inert platinum cathode and aqueous sulfuric acid as the electrolyte.

- (a) Explain, in terms of the electrode reactions, how a piece of aluminium metal could be anodised to be more resistant to corrosion. [3]

- (b) A current of 0.30 mA was switched on for 1 hour to anodise an aluminium frame. Calculate the amount of Al_2O_3 produced from the anodisation. [3]

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

Explain, stating any observations, how the electrode reactions would be different if

- (i) the electrolyte was contaminated with copper(II) sulfate. [2]

- (ii) the aluminium electrode was replaced with another platinum electrode. [2]

- (d) Infra-red (IR) spectroscopy is a common technique used to identify functional groups in organic compounds and to study how the functional groups are affected by other substances.

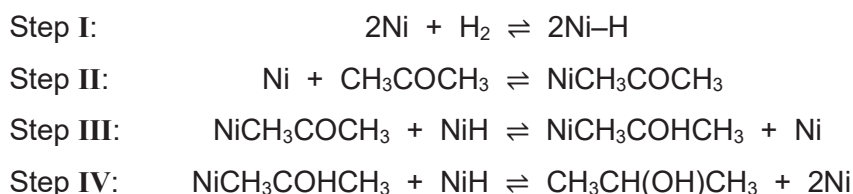
When a beam of IR light of varying energies is shone at an organic compound, its functional groups can absorb certain energies characteristic to it. The energy of IR light is measured in wavenumbers, $\tilde{\nu}$, and is expressed as the reciprocal of its wavelength, λ , with units of cm^{-1} .

$$\tilde{\nu} = \frac{1}{\lambda}$$

For example, carbonyl functional groups absorb IR light at the wavenumber range of 1680 to 1750 cm^{-1} , while alkyl groups absorb IR light at a wavenumber range of 2840 to 3095 cm^{-1} .

The gas-phase kinetics and mechanism of the hydrogenation of propanone using nickel catalyst was studied using IR spectroscopy. Dissociative adsorption of hydrogen gas on solid nickel is known to occur readily (step I). The adsorption of propanone gas onto the nickel catalyst was identified by a wavenumber peaking at 1620 cm^{-1} . The shift in wavenumber from 1680 to 1620 cm^{-1} confirms that it is the C=O functional group that is adsorbed onto the nickel catalyst and not the methyl groups (step II). However, no wavenumber shift corresponding to the alcohol functional group of the product, propan-2-ol, was found. This indicates that when the product is formed, it immediately desorbed from the catalyst (step IV).

Hence, the proposed mechanism for this reaction is as follows.



When the experiment was conducted in a closed vessel of fixed volume at a constant temperature of 363 K , the following data was recorded.

Experiment	Partial pressure of hydrogen / kPa	Partial pressure of propanone / kPa	Relative rate
1	0.5	2.5	1
2	1	2.5	2
3	4	5	16
4	10	5	16
5	50	5	16

- (i) Nickel is acting as a *heterogeneous* catalyst in this reaction.
Define the term *heterogeneous*. [1]
- (ii) Based on experiments 1 to 3, determine the order of reaction with respect to hydrogen and with respect to propanone.
Hence, deduce the rate equation for the hydrogenation of propanone. [3]
- (iii) Based on your answer in (ii), state which step in the proposed mechanism is the rate-determining step. [1]
- (iv) Suggest a reason why the catalyst has to be used in the powdered form. [1]

- (v) Hence, or otherwise, suggest a reason why the rate of reaction stopped increasing in experiments 4 and 5 when the partial pressure of hydrogen exceeded 4 kPa. [1]
- (vi) Sketch an energy distribution diagram to explain how the rate of the reaction would have been different without the use of a catalyst. [3]

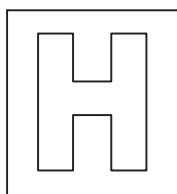
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Candidate Name: _____

Class	Adm No



2017 Preliminary Examinations II

Pre-University 3

H2 CHEMISTRY

Paper 1 Multiple Choice

9647/01

20 Sept 2017

1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Write in soft pencil.

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

Write your name, class and admission number in the spaces provided at the top of this page and on the Multiple Choice Answer Sheet provided.

There are **forty** questions on this paper. Answer **ALL** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the Multiple Choice Answer Sheet provided.

Read the instructions on the Multiple Choice Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this question paper.

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

FOR EXAMINER'S USE	
TOTAL (40 marks)	

This question paper consists of **16** printed pages and **2** blank pages.

Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

- 1 Dolomite is a carbonate-containing mineral with formula $\text{MgZ}(\text{CO}_3)_2$ where **Z** is a metal ion. It is insoluble in water but reacts with acids.

When 2.00 g of dolomite was completely dissolved in an excess of hydrochloric acid, 0.759 g of carbon dioxide was given off. What is the identity of the metal **Z**?

- A** Ba **B** Ca **C** Ra **D** Sr

- 2 Sulfur dioxide gas is an irritant to the eyes and respiratory system. The maximum safe toleration level of sulfur dioxide in air is 0.014 mg dm^{-3} .

How many molecules of sulfur dioxide gas are present in 1 dm^3 of air at this toleration level?

- A** $\frac{0.014}{6.02 \times 10^{23}} \times 64.1$ **B** $\frac{0.014}{1000} \times \frac{1}{64.1} \times 6.02 \times 10^{23}$
C $\frac{0.014}{64.1} \times 6.02 \times 10^{23}$ **D** $\frac{0.014}{1000} \times 64.1 \times 6.02 \times 10^{23}$

- 3 The element technetium, Tc (mass number 99; atomic number 43), was discovered in 1937 by two Italian scientists, Segre and Perrier.

Under suitable conditions, technetium reacts with fluorine to form TcF_6 .

Which of the following options shows the correct number of protons, neutrons and electrons in Tc^{6+} ?

	number of protons	number of neutrons	number of electrons
A	43	43	56
B	43	56	37
C	49	43	37
D	43	56	49

4 Which of the following atoms has three unpaired electrons?

- A Br **B** Co C Ga D Sc

5 Under standard conditions, water exists in the liquid state but hydrogen sulfide exists in the gaseous state.

Which of the following best explains this phenomenon?

- A Water has a higher relative molecular mass than hydrogen sulfide.
B The O-H covalent bond in water is stronger than the S-H covalent bond in hydrogen sulfide.
C The hydrogen bonds between water molecules are stronger than the Van der Waals' forces between hydrogen sulfide molecules.
D Hydrogen sulfide has a more spherical structure compared to water.

6 Antimony, Sb, is in Group V of the Periodic Table. It was proposed that antimony is able to form SbF_4^{n-} anion, the structure of which is of square planar shape.

Which of the following shows the correct value of n and the oxidation number of Sb in this anion?

	value of n	oxidation number of Sb
A	1	+3
B	1	+5
C	3	+1
D	3	+3

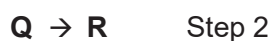
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- 7 **X** and **Y** are ideal gases that do not react with one another. The molar mass of **X** is twice that of **Y**.

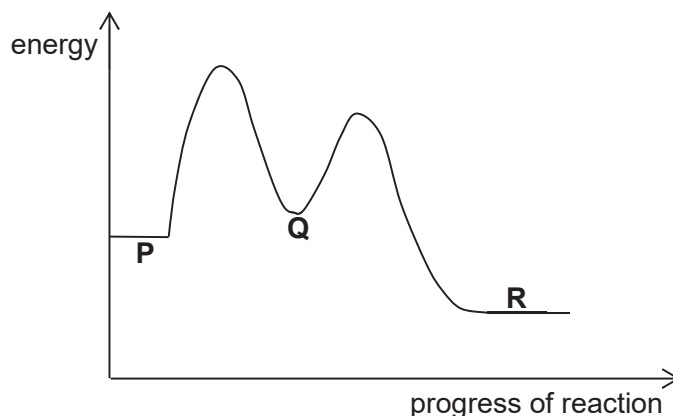
If all measurements are taken at room temperature and pressure, which statement correctly describes **X** and **Y**?

- A** The volume occupied by 2 g of **X** is half that occupied by 2 g of **Y**.
B The mass of 5 dm³ of **X** is half that of 5 dm³ of **Y**.
C The volume occupied by 2.5 g of **X** is equal to the volume occupied by 5 g of **Y**.
D On mixing 1 dm³ of **X** with 1 dm³ of **Y**, the partial pressure of **X** is twice that of **Y**.

- 8 The two steps in the conversion of compound **P** to compound **R** are shown below.



The energy profile of the reaction is shown below.



Which of the following statements about the reaction can be deduced from the information given?

- A** The enthalpy change for the reaction is endothermic.
B **Q** acts as a catalyst in the reaction.
C Step 1 is the rate determining step.
D **R** is thermodynamically less stable than **P**.

- 9 When liquid SOCl_2 is added to Ba(OH)_2 , a vigorous reaction occurs and the temperature decreases from $25\text{ }^\circ\text{C}$ to $5\text{ }^\circ\text{C}$.

What are the correct signs of ΔH , ΔS and ΔG for this reaction?

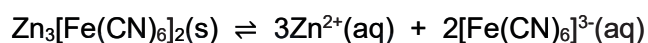
	ΔH	ΔS	ΔG
A	+	+	-
B	+	-	+
C	-	+	-
D	-	-	+

- 10 A sample of finely ground copper was contaminated with zinc powder. Treatment of the sample with an excess of hydrochloric acid produced 120 cm^3 of hydrogen gas, measured at room temperature and pressure. The remaining copper was then reacted with acidified potassium manganate(VII). It was found that 0.00424 mol of potassium manganate(VII) was required for complete oxidation of copper to copper(II) ions.

What is the percentage by mass of copper in the sample?

- A** 45.2% **B** 65.8% **C** 67.3% **D** 90.4%

- 11 Zinc(II) reacts with the complex anion hexacyanoferrate(III), $[\text{Fe(CN)}_6]^{3-}$, to give a sparingly soluble salt which dissociates in water according to the following equilibrium.



If the solubility product, K_{sp} , of $\text{Zn}_3[\text{Fe(CN)}_6]_2$ is X , what is the concentration of $\text{Zn}^{2+}(\text{aq})$ at equilibrium?

