Class Adm No

Candidate Name: ____________________

H

millennia
institute

2021 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions

16 Sep 2021

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	6	Total
Marks	/ 13	/ 7	/ 18	/ 13	/ 9	/ 15	/ 75

This question paper consists of **17** printed pages and **1** blank page.

Answer all questions in the spaces provided.

1 **(a)** Explain why the ions of Group 2 elements increase in size down the Group.

....

....

....

.... [2]

(b) Magnesium is a Group 2 element. Magnesium nitrate decomposes to form an oxide and two gases when heated strongly.

(i) Write a balanced chemical equation, with state symbols, for the decomposition of magnesium nitrate.

.... [1]

(ii) Describe and explain the relative thermal stability of magnesium nitrate and barium nitrate.

....

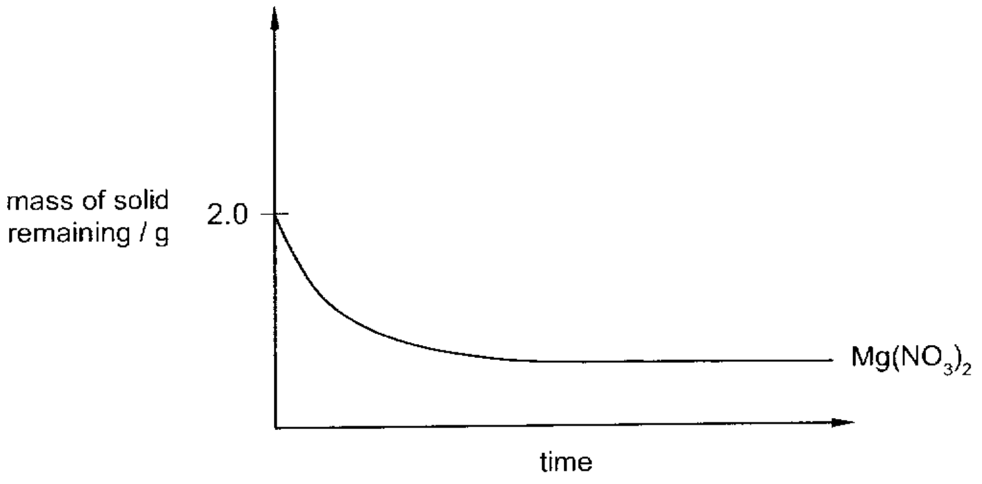
....

....

.... [2]

(iii) 2.0 g of magnesium nitrate was heated strongly with a non-luminous Bunsen flame until it was completely decomposed.

On the same axes, sketch a graph showing the progress of reaction as 2.0 g of barium nitrate was strongly heated with the same Bunsen flame until it was completely decomposed.



[1]

(c) One of the products of the decomposition of Group 2 nitrates is the metal oxide.

Metal oxides are ionic compounds with attractive forces existing within them that can be quantified by the lattice energy.

(i) Using the following data and relevant data from the Data Booklet, construct a Born-Haber cycle and use it to calculate the lattice energy of calcium oxide.

standard enthalpy change of formation of calcium oxide	=	–636 kJ mol^{-1}
standard enthalpy change of atomisation of calcium	=	+178 kJ mol^{-1}
first electron affinity of oxygen	=	–141 kJ mol^{-1}
second electron affinity of oxygen	=	+744 kJ mol^{-1}

[4]

(ii) The melting point of calcium oxide is 2886 K.

Using appropriate values from the Data Booklet, estimate the melting point of magnesium oxide.
Show all your working clearly.

[3]

[Total: 13]

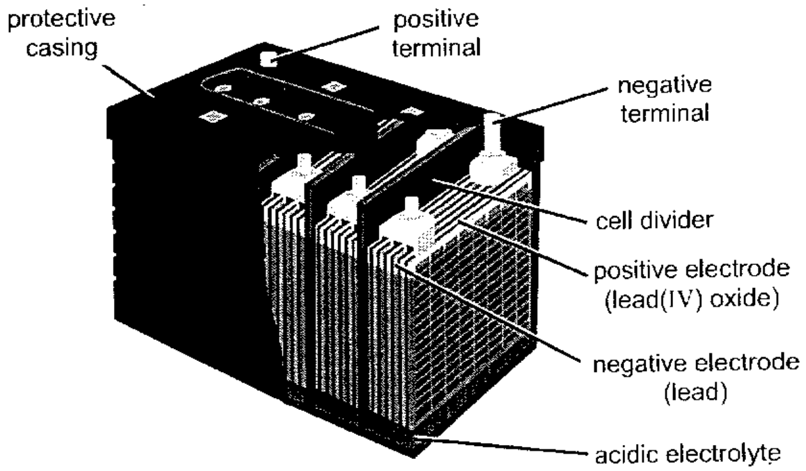
[Turn over

2 Car batteries generate electricity to power the appliances in cars.

The electrical flow is generated with a spontaneous redox reaction across the two electrodes.

As the battery operates, it becomes discharged, and the two electrodes are converted into by-products.

A common arrangement for a car battery would be 6 cells each generating 2 volts, connected in series to form a 12-volt battery.



(a) Using suitable electrode reactions, prove that the $E_{cell}^{\ominus}$ of one battery cell discharging is +1.60 V.

[3]

(b) Aqueous sulfuric acid is used as the electrolyte.

Suggest one possible reason why the voltage of one car battery cell is larger than 1.60 V.

....

....

.... [1]

(c) A fully-charged 12-volt battery contains 18.6 kg of electrodes with equal masses of positive and negative electrodes.

Calculate the quantity of charge provided by the 12-volt battery after it is fully discharged.

[3]

[Total: 7]

[Turn over

3 Hydrogen peroxide decomposes on its own due to the weak O–O bond.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

However, at room temperature and pressure, the decomposition is very slow.

The decomposition of hydrogen peroxide is a first-order reaction.

(a) By measuring the volume of oxygen formed over time, the initial rate of the decomposition of a certain concentration of hydrogen peroxide solution can be found.

initial concentration of H_2O_2 / mol dm^{-3}	initial rate of decomposition / mol dm^{-3} s^{-1}
0.100	1.44×10^{-6}

Calculate the time taken for the concentration of hydrogen peroxide to drop to half its original value.

[2]

(b) When aqueous potassium iodide is added into hydrogen peroxide, the decomposition occurs rapidly.

Potassium iodide speeds up the decomposition of hydrogen peroxide in two reaction steps with the following reversible reaction:

$$IO^- + 2H^+ + 2e^- \rightleftharpoons I^- + H_2O$$

(i) Hydrogen peroxide reacts with I^- in the first step, and I^- is regenerated in the second step.

Write two equations to show the mechanism of iodide ions speeding up the decomposition of hydrogen peroxide.

step 1 ....

step 2 .... [2]

(ii) Use bond energies to calculate the enthalpy change for the first step, ΔH_1.

[Bond energy of I–O = 201 kJ mol^{-1}]

[2]

(iii) Explain why the enthalpy change calculated using bond energy values in **(ii)** is only an estimation of the actual value.

....

.... [1]

(iv) The enthalpy change for the second step, ΔH_2, is -145 kJ mol^{-1}.

Draw an energy profile diagram to show the energy changes and chemical species involved in each of the two reaction steps.

[3]

(c) Manganese(IV) oxide can also be used to speed up the decomposition of hydrogen peroxide.

(i) Draw the electron-in-box diagram for the electronic configuration of the manganese species in manganese(IV) oxide.

[1]

(ii) With reference to the configuration in **(i)**, explain how manganese(IV) oxide allows hydrogen peroxide molecules to interact with it.

....

....

.... [1]

(iii) Using a Maxwell-Boltzmann energy distribution, explain how manganese(IV) oxide speeds up the decomposition of hydrogen peroxide.

....

....

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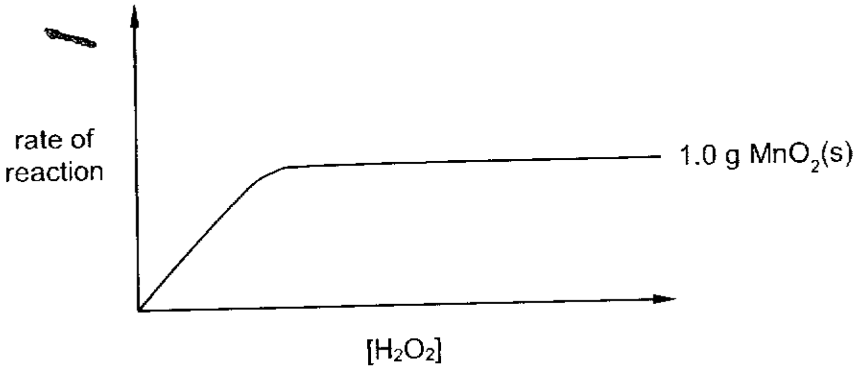
....

....

.... [5]

(iv) In a series of experiments, 1.0 g of manganese(IV) oxide powder was added into hydrogen peroxide solutions of various concentrations to measure the rates of reaction.

On the same axes below, sketch the results obtained when 2.0 g of manganese(IV) oxide powder was used for another series of experiments.

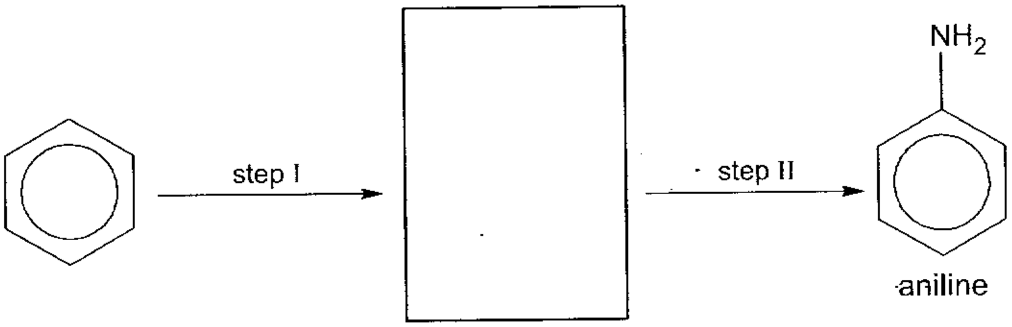


[1]

[Total: 18]

4 Aniline is conventionally synthesised with benzene as the starting organic material.

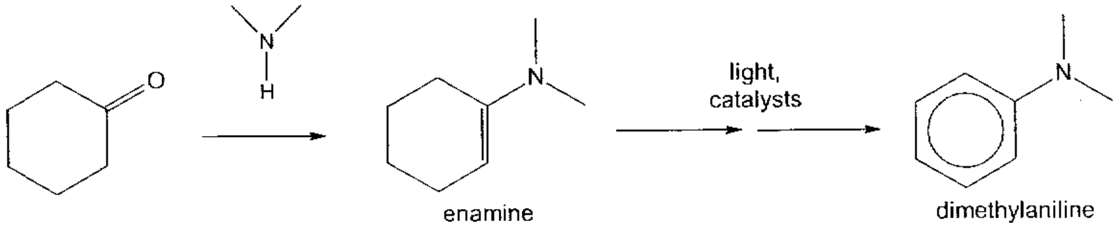
(a) State the reagents and conditions for the 2 steps in the reaction scheme below.
Draw the structure of the intermediate in the box provided.



step I ....

step II .... [3]

(b) In 2020, Dighe *et. al.* researched a new technique, photochemical dehydrogenative amination, to produce dimethylaniline starting from cyclohexanone and dimethylamine. The method is novel because benzene, an aromatic compound, is not required as a starting material.



(i) Describe a chemical test, with appropriate observations, which would confirm the identity of cyclohexanone.

....

....

.... [2]

(ii) The dimethylamine required in the novel method can be produced from methylamine.

State the reagents and conditions, and write a balanced chemical equation for the synthesis of dimethylamine from methylamine as a starting material.

reagents and conditions..

equation.. [2]

[Turn over

(iii) The first reaction step in the novel synthesis involves the formation of an enamine.