- A** $\left(\frac{3X}{2}\right)^{\frac{1}{3}}$ **B** $\left(\frac{3X}{2}\right)^{\frac{1}{5}}$ **C** $\left(\frac{9X}{4}\right)^{\frac{1}{3}}$ **D** $\left(\frac{9X}{4}\right)^{\frac{1}{5}}$

[Turn over

- 12 Which of the following statements about the rate constant, k , of chemical reactions is **not** true?
- A The rate constant increases when temperature increases.
 - B** The rate constant increases when the concentration of the reactant increases.
 - C The rate constant decreases when the activation energy increases.
 - D The units of the rate constant depends on the overall order of reaction.
- 13 A Period 3 element forms an oxide that is soluble in both water and aqueous sodium hydroxide. Which of the following could be the identity of this element?
- A aluminium
 - B silicon
 - C sodium
 - D** sulfur
- 14 In which of the following pairs is the radius of the first species greater than that of the second species?
- A** Mg, Al
 - B Ca, Ba
 - C Mg^{2+} , Na^+
 - D K^+ , Ar
- 15 Which of the following properties of the Group II elements and their compounds decreases down the group?
- A Ease of oxidation of the elements
 - B** Electronegativity of the elements
 - C Reactivity of elements with chlorine
 - D Thermal stability of nitrates
- 16 With reference to the chemistry of Group VII elements and their compounds, which of the following would be a correct prediction for astatine?
- A Astatine reacts vigorously with hydrogen at room temperature.
 - B Astatine exists as a gas at room temperature.
 - C** Astatine reacts with cold aqueous hydroxide to form AtO^- and At^- .
 - D Molten At/At_3 can conduct electricity.

17 Which of the following products is **least** likely to act as a ligand?

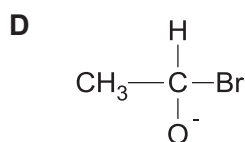
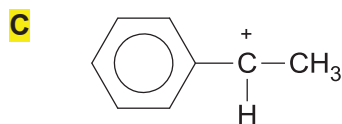
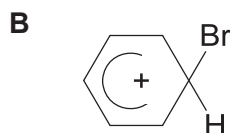
- A** AlH_3 **B** CO **C** $\text{C}_2\text{H}_5\text{OH}$ **D** CH_3NH_2

18 The use of *Data Booklet* is relevant to this question.

An element **G** has an atomic number of 23. Which of the following compounds of **G** is **not** likely to exist?

- A** KGO_3 **B** G_2O_5 **C** K_2GO_4 **D** GOCl_2

19 Which of the following species could be an intermediate in an electrophilic addition reaction?



20 How many structural isomers with the molecular formula $\text{C}_5\text{H}_{10}\text{O}$ gives an orange precipitate with Brady's reagent and a yellow precipitate with alkaline aqueous iodine?

- A** 1 **B** 2 **C** 3 **D** 4

[Turn over

- 21 In an experiment, it was found that during the free radical substitution of alkanes, primary, secondary and tertiary hydrogen atoms were replaced by bromine atoms at different rates, as shown in the table below.

Reaction	Relative Rate
Primary : $\text{RCH}_3 \rightarrow \text{RCH}_2\text{Br}$	1
Secondary : $\text{R}_2\text{CH}_2 \rightarrow \text{R}_2\text{CHBr}$	8
Tertiary : $\text{R}_3\text{CH} \rightarrow \text{R}_3\text{CBr}$	20

With reference to the information given, which of the following shows the 2 products obtained from the reaction of 2,3-dimethylbutane with bromine gas under UV light and their relative ratio?

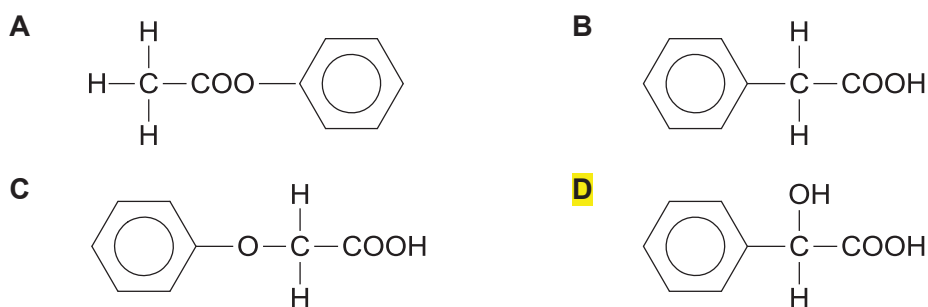
- A** $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{CH}_2\text{Br} : (\text{CH}_3)_2\text{CBrCH}(\text{CH}_3)_2 = 3 : 10$
- B** $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{CH}_2\text{Br} : (\text{CH}_3)_2\text{CBrCH}(\text{CH}_3)_2 = 1 : 20$
- C** $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{Br} : (\text{CH}_3)_3\text{CCHBrCH}_3 = 3 : 8$
- D** $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{Br} : (\text{CH}_3)_3\text{CCHBrCH}_3 = 3 : 20$
- 22 Concentrated ammonia was heated in a sealed tube with excess bromoethane. Which of the following products will **not** be formed?
- A** $\text{C}_2\text{H}_7\text{N}$ **B** $\text{C}_3\text{H}_9\text{N}$ **C** $\text{C}_4\text{H}_{11}\text{N}$ **D** $\text{C}_8\text{H}_{20}\text{NBr}$
- 23 Which of the following statements about phenol is **incorrect**?

- A** Acidic hydrolysis of phenylethanoate will give ethanoic acid and phenol.
- B** Phenol reacts with ethanoic acid to give phenylethanoate.
- C** Phenol gives violet colouration with neutral FeCl_3 .
- D** Phenol gives a white precipitate with aqueous bromine.

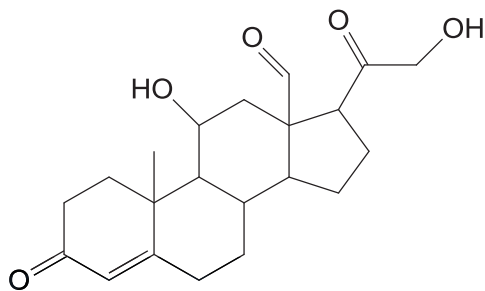
- 24 Several reactions that involve the 'insertion' of carbon monoxide into organic molecules are of industrial importance. One of such reactions is the synthesis of hydroxyethanoic acid from methanal.



Which of the following shows the product formed when benzaldehyde undergoes a similar reaction with carbon monoxide in the presence of water?



- 25 Aldosterone is a hormone essential for sodium conservation in the kidney, salivary glands and colon.



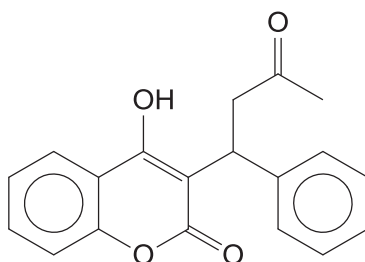
aldosterone

How many chiral carbons are there in the product of the reaction between aldosterone and LiAlH_4 in dry ether?

- A** 7 **B** 8 **C** 9 **D** 10

[Turn over

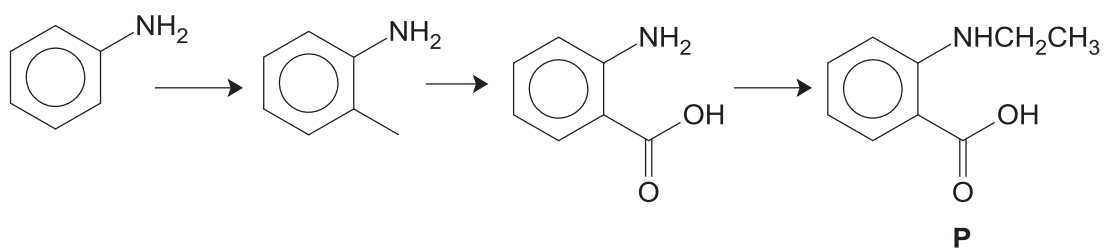
- 26 Warfarin is a drug used as an anticoagulant to prevent stroke in people who have heart disease.



warfarin

Which of the following statements is true about warfarin?

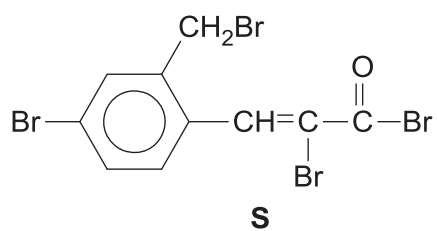
- A** 1 mole of warfarin reacts with 2 moles of 2,4-dinitrophenylhydrazine.
B Warfarin can undergo substitution reaction with SOCl_2 .
C Warfarin reacts with I_2 and dilute NaOH to give a colourless solution.
D There are 16 sp^2 hybridised carbon atoms in 1 molecule of warfarin.
- 27 Which of the following amino acids is **not** involved in the formation of proteins in the body?
- A** $\text{H}_2\text{NCH}(\text{COOH})\text{CH}(\text{CH}_3)_2$ **B** $\text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2\text{COOH}$
C $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{COOH}$ **D** $\text{H}_2\text{NCH}(\text{CH}_2\text{C}_6\text{H}_5)\text{COOH}$
- 28 Why are amides less basic than amines?
- A** Amides form a zwitterion, causing its nitrogen atom to carry a positive charge.
B The amide carbonyl group withdraws lone pair of electrons from nitrogen atom, releasing the H atom on NH_2 as proton.
C The C-N bond in amides is stronger than that in amines.
D The resonance structure of amides causes the movement of a pair of electrons from the nitrogen atom to the oxygen atom.
- 29 The reaction scheme below shows the synthesis of compound **P** from phenylamine.



Which of the following types of reaction is **not** involved in the reaction scheme shown?

- A** electrophilic substitution **B** nucleophilic addition
C nucleophilic substitution **D** oxidation

30 The structure of compound **S** is shown below.



0.01 mol of **S** is reacted with excess hot ethanolic silver nitrate. What is the mass of the silver bromide formed from the reaction?

- A** 1.878 g **B** 3.758 g **C** 5.634 g **D** 7.512 g

Section B

[Turn over

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

31 Which of the following types of bonding are present in $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]\text{Cl}_2$?

- 1** covalent bonding
- 2** dative bonding
- 3** ionic bonding

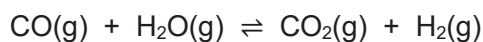
32 Which of the following are **incorrect** assumptions made in the kinetic theory about an ideal gas?

- 1** The gaseous particles are in constant random motion.
- 2** The gaseous particles have constant interactions with one another.
- 3** The volume of the container is negligible.

- 33 When 290 C of electricity are passed through a molten compound of a metal, 0.001 mol of atoms of the metal is deposited at the cathode.

What could the metal be?

- 1 aluminium
 - 2 copper
 - 3 silver
- 34 The following reaction between carbon monoxide and steam occurs in the presence of a suitable catalyst.



The standard enthalpy changes of formation of the compounds involved in the reaction are given below.

Compound	Standard enthalpy change of formation / kJ mol ⁻¹
CO(g)	-111
H ₂ O(g)	-242
CO ₂ (g)	-394

Which of the following changes would increase the yield of H₂(g) in the reaction above?