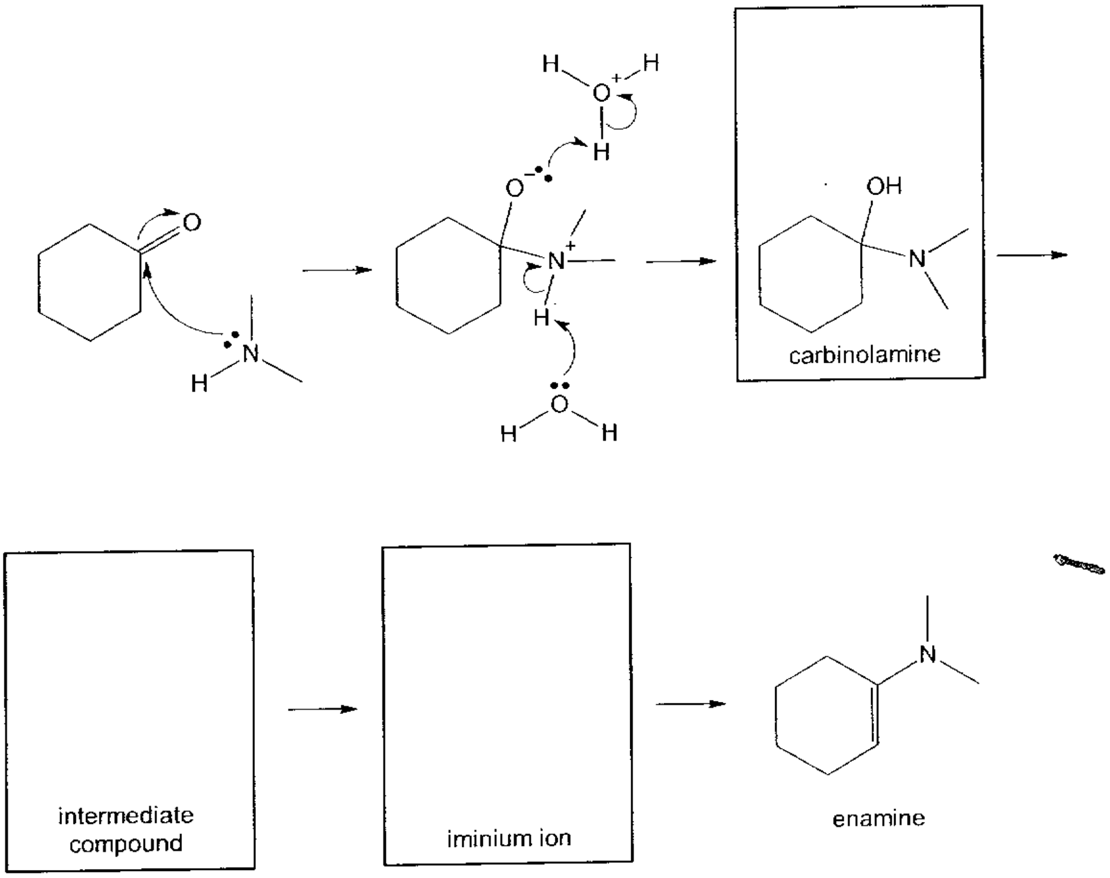
Enamines contain a carbon-carbon double bond (C=C) next to a nitrogen atom.

As part of the reaction mechanism, a carbinolamine is formed.

The oxygen atom on the carbinolamine is protonated by an acid, H^+, forming an intermediate compound.

The lone pair of electrons on the nitrogen atom push the leaving group out, forming an iminium ion and H_2O. This is achieved by forming a C=N double bond, resulting in a positively-charged nitrogen atom. The C–O bond breaks, forming H_2O.

Complete the mechanism of the reaction in the boxes below to form the enamine, starting from carbinolamine to iminium ion. Include the species that protonated carbinolamine, lone pairs of electrons, curly arrows to represent electron movement, the intermediate compound formed, and the iminium ion.



[4]

(iv) Aniline is often preferred over benzene as the starting material for the formation of substituted aromatic compounds.

Explain the relative reactivity of aniline towards bromine compared to benzene.

....

....

....

.... [2]

[Total: 13]

5 **(a)** Group 17 elements form molecular compounds with hydrogen, **HX**.

Table 5.1

HX	boiling point of HX / °C
HF	19.5
HC*l*	–85.1
HBr	–66.8
HI	–35.4

(i) Explain why the boiling points of HX follow the trend shown in **Table 5.1**.

....

....

....

....

....

.... [3]

[Turn over

(ii) **HX** molecules dissociate in water, forming acidic solutions.

$$H\mathbf{X}(aq) \rightleftharpoons H^+(aq) + \mathbf{X}^-(aq)$$

State and explain the trend down the Group in the extent of dissociation for the **HX** molecules.

....

....

....

....

....

.... [3]

(b) To a 90 cm^3 solution containing 0.00100 mol dm^{-3} Cl^- ions, 10 cm^3 of 0.00100 mol dm^{-3} silver nitrate solution was added.

0.001431 g of precipitate was formed.

Calculate the solubility product, K_{sp}, of the precipitate formed.

[3]

[Total: 9]

6 Ultraviolet-visible spectroscopy (UV-VIS) is a technique used to measure differences in energy levels within a compound.

Light of the ultraviolet to visible wavelength range is passed through a sample.

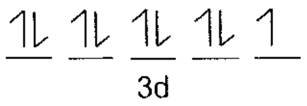
Electrons absorb the incoming light energy to promote to a higher energy level orbital.

The energy of the light absorbed corresponds to the difference in the initial and final energy levels.

By detecting the wavelengths of light which are not transmitted through the sample, information about the electronic structure of the substance can be obtained.

(a) Copper(II) ions exist as a hexahydrate in aqueous solution, $[Cu(H_2O)_6]^{2+}$.

Due to the approach of the six water molecules, the orbitals in the 3d subshell of the copper(II) ion are split into two separate energy levels.



(i) Complete the diagram above, labelling all five 3d orbitals. [1]

(ii) Explain why the 3d orbital energy levels are arranged in such a way.

....

....

....

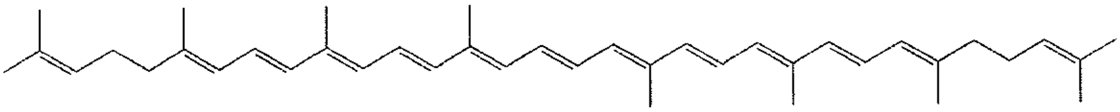
.... [2]

(b) Another type of electronic structure that can be detected by UV-VIS spectroscopy is a system of conjugated C=C bonds.

A conjugated system consists of C=C bonds alternating with C–C bonds.

The p orbitals of each carbon atom overlap sideways, forming a π–system.

Lycopene is an example of a molecule containing a conjugated system. It is an intense pigment found in many different types of food.



lycopene

λ_{max} is the wavelength (in nanometres) at which a substance containing conjugated C=C double bonds absorbs the most light. It can be predicted using Fieser-Kuhn rules:

$$\lambda_{max} = 114 + 5\boldsymbol{M} + \boldsymbol{n}(48 - 1.7\boldsymbol{n})$$

where $\boldsymbol{M}$ = total number of methyl substituents in the conjugated system
$\boldsymbol{n}$ = number of C=C double bonds in the conjugated system

(i) Calculate the predicted λ_{max} of lycopene.

[2]

(ii) Light of different wavelengths correspond to different colours.

When a sample absorbs light of a particular colour, the sample would appear as the complementary colour of the light absorbed.

With reference to the information given in **Table 6.1** and your answer in **(b)(i)**, state the expected colour of lycopene.

Table 6.1

colour	wavelengths / nm	complementary colour
violet	380 – 430	yellow
blue	430 – 490	orange
green	490 – 560	red
yellow	560 – 580	violet
orange	580 – 620	blue
red	620 – 700	green

.... [1]

When a pair of atomic orbitals overlap, two new molecular orbitals are formed.

The molecular orbitals – the bonding orbital and the antibonding orbital – are of lower and higher energies than the originating atomic orbitals respectively (**Fig 6.1**).

When multiple atomic orbitals overlap sideways in a π–system, the resulting molecular orbitals will adopt two separate stacks of energy levels – the lower energy bonding orbitals and higher energy antibonding orbitals.

The more of such atomic orbitals overlapping, the more the resultant molecular orbitals will split in energy to form larger stacks (**Fig 6.2**).

The π–overlapping of atomic orbitals also results in a lower energy molecule.

Fig 6.1

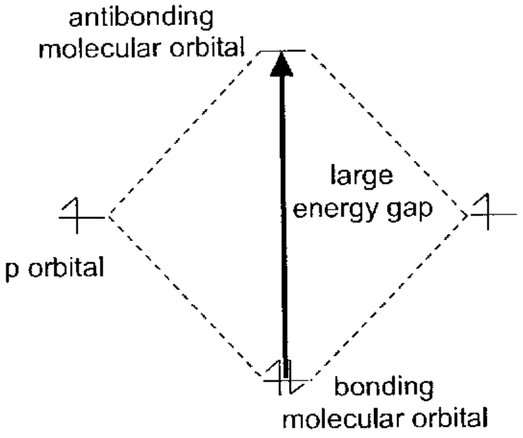
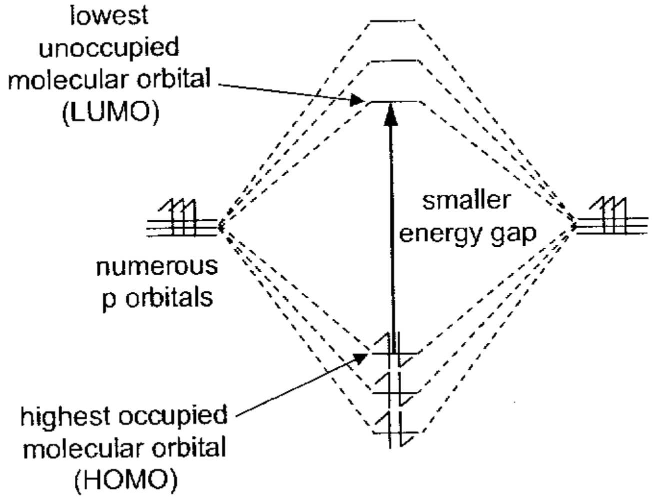


Fig 6.2



When electrons absorb light energy, they promote to a higher energy antibonding orbital, with the energy difference between the antibonding orbital (LUMO) and the starting bonding orbital (HOMO) equal to the energy of the light.

The higher the light energy, the shorter the wavelength λ_{max}.

(iii) Explain how having more atomic orbitals overlapping will result in

- a relatively high λ_{max}.

....

.... [1]

- a lower energy molecule.

....

.... [1]

[Turn over

(iv) Lycopene stains are persistent and difficult to remove. One way to remove them is by applying bleach.

Bleach is formed by dissolving chlorine in water.

$$Cl_2(g) + H_2O(l) \rightarrow HCl(aq) + HClO(aq)$$

Using oxidation numbers, explain why the formation of bleach is a redox reaction.

....

....

....

.... [2]

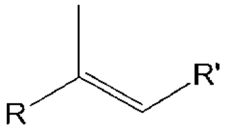
(v) Draw the dot-and-cross diagram for a molecule of bleach, HC*l*O.

[1]

(vi) Bleach molecules react with C=C double bonds.

In the first step, the electron-deficient chlorine atom in the bleach molecule reacts with the C=C double bond to form a carbocation.

Based on the information given above, outline the mechanism of the reaction between bleach and one C=C double bond in a section of lycopene. You may represent lycopene as the structure below.



[2]

(vii) Explain how using bleach removes lycopene stains.

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....

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.... [2]

[Total: 15]

END OF PAPER

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	Class	Adm No
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2021 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions

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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	6	Total
Marks	/ 13	/ 7	/ 18	/ 13	/ 9	/ 15	/ 75

This question paper consists of **17** printed pages and **1** blank page.

Answer all questions in the spaces provided.

1 **(a)** Explain why the ions of Group 2 elements increase in size down the Group. [2]

Although both nuclear charge and shielding effect increases, the distance between the valence electron and the nucleus increases. ;

The electrostatic forces of attraction between the positive nucleus and the outermost electron decreases and valence electrons are pulled less closely. ;

(b) Magnesium is a Group 2 element. Magnesium nitrate decomposes to form an oxide and two gases when heated strongly.