- 1 decrease in temperature
- 2 adding sodium hydroxide into the system
- 3 adding more catalyst into the system

[Turn over

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

35 Which of the following statements are true for the hydrogen halides HCl, HBr and HI?

- 1** Hydrogen iodide is the strongest acid.
- 2** Hydrogen iodide has the lowest thermal stability.
- 3** Hydrogen chloride has the lowest boiling point.

36 Which of the following properties of copper and calcium are likely to differ?

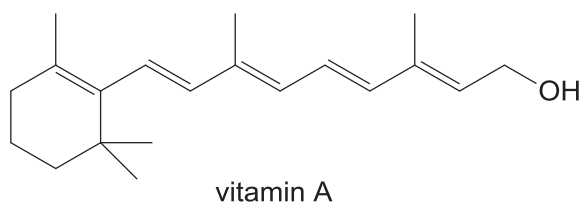
- 1** density
- 2** ability to display variable oxidation states
- 3** reactivity with acid

37 In the catalytic converter in the exhaust system of a car, harmful gases are converted to less harmful ones.

Which of the following processes take place in the catalytic converter?

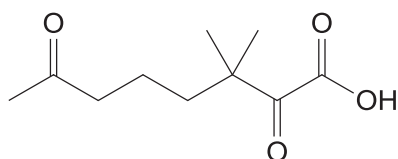
- 1** hydrocarbons + oxides of nitrogen → carbon dioxide + water + nitrogen
- 2** carbon monoxide + oxides of nitrogen → carbon dioxide + nitrogen
- 3** carbon dioxide + oxides of nitrogen → carbon + nitrogen + water

38 The structure of vitamin A is shown below.

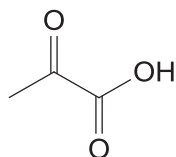


Which of the following are possible products of the reaction of vitamin A with excess hot acidified potassium manganate(VII)?

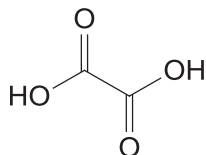
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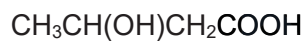


3



39 Which compound reacts with an excess of sodium metal to give one mole of $\text{H}_2(\text{g})$ per mole of the compound?

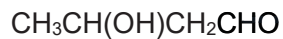
1



2



3



[Turn over

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 40** Hippuric acid can be produced by adding benzoyl chloride to aminoethanoic acid. Which changes in bonding occur during this synthesis?



hippuric acid

- 1** A carbon-chlorine bond is broken.
- 2** A carbon-nitrogen bond is formed.
- 3** A hydrogen-chlorine bond is formed.

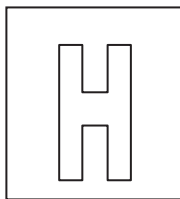
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Candidate Name: _____

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2017 Preliminary Examination II

Pre-university 3

H2 CHEMISTRY**9647/02**

Paper 2 Structured Questions

12th Sept 2017**2 hours**

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST**Do not turn over this question paper until you are told to do so**

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

Write in dark blue or black pen.

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

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

Answer **all** questions.

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

A Data Booklet is provided.

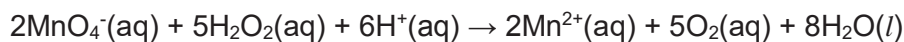
At the end of the examination, fasten all your work securely together.

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

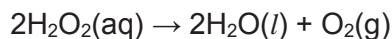
Question	1	2	3	4	5	Total
Marks	12	14	15	11	20	72

1 Planning (P)

Hydrogen peroxide undergoes a redox reaction with acidified KMnO_4 as follows:



By itself, hydrogen peroxide decomposes slowly in accordance to the following equation:



It is found that the decomposition reaction is first order with respect to H_2O_2 . The reaction can be accelerated by using solid manganese(IV) oxide as the catalyst.

(a) Write the rate equation for the decomposition of hydrogen peroxide.

..... [1]



(b) Using the information given, you are required to write a plan to determine the rate constant for the decomposition of hydrogen peroxide using the continuous titration method.

You may also assume that you are provided with:

- 250 cm^3 of 0.0100 mol dm^{-3} acidified KMnO_4 ;
- 250 cm^3 of 0.0250 mol dm^{-3} H_2O_2 solution;
- Solid manganese(IV) oxide;
- 25.0 cm^3 pipette;
- Stopwatch;
- the apparatus normally found in a school or college laboratory.

Your plan should include:

- practical details of how you would
 - determine if dilution of the reaction mixture is needed for titration against H_2O_2 ;
 - ensure the reaction is complete;
 - carry out the titration;
- a sketch of the graph you would expect to obtain;
- brief, but specific, details of how the results would then be used to obtain
 - the initial rate of reaction of decomposition in $\text{mol dm}^{-3} \text{min}^{-1}$.
 - the rate constant for the reaction

Since two volumes used are within the capacity of the apparatus used, no dilution of the solutions needed;

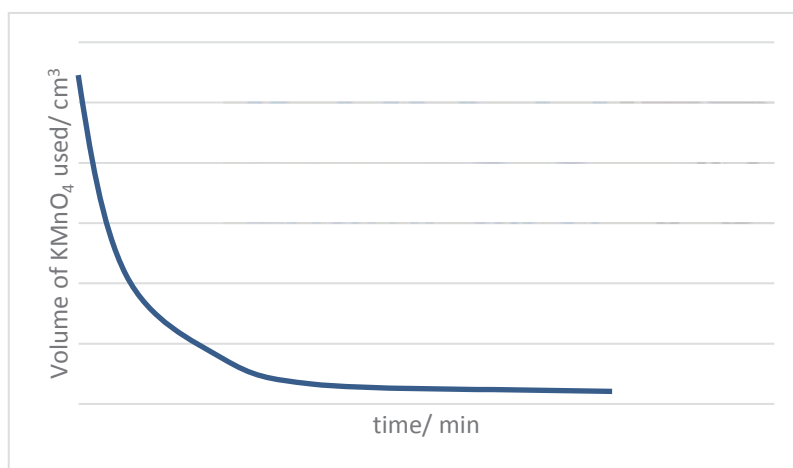
Procedure:

1. From the 250 cm^3 of $0.0250 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$ solution, pipette 25.0 cm^3 into another conical flask.
2. Fill up the 50.00 cm^3 burette with the standard acidified KMnO_4 solution.
3. Take the initial burette reading.
4. Titrate the solution with acidified KMnO_4 . Swirl continuously during the addition of the titrant.
5. Toward the end-point, add the KMnO_4 solution dropwise and swirl. Stop the addition of the titrant when one drop of titrant causes the solution in the conical flask to change from colourless to pale pink.
6. Record the final burette reading. Calculate the volume of acidified KMnO_4 solution needed to react with the hydrogen peroxide solution. (This titre volume would give us the concentration of the H_2O_2 solution at that instant of decomposition).
7. Add some solid manganese(IV) oxide into the 500 cm^3 conical flask containing the H_2O_2 solution. Start the stopwatch. Swirl gently.
8. At every 1 min (student can put a range from 30 s to 10 min) interval, pipette 25.0 cm^3 aliquots of the solution containing 20 cm^3 of cold water.
9. Repeat steps 2 to 7 at 1st, 2nd, 3rd, 4th and 5th min.

Table of results

Time/min	0	1	2	3	4	5
Initial burette reading/ cm^3						
Final burette reading/ cm^3						
Titre volume/ cm^3						

Sketch of graph



Since the gradient of the graph at $t = 0$ is $x \text{ cm}^3 \text{ min}^{-1}$,

Initial rate of reaction = $(x/1000 \times 0.01 \times 5/2) \div 25/1000 \text{ mol dm}^{-3} \text{ min}^{-1}$

Since rate = $k [\text{H}_2\text{O}_2]$,

$k = [(x/1000 \times 0.01 \times 5/2) \div 25/1000] / 0.025$

- 2 Hydrogen iodide can undergo decomposition to give a mixture of hydrogen gas and iodine gas.



- (a) State Le Chatelier's Principle.

.....
 [1]

Le Chatelier's Principle states that when a system in equilibrium is disturbed, the position of the equilibrium will shift in a direction that tends to reduce that change so as to re-establish the equilibrium.

- (b) Predict and explain the effect of the following changes on the position of the above equilibrium, if any.

- (i) Increasing the temperature

.....

 [2]

When temperature of the system is increased, by Le Chatelier's Principle, the equilibrium position shifts to the right towards the endothermic reaction to remove the excess heat

- (ii) Reducing the pressure

.....

 [1]

When pressure is reduced, by Le Chatelier's Principle, the equilibrium position does not shift as the number of gaseous particles on both the reactants and products are the same.

- (iii) Addition of catalyst

.....

 [1]

Catalyst catalyses both forward and backward reactions to the same extent in a reversible reaction, hence there is no shift in equilibrium position.

- (c) When 1.4 mol of hydrogen iodide is heated in a closed vessel at 550 K, the total pressure at equilibrium was 6 atm.

Given that the mole ratio of hydrogen iodide to iodine gas at equilibrium is 9:4, calculate the equilibrium constant, K_p , at 550 K.

[3]

$$P_{H_2} = P_{I_2} = (4/17) \times 6 = 1.41 \text{ atm ;}$$

$$P_{HI} = (9/17) \times 6 = 3.18 \text{ atm ;}$$

$$K_p = (1.411)^2 / (3.176)^2 = 0.198 ;$$

- (d) Hydrogen chloride and hydrogen bromide also undergoes a similar decomposition to give hydrogen gas and its respective halogens.

Describe the trend in the volatility and colours of the halogens.

.....