(i) Write a balanced chemical equation, with state symbols, for the decomposition of magnesium nitrate. [1]

$2\,Mg(NO_3)_2\,(s) \rightarrow 2\,MgO\,(s) + 4\,NO_2\,(g) + O_2\,(g)$

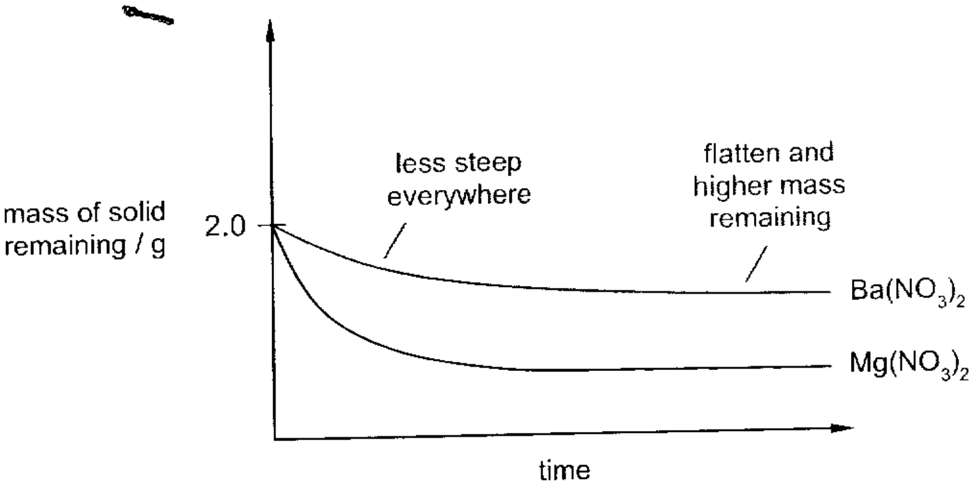
(ii) Describe and explain the relative thermal stability of magnesium nitrate and barium nitrate. [2]

Ba^{2+} ion is larger than Mg^{2+} ion while charge is the same, thus Ba^{2+} has a lower charge density and polarises NO_3^- less. ;

N–O bond is weakened less and $BaNO_3$ is more thermally stable. ;

(iii) 2.0 g of magnesium nitrate was heated strongly with a non-luminous Bunsen flame until it was completely decomposed.

On the same axes, sketch a graph showing the progress of reaction as 2.0 g of barium nitrate was strongly heated with the same Bunsen flame until it was completely decomposed.



[1]

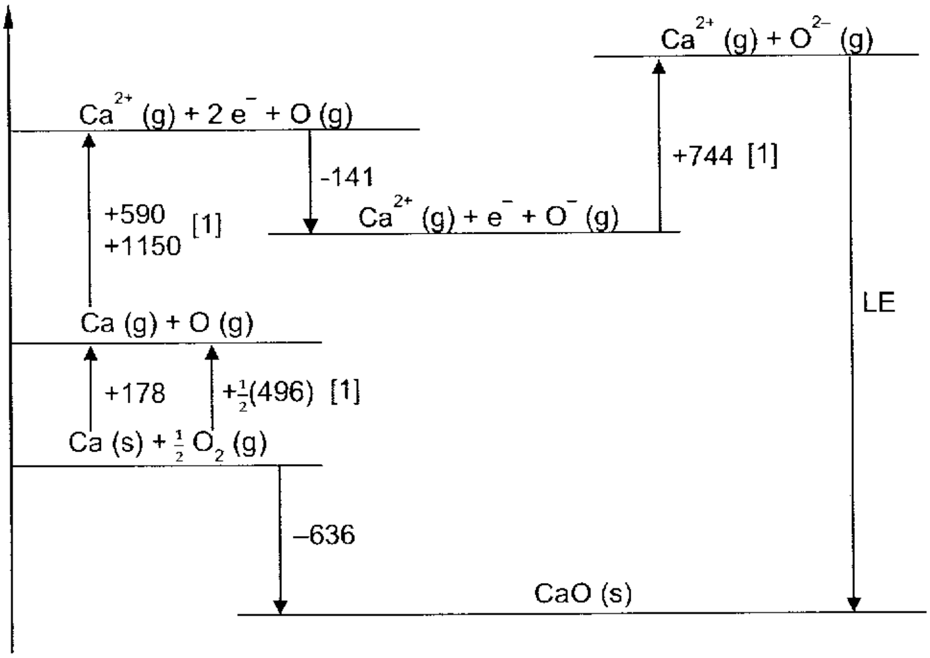
(c) One of the products of the decomposition of Group 2 nitrates is the metal oxide.

Metal oxides are ionic compounds with attractive forces existing within them that can be quantified by the lattice energy.

(i) Using the following data and relevant data from the Data Booklet, construct a Born-Haber cycle and use it to calculate the lattice energy of calcium oxide.

standard enthalpy change of formation of calcium oxide = $-636\ \text{kJ mol}^{-1}$
standard enthalpy change of atomisation of calcium = $+178\ \text{kJ mol}^{-1}$
first electron affinity of oxygen = $-141\ \text{kJ mol}^{-1}$
second electron affinity of oxygen = $+744\ \text{kJ mol}^{-1}$

[4]



$-636 = +178 + \frac{1}{2}(496) + 590 + 1150 - 141 + 744 + \text{LE}$

LE(CaO) = $\mathbf{-3405\ kJ\ mol^{-1}}$ [1]

accept −3410

(ii) The melting point of calcium oxide is 2886 K.

Using appropriate values from the Data Booklet, estimate the melting point of magnesium oxide.
Show all your working clearly.

[3]

LE(CaO) = k $\frac{q_+ \times q_-}{r_+ + r_-}$ = k $\frac{(+2)\times(-2)}{0.099 + 0.140}$ = –3405
k = 203.44875 ;

LE(MgO) = 203.44875 $\frac{(+2)\times(-2)}{0.065 + 0.140}$ = –3969.73 kJ mol^{-1} ;

estimated melting point of MgO = 2886 × $\frac{3969.73}{3405}$ = **3360 K** ;

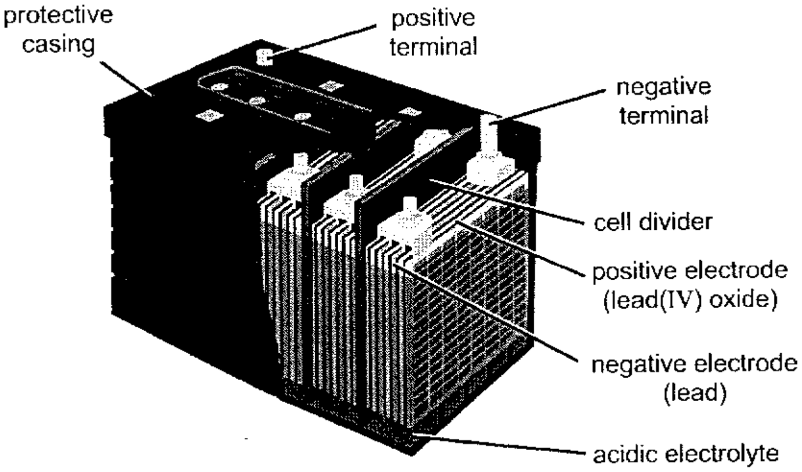
[Total: 13]

2 Car batteries generate electricity to power the appliances in cars.

The electrical flow is generated with a spontaneous redox reaction across the two electrodes.

As the battery operates, it becomes discharged, and the two electrodes are converted into by-products.

A common arrangement for a car battery would be 6 cells each generating 2 volts, connected in series to form a 12-volt battery.



(a) Using suitable electrode reactions, prove that the $E_{cell}^{\ominus}$ of one battery cell discharging is +1.60 V.

[3]

cathode: $PbO_2 + 4\ H^+ + 2\ e^- \rightarrow Pb^{2+} + 2\ H_2O$ +1.47 ;
anode: $Pb \rightarrow Pb^{2+} + 2\ e^-$ +0.13 ;
$E_{cell}^{\ominus} = +1.47 + 0.13 = \mathbf{+1.60\ V}$;

(b) Aqueous sulfuric acid is used as the electrolyte.

Suggest one possible reason why the voltage of one car battery cell is larger than 1.60 V.

[1]

any 1:

lead(II) sulfate precipitate is formed
shifting equilibrium position right hence increasing E_{cell}

electrolyte / acid concentration is higher than 1.00 mol dm^{-3}

engine temperature is higher than 25 °C

(c) A fully-charged 12-volt battery contains 18.6 kg of electrodes with equal masses of positive and negative electrodes.

Calculate the quantity of charge provided by the 12-volt battery after it is fully discharged. [3]

since PbO_2 has a higher M_r than Pb
and $\frac{\eta_{PbO_2}}{\eta_{Pb}} = \frac{1}{1}$
limiting reagent is PbO_2 ;

mass of $PbO_2 = \frac{18600\ g}{2} = 9300$ g
$\eta_{PbO_2} = \frac{9300\ g}{239.2\ g/mol} = 38.8796$ mol
since $\frac{\eta_{e^-}}{\eta_{PbO_2}} = \frac{2}{1}$, $\eta_{e^-} = 38.8796$ mol × 2 = 77.759 mol ;

Q = nF = 77.759 mol × 96500 C/mol = **7.50×10^6 C** ;

[Total: 7]

3 Hydrogen peroxide decomposes on its own due to the weak O–O bond.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

However, at room temperature and pressure, the decomposition is very slow.

The decomposition of hydrogen peroxide is a first-order reaction.

(a) By measuring the volume of oxygen formed over time, the initial rate of the decomposition of a certain concentration of hydrogen peroxide solution can be found.

initial concentration of H_2O_2 / mol dm^{-3}	initial rate of decomposition / mol dm^{-3} s^{-1}
0.100	1.44×10^{-6}

Calculate the time taken for the concentration of hydrogen peroxide to drop to half its original value.

[2]

rate = $k[H_2O_2]$

$k = \frac{rate}{[H_2O_2]} = \frac{1.44 \times 10^{-6}\ mol\ dm^{-3}\ s^{-1}}{0.100\ mol\ dm^{-3}} = 1.44 \times 10^{-5}\ s^{-1}$;

$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{1.44 \times 10^{-5}\ s^{-1}} = \mathbf{48100\ s}$;

(b) When aqueous potassium iodide is added into hydrogen peroxide, the decomposition occurs rapidly.

Potassium iodide speeds up the decomposition of hydrogen peroxide in two reaction steps with the following reversible reaction:

$$IO^- + 2H^+ + 2e^- \rightleftharpoons I^- + H_2O$$

(i) Hydrogen peroxide reacts with I^- in the first step, and I^- is regenerated in the second step.

Write two equations to show the mechanism of iodide ions speeding up the decomposition of hydrogen peroxide.

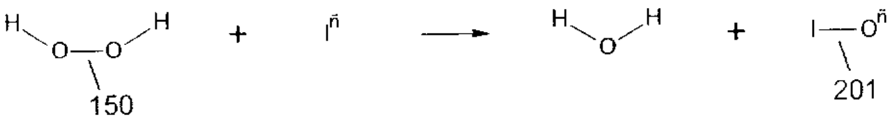
[2]

step 1: $H_2O_2 + I^- \longrightarrow H_2O + IO^-$
step 2: $H_2O_2 + IO^- \longrightarrow O_2 + H_2O + I^-$

(ii) Use bond energies to calculate the enthalpy change for the first step, ΔH_1.

[Bond energy of I–O = 201 kJ mol^{-1}]

[2]



$\Delta H_1 = 150 - 201 = \mathbf{-51\ kJ\ mol^{-1}}$

[1] correct $E_{absorbed}$ or $E_{released}$
[1] correct final answer

(iii) Explain why the enthalpy change calculated using bond energy values in **(ii)** is only an estimation of the actual value.

[1]

any 1:

bond energy values assume gaseous state, but chemicals are aqueous / liquid state

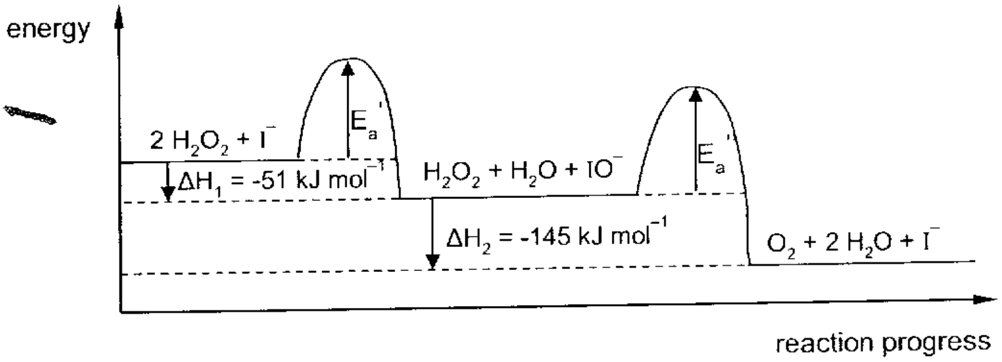
bond energy values are only averages

the IO^- ion is charged, affecting bond energy

(iv) The enthalpy change for the second step, ΔH_2, is –145 kJ mol^{-1}.