 [3]

Volatility decreases down the group for halogens; colour intensity increases down the group;

Chlorine: yellowish-green gas

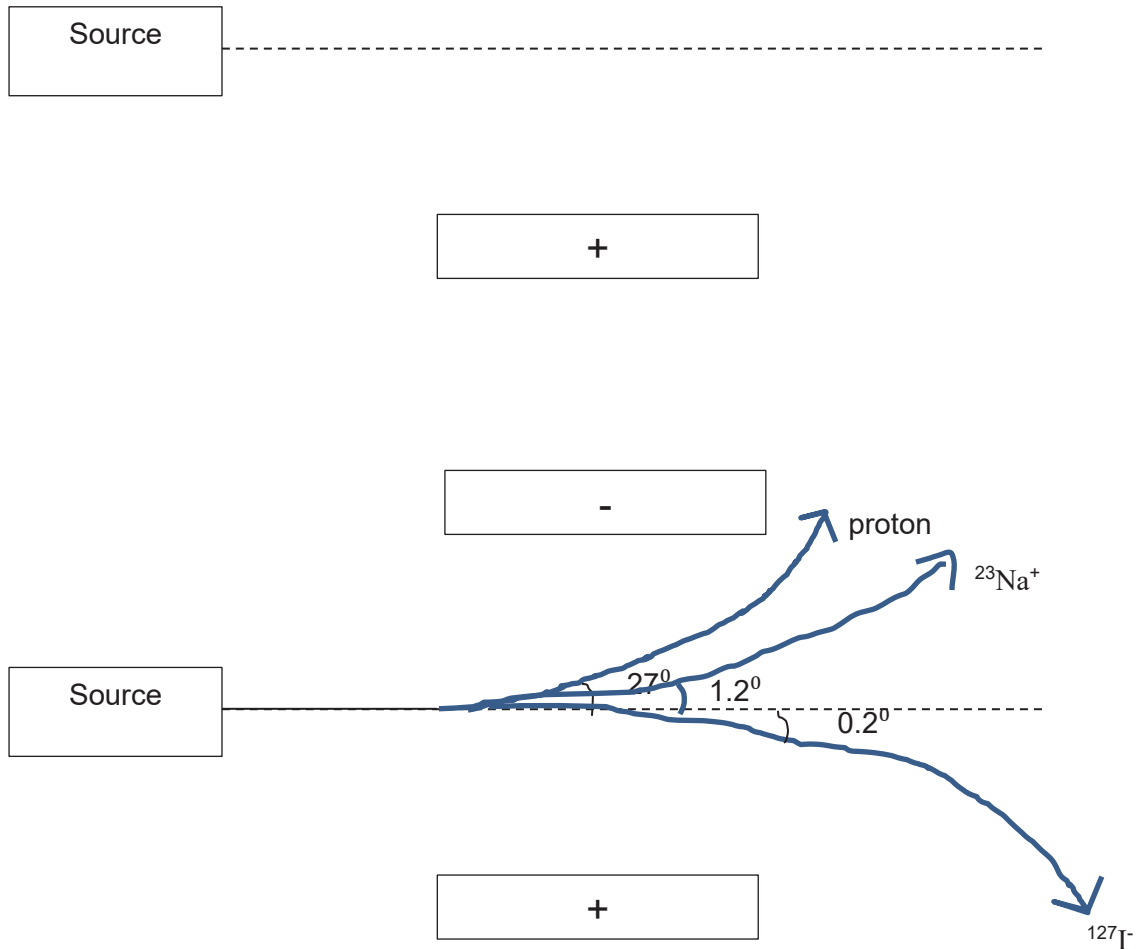
Bromine: reddish-brown liquid

- (e) It was observed that a beam of protons gives an angle of 27° in the following electric field.

Indicate on the diagram below how a beam of protons, $^{127}\text{I}^-$ and $^{23}\text{Na}^+$ ions, travelling at the same speed, behave in the same electric field. Calculate the respective angles of deflection.



[Turn over



[3]

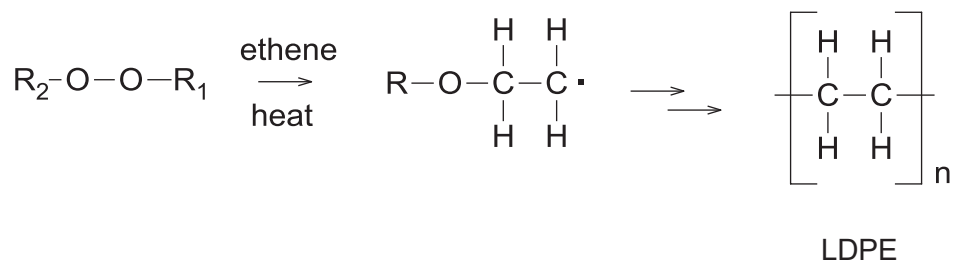
Angle of deflection for $\text{H}^+ = 1/1 \times 27^\circ = 27^\circ$

Angle of deflection for $\text{Na}^+ = 1/23 \times 27^\circ = 1.2^\circ$

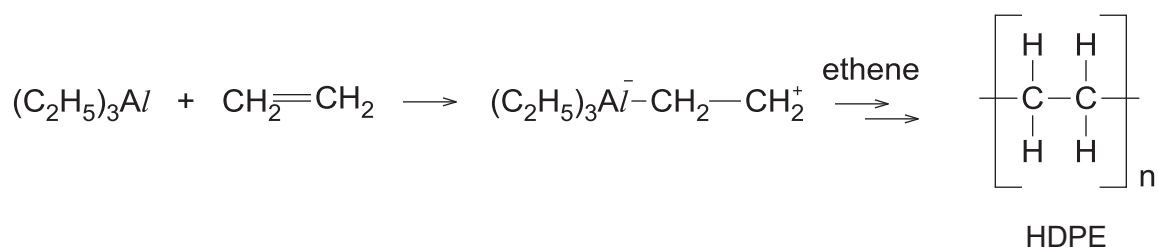
Angle of deflection for $\text{I}^- = 1/127 \times 27^\circ = 0.2^\circ$

[Total: 14]

- 3 In 1933, chemists in Britain discovered that when ethene was subjected to high pressures in the presence of a trace amount of oxygen or organic peroxide, it produced low-density poly(ethene) (LDPE). The radical mechanism using organic peroxides is shown below.



Using triethylaluminium, also known as Ziegler-Natta catalyst, developed by Karl Ziegler and Giulio Natta in 1953, ethene can be polymerised at much lower pressures to produce high-density poly(ethene) (HDPE). In the first step, triethylaluminium can accept the pair of π electrons of ethene to form a carbocation which is very similar to that found in the usual electrophilic addition reactions. This carbocation then undergoes an addition reaction with another ethene molecule. Eventually, long chains of ethene units form.



The major differences between the structures of LDPE and HDPE are that:

- the average chain length of LDPE is much shorter than that of HDPE
- the chains of LDPE are branched, while the chains of HDPE are unbranched.

The table below compares the physical properties of LDPE and HDPE.

Property	Polymer	
	LDPE	HDPE
Density	Low	High
Melting Point	Approximately 130 °C	Approximately 160 °C
Tensile strength	Low	High
Flexibility	Very flexible	Much more rigid

- (a) (i) Using structure and bonding, explain the difference in melting point between LDPE and HDPE.
-

.....

 [2]

Both have simple molecular structures with weak van der Waals forces of attraction between molecules. HDPE have are straight chain molecules which have **larger** surface area of contact between adjacent molecules than the branched-chain LDPE which is more spherical and packed less closely together. Hence, more energy is needed to break the more extensive van der Waals forces between HDPE, resulting in higher melting point.

Or

Both have simple molecular structures with weak van der Waals forces of attraction between molecules. HDPE has a longer chain length as compared to LDPE, thus resulting in a larger electron cloud size. Hence, more energy is needed to break the more extensive van der Waals forces between HDPE, resulting in higher melting point.

- (ii) Suggest why LDPE has a lower density than HDPE.

.....

 [1]

Since HDPE chains are unbranched, they have a more regular arrangement, thus giving a more compact arrangement.

- (b) (i) Write an equation to represent the first step in the radical mechanism.

..... [1]



- (ii) With reference to the mechanism given, explain why the production of LDPE only starts upon heating.

.....
 [1]

Heat is needed to cause homolytic fission of the O-O bond of organic peroxide to produce the alkoxy radicals that will react with the ethene molecules.

- (iii) Suggest why the chains of LDPE are branched.

.....
 [1]

During propagation step, due to the high reactivity of organic free radicals, the primary radical can abstract the hydrogen from the carbon atom in the middle of the chain.

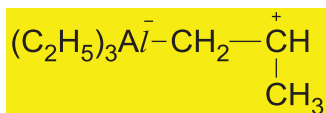
- (c) (i) State the role of triethylaluminium in the reaction using Ziegler-Natta catalysts.

..... [1]

Triethylaluminium acts as an electrophile.

- (ii) Similar to ethene, propene can be polymerised using the Ziegler-Natta catalysts. Show the structure of the carbocation intermediate formed in the first step.

[1]



- (d) Use the table of characteristics values for the infra-red absorption in the Data Booklet to answer this question.

Infra-red absorptions can be used to identify functional groups in organic compounds. For example, ethanol shows absorptions at $1000\text{-}1300\text{ cm}^{-1}$ and $3230\text{-}3550\text{ cm}^{-1}$.

Use the table to identify the infra-red absorption range that will be shown by

- (i) Ethene but not by poly(ethene)

..... cm^{-1}

1610-1680 cm^{-1}

(ii) Propyl ethanoate but not by propene

..... cm⁻¹

1000-1300 and 1680-1750 cm⁻¹

[3]

(e) The four methods used to dispose polymers are incineration, recycling, depolymerisation and bacterial fermentation.

(i) Combustion of the polymers during incineration can lead to the formation of pollutants such as carbon monoxide which is toxic to humans, if the conditions are not carefully controlled.

In terms of the bonding involved, explain how carbon monoxide prevents oxygen from being transported around the body.

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

Oxygen molecule is reversibly bonded to the haem group.

⇒ the Fe²⁺-O₂ bond is weak allowing oxygen to be easily given up to the cells.

In the presence of CO, which is a stronger ligand than O₂, ligand exchange takes place and CO is strongly and irreversibly adsorbed at this site, destroying haemoglobin's oxygen carrying capacity.

(ii) State two advantages of recycling.

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

Recycling saves energy; recycling conserves the resources needed to process the new polymers; recycling produces less pollution to the air, land and water.

[Total: 15]

4 Iron is a transition element in Period 4 of the Periodic Table.

(a) Explain what is meant by a transition element.

..... [1]

A transition element is a **d-block element** which forms **at least one simple ion**, in compounds, with a **partially filled d-subshell**.

(b) Most iron oxide samples have a mole ratio of iron to oxygen in a range between 0.84 : 1 to 0.96 : 1. Suggest why these samples have variable compositions.

.....
 [1]

Since iron can exist in both +2 and +3 oxidation states, some of the iron (II) ions in iron (II) oxide is oxidised to iron(III) ions.

(c) The reaction between peroxodisulfate ions, $S_2O_8^{2-}$ and iodide ions is very slow at room conditions, while addition of iron(III) ions can speed up the reaction rate.

(i) Suggest why the reaction between $S_2O_8^{2-}$ and iodide ions is very slow.

.....
 [1]

The reaction involves collision of ions of the same charge, $S_2O_8^{2-}$ and I^- , hence the number of effective collisions are small due to electronic repulsion.

(ii) Construct ionic equations to outline the catalytic role of iron(III) ions in the reaction.

.....
 [2]



(iii) State another iron species that can also act as a catalyst for the reaction.

..... [1]

Fe²⁺ ion

(d) When thiocyanate ligand, SCN^- , is added to the yellow solution of FeCl_3 , a deep red solution **H** is obtained.

(i) Suggest the formula of the complex responsible for the deep red solution **H**.

..... [1]



(ii) State the type of reaction when FeCl_3 forms **H**.

..... [1]

Ligand exchange reaction

(iii) Explain why aqueous Fe^{3+} solutions are coloured.