Draw an energy profile diagram to show the energy changes and chemical species involved in each of the two reaction steps.

[3]

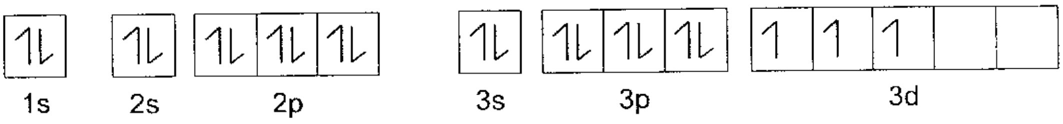


intermediate products and final products [1]
two activation energies with labels [1]
two enthalpy changes with labels [1]

(c) Manganese(IV) oxide can also be used to speed up the decomposition of hydrogen peroxide.

(i) Draw the electron-in-box diagram for the electronic configuration of the manganese species in manganese(IV) oxide.

[1]



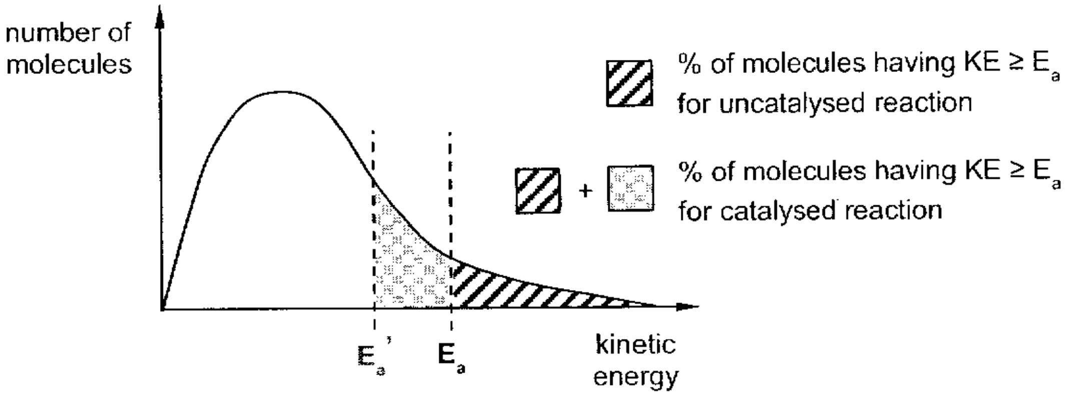
(ii) With reference to the configuration in **(i)**, explain how manganese(IV) oxide allows hydrogen peroxide molecules to interact with it.

[1]

Mn^{4+} has energetically-accessible vacant 3d orbitals
that can accept lone pair electrons / dative bonds from hydrogen peroxide

(iii) Using a Maxwell-Boltzmann energy distribution, explain how manganese(IV) oxide speeds up the decomposition of hydrogen peroxide.

[5]



[1]
- axes labels for number of molecules, energy
- correct graph shape (start from origin, peak at the left, taper off)
- E_a and E_a' both marked out correctly on the x-axis

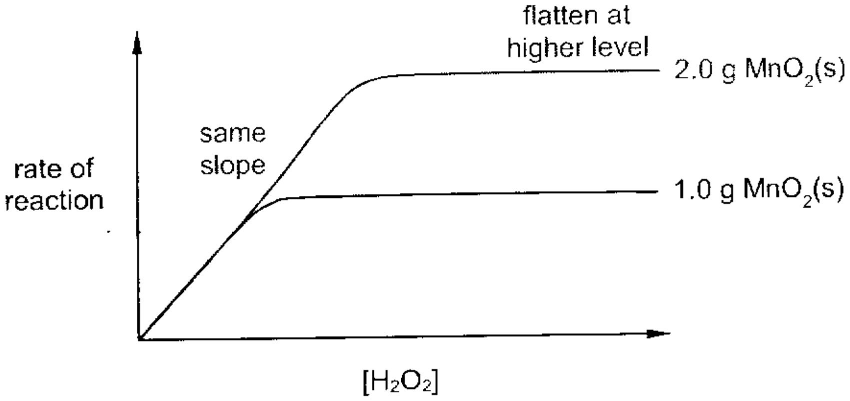
[1]
- label zone for % of molecules having KE ≥ E_a for uncatalysed reaction
- label additional zone for % of molecules having KE ≥ E_a for catalysed reaction

any two [2]
- increased concentration of molecules at MnO_2 surface, increasing frequency of collisions
- provides alternative reaction mechanism of lower activation energy, increasing percentage of molecules having energy greater than or equal to activation energy
- increased percentage of molecules having correct orientation

[1]
increasing frequency of effective collisions, increasing rate of reaction

(iv) In a series of experiments, 1.0 g of manganese(IV) oxide powder was added into hydrogen peroxide solutions of various concentrations to measure the rates of reaction.

On the same axes below, sketch the results obtained when 2.0 g of manganese(IV) oxide powder was used for another series of experiments.



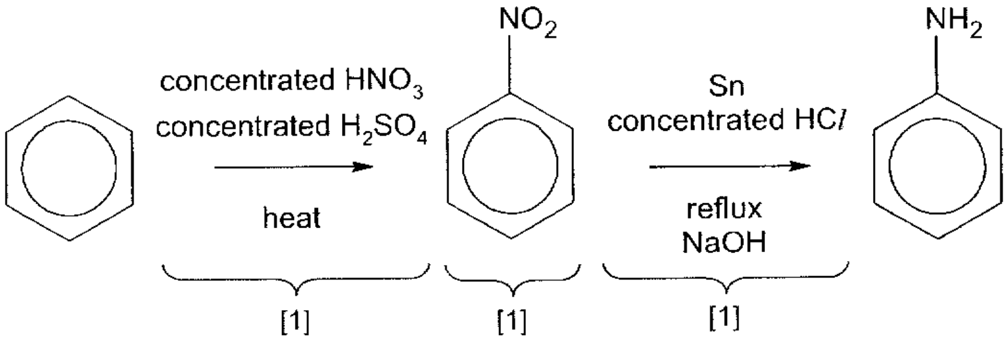
[1]

[Total: 18]

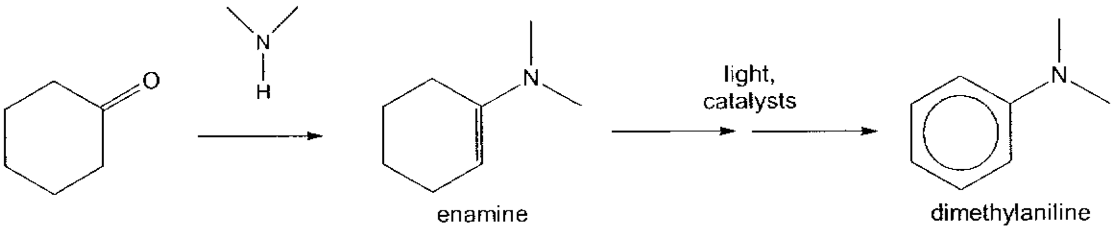
4 Aniline is conventionally synthesised with benzene as the starting organic material.