.....

.....

.....

..... [3]

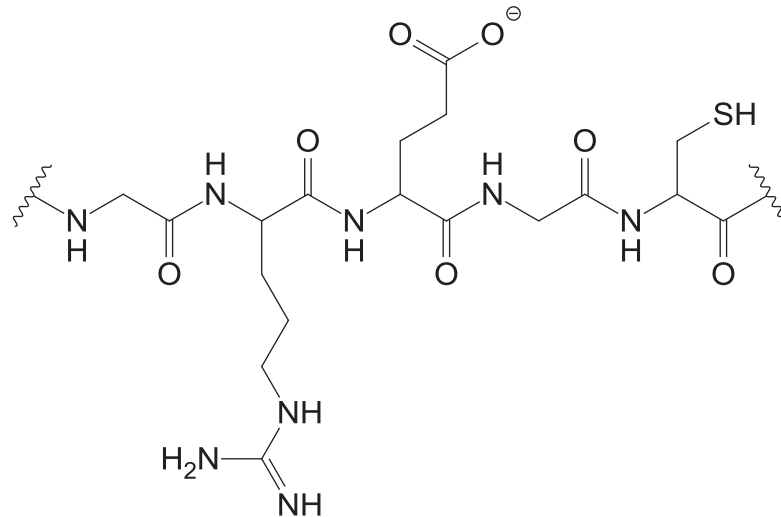
For $\text{Fe}^{3+}(\text{aq})$, in the presence of ligands, partially-filled 3d orbitals in vanadium ions are split into two levels (i.e. become non-degenerate) with an energy gap, ΔE , falling within the energy range of the visible spectrum of light.

When light falls on the complex, a particular wavelength of light corresponding to ΔE is absorbed and this causes the electrons from the lower energy d orbitals to be promoted to a vacant higher energy level d orbital; a process known as the d-d electron transition. The colour observed is the complement of the colour absorbed.

[Total: 11]

5 The pancreas produces the protein insulin that regulates the metabolism of carbohydrates, fats and proteins.

The structure of a portion of the insulin molecule is shown below. This portion contains a number of amino acids.



(a) Describe the tertiary structure of insulin.

.....

.....

..... [2]

Tertiary structure refers to the overall 3D conformation of the protein involving folding or coiling of the chains via side-chain (R groups) interactions. Side-chain interactions which hold the tertiary structure in its shape are ionic bonds, disulfide, hydrogen bonding or van der Waals interactions;

(b) (i) What is meant by the term *denaturation*?

.....

..... [1]

Denaturation of proteins involves the disruption of the secondary, tertiary and quaternary structures as these are held together by relatively weak attractions, forming random coil of polypeptide chain.

(ii) Suggest a brief outline of one method by which insulin may be denatured.

.....

.....

.....

..... [2]

Addition of H^+ or OH^- protonates or deprotonates the ionic R groups and hence disrupts the polar side chain interactions such as ionic bonds and hydrogen bonds holding the tertiary and quaternary structure of the protein. OR

When heat is applied, weak bonds, such as Van der Waals' forces and hydrogen bonds, holding together the quaternary, tertiary and secondary structures of the protein can be broken.

The increase in temperature increases the vibration of molecules, and the molecules can vibrate so strongly that the intermolecular interactions of the α -amino acid residues are destroyed causing denaturation. OR

Mechanical actions such as beating, whipping, shaking and kneading can also disrupt the intramolecular interactions within the protein molecules, destabilising the protein structure leading to the loss of the tertiary and secondary structures and hence denaturation. OR

The addition of heavy metal ions such as Ag^+ , Hg^+ , and As^+ which can combine permanently and preferentially with the sulfur atoms in -SH groups, destroying the disulfide (S-S) covalent bonds and thus changing the structure.

Heavy metals form salts or complex ions, hence breaking the ionic interactions

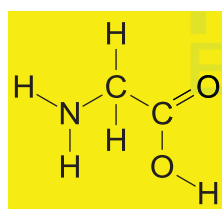
- (iii) State the reagent and conditions required for complete hydrolysis of protein in the laboratory.

..... [1]

Heat under reflux with $6 \text{ mol dm}^{-3} \text{ HCl}$ for 6 hours

- (iv) One of these amino acid residues are present more than once in the above portion of the insulin molecule. Draw a displayed formula for this amino acid residue.

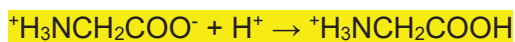
[1]



- (v) Explain, with the aid of equations, how the zwitterionic form of the amino acid in (b)(iv) act as a buffer.

..... [2]

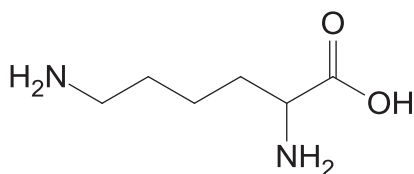
When little amount of acid is added,



When little amount of base is added,



- (c) Lysine is a α -amino acid that is used in the biosynthesis of proteins.



- (i) Explain what is meant by the term pK_a as applied to a weak acid HA.

..... [1]

$$pK_a = -\log K_a$$

- (ii) State the functional groups present in lysine.

..... [1]

Primary amine and carboxylic acid

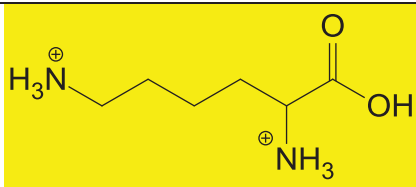
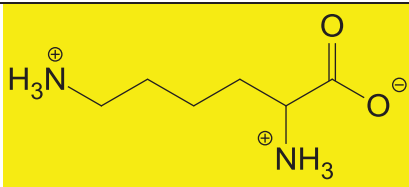
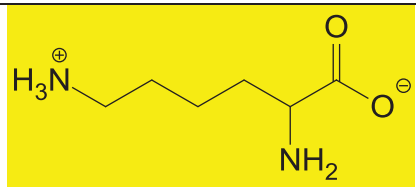
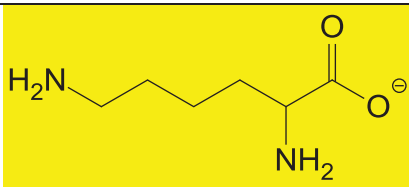
- (iii) There are three pK_a values associated with lysine: 2.1, 8.9 and 10.5.

Make use of these pK_a values to suggest the major species present in the solutions of the amino acid with the following pH values.

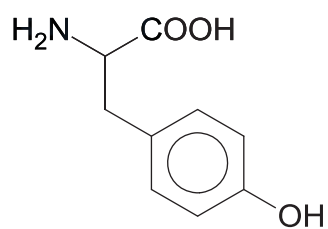
pH 1	pH 4

pH 9	pH 12

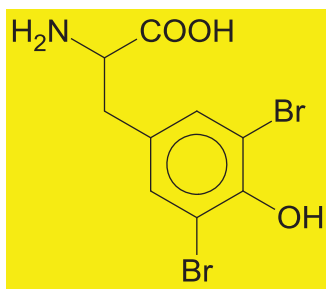
[4]

pH 1	pH 4
	
pH 9	pH 12
	

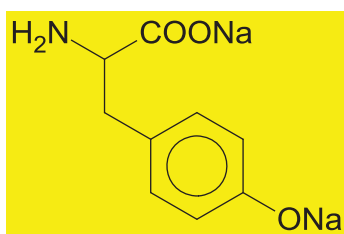
(d) Tyrosine is another amino acid present in insulin.



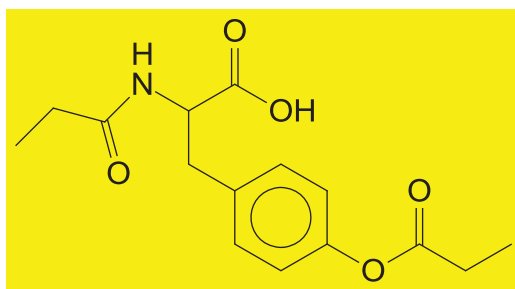
Draw the organic products when tyrosine undergoes reaction with

(i) $\text{Br}_2(\text{aq})$ 

[1]

(ii) $\text{NaOH}(\text{aq})$ 

[1]

(iii) excess $\text{CH}_3\text{CH}_2\text{COCl}$ 

[1]

(e) State the type of reactions for reaction with

 $\text{Br}_2(\text{aq})$ $\text{NaOH}(\text{aq})$

[2]

Reaction with $\text{Br}_2(\text{aq})$: electrophilic substitutionReaction with $\text{NaOH}(\text{aq})$: acid-base reaction

[Total: 20]

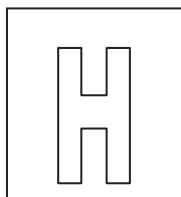
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Candidate Name: _____

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2017 Preliminary Examination II Pre-University 3

H2 CHEMISTRY

9647/03

Paper 3 Free Response

15th Sept 2017

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper

Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

Write in dark blue or black pen.

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

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

Answer any **four** questions.

A Data Booklet is provided.

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

You are reminded of the need for good English and clear presentation in your answers.

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

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

Question	1	2	3	4	5	Total
Marks	20	20	20	20	20	80

1 (a) Graphite is a naturally-occurring form of crystalline carbon and is found in metamorphic and igneous rocks. Graphite is extremely soft and cleaves with very light pressure yet it is extremely resistant to heat and nearly inert in contact with almost any other material. These extreme properties give it a wide range of uses in metallurgy and manufacturing.

(i) With reference to the structure, account for the following properties of graphite.

- Soft
- Heat resistant and inert

[3]

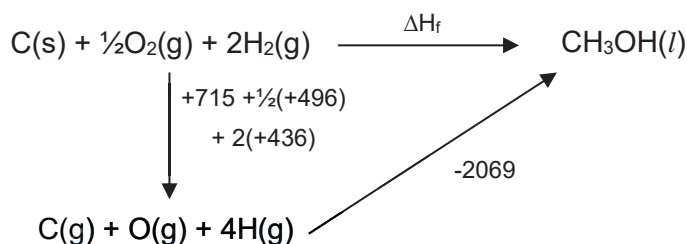
Graphite has a **giant covalent structure**(;). The bonding between the layers is **weak temporary dipole – induced dipole forces**(;) which can be **easily overcome**, allowing the layers to **slide over** each other easily and thus graphite is soft.

Large amount of thermal energy is required to break the **strong covalent bonds**(;) between the carbon atoms within the layers which account for its resistance to heat.

(ii) The following table shows some thermochemistry data.

Reaction	$\Delta H / \text{kJ mol}^{-1}$
Standard enthalpy change of atomisation of carbon	+715
Enthalpy change of $4\text{H}(\text{g}) + \text{O}(\text{g}) + \text{C}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$	-2069

With the use of relevant data from the *Data Booklet* and the above information, calculate the enthalpy change of formation of methanol. [3]



$$\Delta H_f = +715 + \frac{1}{2}(+496) + 2(+436) + (-2069) = -234 \text{ kJ mol}^{-1}$$

(b) A butane burner is used to heat the air in a hot air balloon. The hot air balloon has a volume of 2.1 m^3 and its volume does not change when the enclosed air is heated.

(i) Using the ideal gas equation, calculate the amount of gas molecules the balloon contains at temperature 800 K and a pressure of $1.0 \times 10^6 \text{ Pa}$. [1]

$$pV = nRT$$

$$1.0 \times 10^6 \times 2.1 = n \times 8.31 \times 800$$

$$n = 316 \text{ mol}$$

- (ii) Hence calculate the mass of air it contains, assuming an average relative molecular mass of 29. [1]

$$\text{Mass} = 315.9 \times 29 = 9160\text{g}$$

- (iii) The standard enthalpy change of combustion of butane is $-2877.5 \text{ kJ mol}^{-1}$. It requires 1.0 J of energy to raise the temperature of 1.0 g of air by 1.0 K. Using your answer in (b)(ii), calculate the mass of butane that needs to be burnt to raise the temperature of the air in the balloon by 20 K. Assume that the hot air balloon is a closed system. [2]

$$Q = mc\Delta T = 9160 \times 1.0 \times 20 = 183213 \text{ J}$$

$$\Delta H = - \frac{Q}{\text{Amt of butane}} \times \text{coeff}$$

$$-2877.5 = - \frac{183213 \div 1000}{\text{amt of butane}} \times 1$$

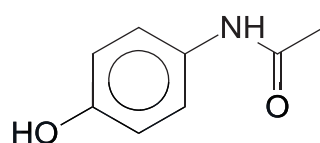
$$\text{Amount of butane} = 0.06367 \text{ mol}$$

$$\text{Mass of butane} = 0.06367 \times (4 \times 12.0 + 1.0 \times 10) = 3.69\text{g}$$

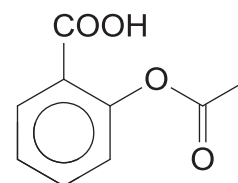
- (iv) The actual mass of butane that needs to be burnt to raise the temperature of the air in the balloon by 20 K was found to be 3.81 g. Suggest why this differs from your answer in (b) (iii). [1]

More butane needs to be burnt due to heat loss.

- (c) Paracetamol and aspirin are effective at pain and fever relief due to their ability to dissolve quickly in the blood stream and are soluble in fatty compounds found in cell membrane.



Paracetamol



Aspirin

- (i) Account for these properties based on the structure and bonding of aspirin. [2]

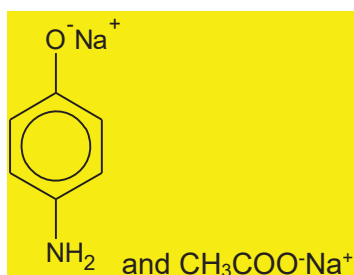
Aspirin has a simple molecular structure. The presence of COOH forms ion-dipole interactions (when hydrolysed to form COO^-) / hydrogen bonding with water.

The presence of benzene ring forms favourable van der Waals' forces with the fatty compounds which results in the solubility.

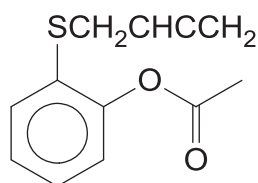
- (ii) One of the pain relievers cause more stomach irritation than the other. With reference to the functional groups present, suggest and explain the pain reliever that you will recommend to someone who suffers from gastric bleeding. [2]

Paracetamol causes less stomach irritation and is recommended(;) as the acidic -COOH group of aspirin will attack the lining of the stomach walls, causing irritation.(;)

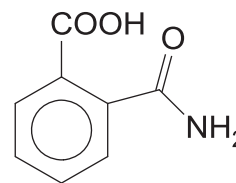
- (iii) Write the structural formula of the organic product(s) formed when paracetamol tablet is refluxed with sodium hydroxide. [2]



- (iv) Extensive research has been made to improve the effectiveness of the pain-relievers. Two proposals were made to modify aspirin.



Drug A



Drug B

Given that the melting points of Drugs **A** and **B** are 179°C and 154°C respectively, account for the melting point in terms of structure and bonding. [2]

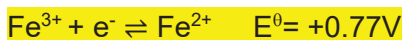
Both drugs have simple molecular structure. Drug A has a higher melting point as the van der Waals' forces of attraction is more extensive and stronger than the hydrogen bonding in Drug B. More energy is needed to overcome the stronger van der Waals' forces of attraction between Drug A.

- (v) State the relative solubility of Drugs **A** and **B** in water. [1]

Drug **A** is less soluble in water than drug **B**.

- 2 Halogens and their compounds can be toxic but some are essential for the human body's functioning and are used in daily products. The oxidising power of chlorine allows it to act as a good disinfectant.

(a) With the use of *Data Booklet*, explain why FeCl_3 exists but FeI_3 does not. [4]



For FeCl_3 , initial species present: Fe^{3+} and Cl^-



$$E^0_{\text{cell}} = +0.77 - (+1.36) = -0.59\text{V} < 0$$

Hence, the species cannot undergo further redox. Thus FeCl_3 exists.



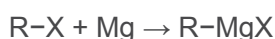
For FeI_3 , initial species present: Fe^{3+} and I^-



$$E^0_{\text{cell}} = +0.77 - (+0.54) = +0.23\text{V} > 0$$

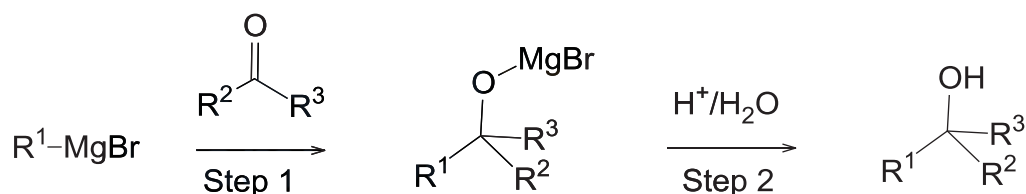
Hence, the species can undergo further redox to form Fe^{2+} and I_2 . Thus FeI_3 does not exist.

(b) Grignard reaction is an important reaction which helps in lengthening the carbon chain. A Grignard reagent has a general formula of R-MgX where R is an alkyl or aryl group and is formed via the reaction of an alkyl or alkyl halide with magnesium powder.



Grignard reagent

Carbonyl compounds react with Grignard reagent to increase the carbon chain.



(i) In the formation of Grignard reagent, it is important to carry out the reaction in a dry environment. Suggest a reason. [1]



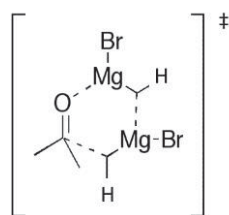
Mg reacts in the presence of water to form magnesium hydroxide and H_2 gas. OR
Grignard reagent can react with water to form the respective alkane.

- (ii) It was observed that the reaction to form the Grignard reagent is very slow at the start when magnesium powder is added to the alkyl halide in diethyl ether solvent. Suggest a reason. [1]

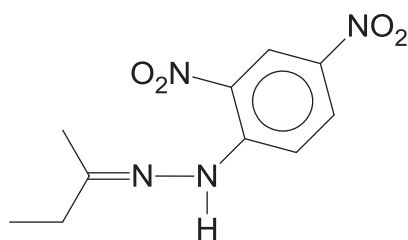
There is an unreactive layer of magnesium oxide coated on the exterior.

- (iii) The addition of the Grignard reagent to the carbonyl typically proceeds through a six-membered ring transition state. For the reaction of each molecule of carbonyl compound, two molecules of Grignard reagents are involved in the formation of the transition state.

Suggest the transition state of Step 1 for the reaction between propanone and CH_3MgBr shown above. [1]

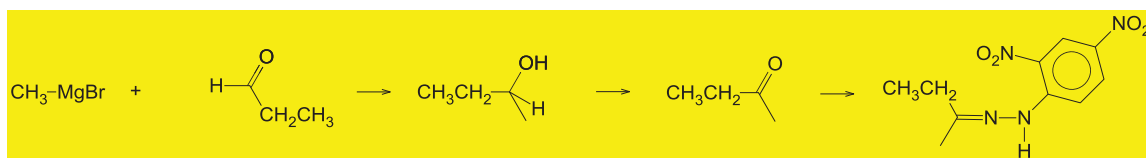


- (iv) Suggest a four-step synthesis of compound **Q**. State the reagents and conditions for each stage and draw structures of the intermediate organic products. The first two steps should involve the use of Grignard reaction between CH_3MgBr and a relevant carbonyl compound.



Compound Q

[5]



- (c) (i) Describe what is observed when NaCl and NaBr reacts with concentrated sulfuric acid respectively. In each case, suggest the products of the reaction and write equations where appropriate. [2]



White fumes of HCl (g) produced. (.)



Orange-brown fumes (mixture of Br₂ and HBr) obtained. (.)

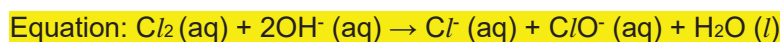
- (ii) Explain any difference in their reactions with concentrated sulfuric acid. [1]

The ease of oxidation of halide ions increases from Cl⁻ to Br⁻. Hence, Br⁻ is oxidised to Br₂ and Cl⁻ is not oxidised at all.

- (d) When cold aqueous sodium hydroxide is added to a yellowish-green solution of chlorine in trichloromethane and shaken together, two immiscible colourless layers (aqueous layer and organic layer) were observed.

- (i) State the type of reaction and give an equation, including state symbols, for this reaction. [2]

Type of reaction: disproportionation of chlorine

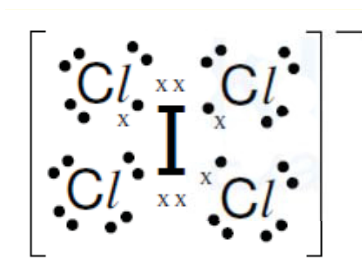


- (ii) Assuming that the starting reagents were added in stoichiometric ratio, suggest the chemical species found in the two immiscible colourless layers respectively. [2]

Aqueous layer: Cl⁻ (aq) + ClO⁻ (aq)

Organic Layer: CHCl₃

- (e) One of the compounds that may be formed between chlorine and iodine is iodine tetrachloride, ICl₄⁻. Construct a 'dot-and-cross diagram' to show the arrangement of electrons in ICl₄⁻. [1]



[Total: 20]

- 3 (a) Hunsdiecker reaction is the organic reaction of silver salts of carboxylic acids with halogens to give organic halides.

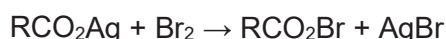
The overall reaction is:



The reaction mechanism of the Hunsdiecker reaction is believed to involve organic radical intermediates.

The steps involved in the reaction mechanism are as follows:

1. The silver salt of the carboxylic acid quickly reacts with bromine to form the acyl hypohalite intermediate, RCO_2Br .



2. The initiation step involves the formation of two radicals from the acyl hypohalite intermediate. One of which is bromine radical.
3. The first step of propagation involves the removal of CO_2 from the radical formed in step 2, forming $\text{R}\bullet$ and CO_2 .
4. $\text{R}\bullet$ recombines with the acyl hypohalite intermediate to form the desired organic halide.

- (i) Write equations to illustrate the reaction mechanism of Hunsdiecker reaction. [3]



Initiation



Propagation (I)



Propagation (II)



Termination



- (ii) Draw the structure of the organic product formed when $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{COOAg}$ reacts with Br_2 . [1]



- (iii) The product in (a)(ii) displays optical isomerism as it has a chiral centre. Explain the term *chiral centre* and label the chiral centre in (a)(ii) with an asterix(*) sign. [2]

A chiral centre is a **C atom bonded to four different substituents.**

- (iv) Chlorine and iodine can be used in place of bromine to react with silver salts of carboxylic acids.

A student wanted to compare the rate of reaction of iodine reacting with silver salts of carboxylic acids with that of bromine. However, he did not label the apparatus and ended up not able to tell which apparatus has the iodine-containing and bromine-containing organic products.

Describe a chemical test which can allow the student to derive correctly the apparatus with the iodine-containing and bromine-containing organic products respectively. Include the observations, if any. [4]

Add NaOH to the respective solutions, followed by HNO₃. Add AgNO₃(aq).

The solution containing a cream precipitate has the bromine-containing product while the solution containing a yellow precipitate has the iodine-containing product.

Add concentrated NH₃ to the respective solutions.

The cream precipitate will dissolve in the concentrated NH₃ while the yellow precipitate will not dissolve in the concentrated NH₃.

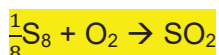
- (b) Write the equations and state the observations of the following reactions, where appropriate.

- Reaction between sodium and oxygen
- Reaction between sulfur and oxygen

[4]



Na burns in oxygen with an orange flame.

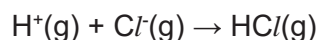


S burns with a blue flame to form SO₂.

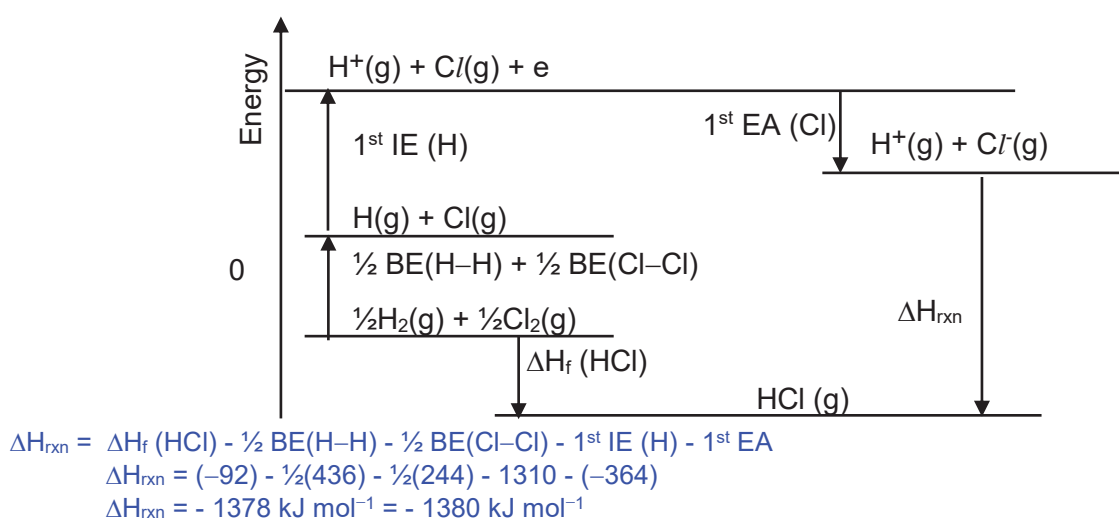
- (c) (i) The following table shows some thermochemistry data.

Reaction	$\Delta H / \text{kJ mol}^{-1}$
enthalpy change of formation of $\text{HCl}(\text{g})$	-92
first electron affinity of $\text{Cl}(\text{g})$	-364

Using the following data, and relevant data from the *Data Booklet*, construct an energy level diagram to calculate the standard enthalpy change for the following reaction.



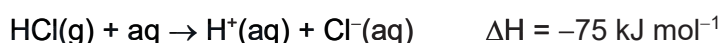
[4]



- (ii) The following reaction is expected to be an endothermic reaction.



However, the following reaction is an exothermic reaction.



Explain the above observations.

[2]

The first reaction involves bond breaking only while the second reaction involves forming ion-dipole interactions between H^+ and water molecules and Cl^- and water molecules. Energy is evolved in the formation of ion-dipole interactions which can more than compensate the heat absorbed to break the $\text{H}-\text{Cl}$ bond in the gaseous state and to ionise the H atom, thus resulting in the enthalpy change of reaction is exothermic.

[Total: 20]

- 4 (a) (i) Heating compound **P**, $C_{10}H_{12}O_3$, with dilute sulfuric acid yields compound **Q**, $C_9H_{12}O_2$, and methanoic acid.

On treatment with dilute nitric acid, compound **Q** forms compound **R** with the formula $C_9H_{11}NO_4$. Compound **Q** also reacts with aqueous bromine to form compound **S**, $C_9H_9O_2Br_3$.

Heating compound **R** with tin in concentrated hydrochloric acid, followed by adding excess aqueous sodium hydroxide to the product gives compound **T**, $C_9H_{12}NO_2Na$.

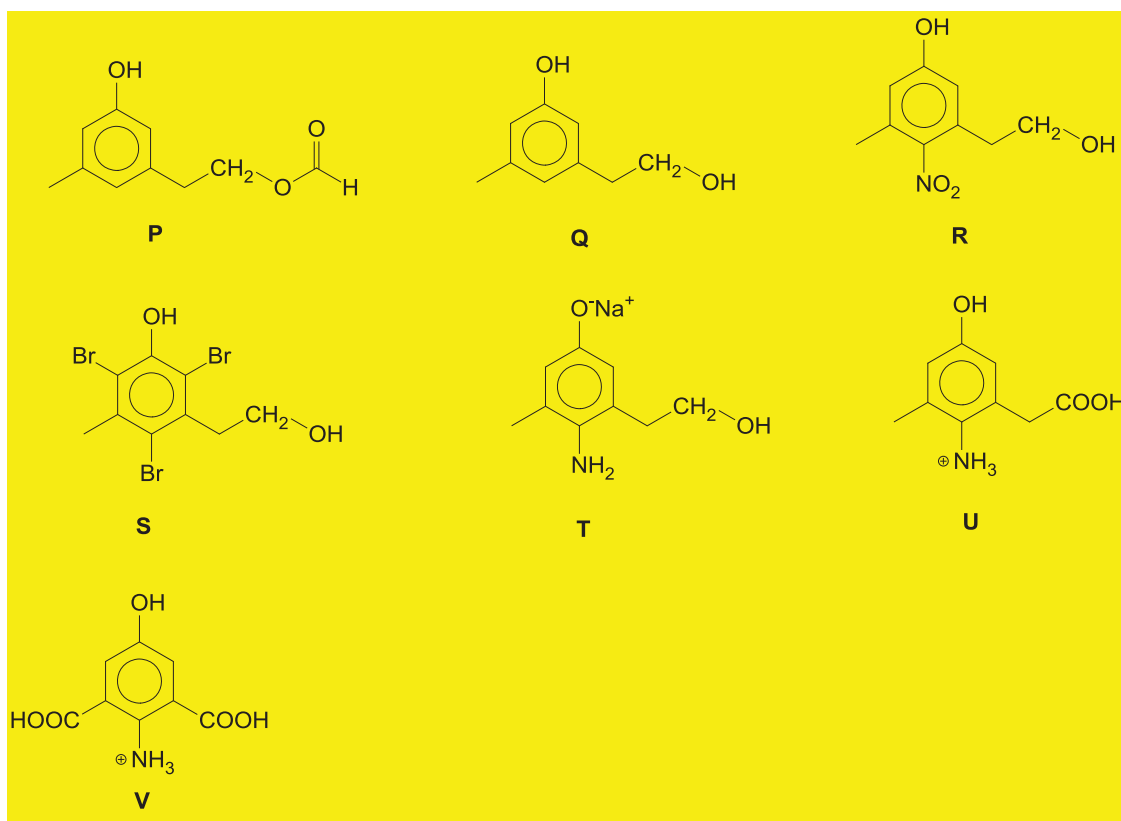
Compound **T** turns hot acidified potassium dichromate solution green and forms compound **U**, $C_9H_{12}NO_3$. 1 mole of compound **U** reacts with 3 moles of aqueous sodium hydroxide. Compound **T** reacts with hot acidified potassium manganate(VII) and forms compound **V**, $C_8H_8NO_5$.

Suggest structures for compounds **P–V** and give an account of the chemistry involved.

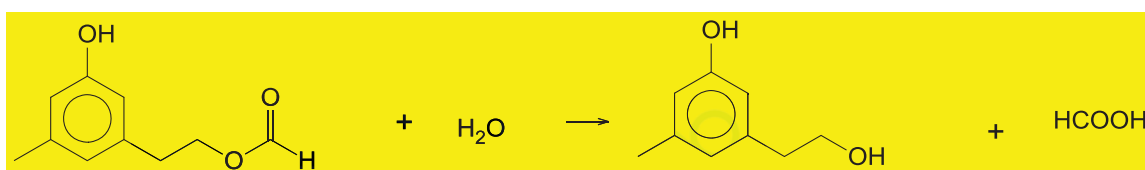
[14]

Observation	Deduction
Heating compound P which has the formula, $C_{10}H_{12}O_3$, with dilute sulfuric acid yields compound Q , $C_9H_{12}O_2$, and methanoic acid	P is an ester P undergoes acidic hydrolysis.
On treatment with dilute nitric acid, compound Q forms compound R	Q contains phenol Q undergoes electrophilic substitution.
Compound Q also reacts with aqueous bromine to form compound S , $C_9H_9O_2Br_3$	Q contains phenol Br is substituted at 2,4 and 6 position in S . Q undergoes electrophilic substitution.
Heating compound R with tin in concentrated hydrochloric acid	Reduction of nitro group to $-NH_2$ R contains $-NO_2$
Adding excess aqueous sodium hydroxide to the product gives compound T , $C_9H_{12}NO_2Na$.	Acid-base reaction Phenoxide ion is produced
Compound T turns hot acidified potassium dichromate solution green and forms compound U , $C_9H_{12}NO_3$.	Oxidation Primary alcohol is present in T Phenoxide ion is acidified and revert to phenol in U

1 mole of compound U reacts with 3 moles of aqueous sodium hydroxide.	U contains 3 acidic groups (1 phenol, 1 ammonium salt group and 1 carboxylic acid group).
Compound T reacts with hot acidified potassium manganate(VII) and forms compound V , $C_8H_8NO_5$.	Oxidation



(ii) Write the equation for the reaction of compound **P** being heated with dilute sulfuric acid. [1]



(b) Ester is an organic molecule which has many uses. Esters with low molecular masses are commonly used as fragrances and are found in essential oils. Phosphoesters form the backbone of DNA molecules.

(i) Given that methyl methanoate and ethyl methanoate are the simplest esters available, suggest a chemical test which can distinguish the two compounds. [3]

To separate solutions of methyl methanoate and ethyl methanoate, add NaOH(aq) and heat it, followed by adding $\text{I}_2(\text{aq})$. The solution that forms a yellow precipitate contains

ethyl methanoate while the solution that contains methyl methanoate does not form yellow precipitate.

(ii) Acyl chlorides and esters are both derivatives of carboxylic acids.

Compare and account for the acidity of methyl methanoate and ethanoyl chloride. [2]

Ethanoyl chloride is more acidic than methyl methanoate(;) as it hydrolyses in water to form HCl which is a strong acid(;).

[Total: 20]

- 5 Vehicle frames are usually made from aluminium as it is lightweight and strong. However, the aluminium frames have to be made more resistant to corrosion as certain parts could be exposed to rainwater and acidic gases in vehicle exhaust.

The industrial process for the anodising of aluminium uses an inert platinum cathode and aqueous sulfuric acid as the electrolyte.

- (a) Explain, in terms of the electrode reactions, how a piece of aluminium metal could be anodised to be more resistant to corrosion. [3]

at the Pt cathode: $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

at the Al anode:



Overall reaction: $2\text{Al}(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g}) ;$

- (b) A current of 0.30 mA was switched on for 1 hour to anodise an aluminium frame.

Calculate the amount of Al_2O_3 produced from the anodisation. [3]

$$Q = It$$

$$Q = 0.30 \times 10^{-3} \times 3600 = 1.08 \text{ C}$$

$$Q = nF$$

$$\text{No. of mol of electrons transferred, } n = Q / F = 1.08 / 96500 = 1.12 \times 10^{-5} \text{ mol ;}$$

[Turn over



For every 12 mol of electron transferred, 2 mol of Al_2O_3 is produced ;

No. of mol of Al oxidised = $1.12 \times 10^{-5} \div 6 = 1.87 \times 10^{-6}$ mol ;

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

Explain, stating any observations, how the electrode reactions would be different if

(i) the electrolyte was contaminated with copper(II) sulfate. [2]

The cathode reaction will instead be the reduction of Cu^{2+} ions to copper solid.



The platinum cathode will be coated with a pink / orange / brown layer of copper ;

(ii) the aluminium electrode was replaced with another platinum electrode. [2]

Platinum is inert and does not get oxidised. Water is oxidised to oxygen gas.



Effervescence of a colourless gas at the anode; (which relights a glowing splint)

(d) Infra-red (IR) spectroscopy is a common technique used to identify functional groups in organic compounds and to study how the functional groups are affected by other substances. When a beam of IR light of varying energies is shone at an organic compound, its functional groups can absorb certain energies characteristic to it. The energy of IR light is measured in wavenumbers, $\tilde{\nu}$, and is expressed as the reciprocal of its wavelength, λ , with units of cm^{-1} .

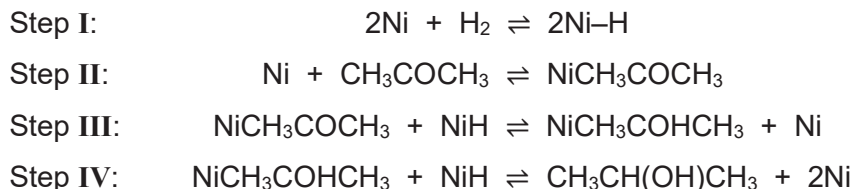
$$\tilde{\nu} = \frac{1}{\lambda}$$

For example, carbonyl functional groups absorbs IR light at the wavenumber range of 1680 to 1750 cm^{-1} , while alkyl groups absorb IR light at a wavenumber range of 2840 to 3095 cm^{-1} .

The gas-phase kinetics and mechanism of the hydrogenation of propanone using nickel catalyst was studied using IR spectroscopy. Dissociative adsorption of hydrogen gas on solid nickel is known to occur readily (step I). The adsorption of propanone gas onto the nickel catalyst was identified by a wavenumber peaking at 1620 cm^{-1} . The shift in wavenumber from 1680 to 1620 cm^{-1} confirms that it is the C=O functional group that is adsorbed onto the nickel catalyst and not the methyl groups (step II). However, no wavenumber shift corresponding to

the alcohol functional group of the product, propan-2-ol, was found. This indicates that when the product is formed, it immediately desorbed from the catalyst (step IV).

Hence, the proposed mechanism for this reaction is as follows.



When the experiment was conducted in a closed vessel of fixed volume at a constant temperature of 363 K, the following data was recorded.

Experiment	Partial pressure of hydrogen / kPa	Partial pressure of propanone / kPa	Relative rate
1	0.5	2.5	1
2	1	2.5	2
3	4	5	16
4	10	5	16
5	50	5	16

- (i) Nickel is acting as a *heterogeneous* catalyst in this reaction.

Define the term *heterogeneous*.

[1]

The catalyst used is in a **different phase / physical state** from the reactants. ;

- (ii) Based on experiments 1 to 3, determine the order of reaction with respect to hydrogen and with respect to propanone.

Hence, deduce the rate equation for the hydrogenation of propanone.

[3]

$$\text{Rate} = k[\text{H}_2]^m[\text{propanone}]^n$$

By comparing experiments 1 and 2,

When partial pressure (concentration) of hydrogen doubled and propanone kept constant, rate doubled.

Reaction is first order with respect to hydrogen, $m = 1$;

By comparing experiments 2 and 3,

$$\frac{\text{rate of expt 3}}{\text{rate of expt 2}} = \frac{k[\text{H}_2]^1[\text{propanone}]^n}{k[\text{H}_2]^1[\text{propanone}]^n}$$

$$\frac{16}{2} = (4)^1 \times \frac{5}{2.5}^n$$

$$2^n = 2$$

$$n = 1$$

Reaction is first order with respect to propanone, $n = 1$;

$$\text{Rate} = k[\text{H}_2][\text{CH}_3\text{COCH}_3] \quad \text{or} \quad \text{rate} = k p_{\text{H}_2} p_{\text{CH}_3\text{COCH}_3} ;$$

- (iii) Based on your answer in (ii), state which step in the proposed mechanism is the rate-determining step. [1]

Step 4. ;

Explanation (not needed)

If slow step is

$$\text{step 1: rate} = k [\text{H}_2]^1 \quad \text{X}$$

$$\text{step 2: rate} = k [\text{CH}_3\text{COCH}_3]^1 \quad \text{X}$$

$$\text{step 3: rate} = k [\text{H}_2]^{0.5} [\text{CH}_3\text{COCH}_3]^1 \quad \text{X}$$

$$\text{step 4: rate} = k [\text{H}_2] [\text{CH}_3\text{COCH}_3]^1 \quad (\text{consistent})$$

Write the expression for K_c for steps 1 to 3, ignoring Ni as it is in solid state. Re-express the rate equation for step 4 in terms of the actual reactants and not leave it in terms of the intermediates.

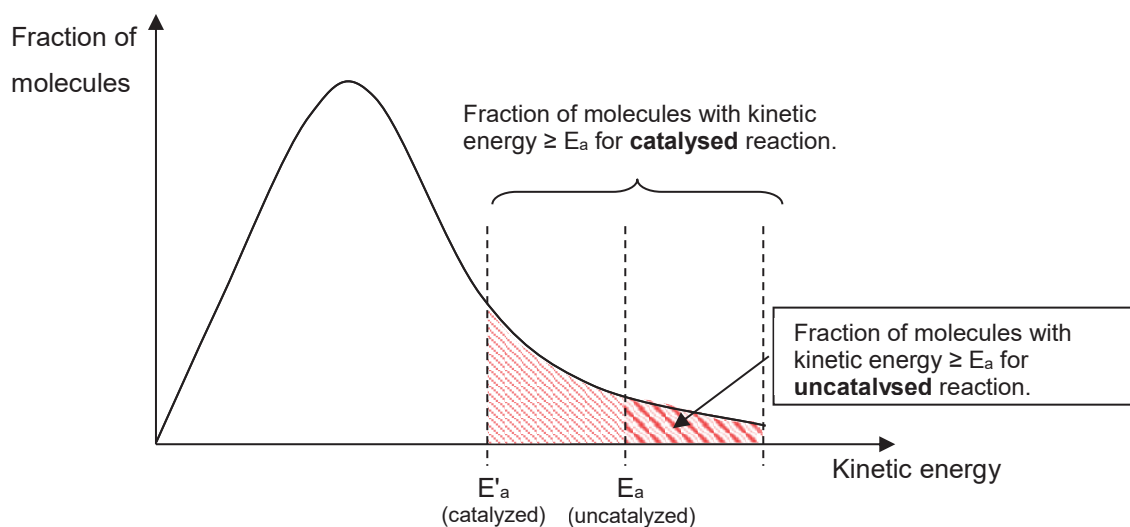
- (iv) Suggest a reason why the catalyst has to be used in the powdered form. [1]

The powdered form provides a larger surface area which increases the frequency of effective collisions, speeding up the reaction. ;

- (v) Hence, or otherwise, suggest a reason why the rate of reaction stopped increasing in experiments 4 and 5 when the partial pressure of hydrogen exceeded 4 kPa. [1]

The **hydrogen gas concentration (substrate concentration) exceeded the available catalyst surface area** for adsorption / reaction to take place. ;

- (vi) Sketch an energy distribution diagram to explain how the rate of the reaction would have been different without the use of a catalyst. [3]



; (1 m for diagram and labels)

- A catalyst provides an **alternative reaction path with lower activation energy (E'_a)** than that for the uncatalysed reaction (E_a).
- Without a catalyst, **fraction of molecules containing energy greater than the activation energy decreases**
- The **frequency of effective collisions is lower without a catalyst.**
- Hence, **rate of reaction decreases.**

:: (0-1 pt = 0m ; 2-3 pts = 1m, all 4 pts = 2m)

[Total: 20]

END OF PAPER

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