(a) State the reagents and conditions for the 2 steps in the reaction scheme below. Draw the structure of the intermediate in the box provided.

[3]



(b) In 2020, Dighe *et. al.* researched a new technique, photochemical dehydrogenative amination, to produce dimethylaniline starting from cyclohexanone and dimethylamine. The method is novel because benzene, an aromatic compound, is not required as a starting material.



(i) Describe a chemical test, with appropriate observations, which would confirm the identity of cyclohexanone.

[2]

Add 2,4-dinitrophenylhydrazine, warm. ;
An orange precipitate forms ;

(ii) The dimethylamine required in the novel method can be produced from methylamine.

State the reagents and conditions, and write a balanced chemical equation for the synthesis of dimethylamine from methylamine as a starting material.

[2]

limited CH_3Br, ethanol, heat in sealed tube ;
$CH_3Br + CH_3NH_2 \longrightarrow (CH_3)_2NH + HBr$;

[Turn over

(iii) The first reaction step in the novel synthesis involves the formation of an enamine.

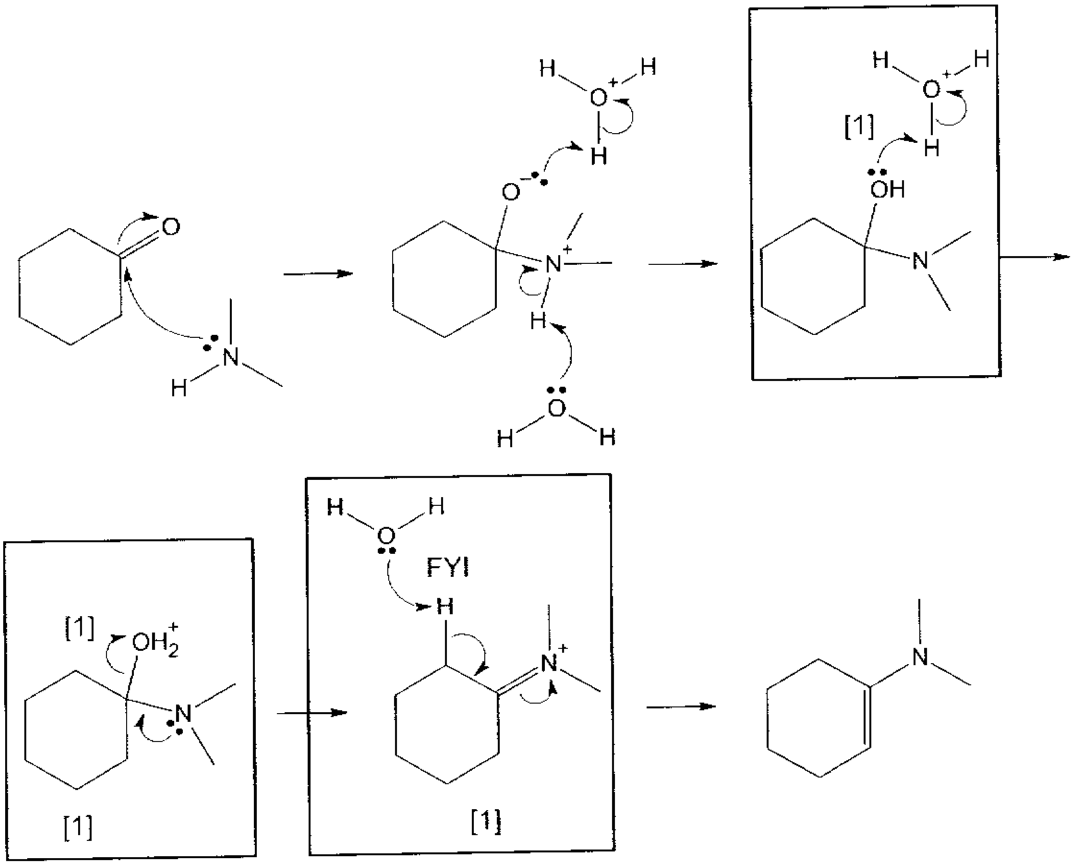
Enamines contain a carbon-carbon double bond (C=C) next to a nitrogen atom.

As part of the reaction mechanism, a carbinolamine is formed.

The oxygen atom on the carbinolamine is protonated by an acid, H^+, forming an intermediate compound.

The lone pair of electrons on the nitrogen atom push the leaving group out, forming an iminium ion and H_2O. This is achieved by forming a C=N double bond, resulting in a positively-charged nitrogen atom. The C–O bond breaks, forming H_2O.

Complete the mechanism of the reaction in the boxes below to form the enamine, starting from carbinolamine to iminium ion. Include the species that protonated carbinolamine, lone pairs of electrons, curly arrows to represent electron movement, the intermediate compound formed, and the iminium ion.



[4]

(iv) Aniline is often preferred over benzene as the starting material for the formation of substituted aromatic compounds.

Explain the relative reactivity of aniline towards bromine compared to benzene.

[2]

The lone pair of electrons on N atom delocalises into the π electron cloud / p orbitals of the benzene ring, ;

increasing the electron density of the benzene ring. Hence aniline is more reactive towards the electrophilic substitution of bromine. ;

[Total: 13]

[Turn over

5 **(a)** Group 17 elements form molecular compounds with hydrogen, H**X**.

Table 5.1

H**X**	boiling point of H**X** / °C
HF	19.5
HC*l*	–85.1
HBr	–66.8
HI	–35.4

(i) Explain why the boiling points of H**X** follow the trend shown in **Table 5.1**. [3]

Number of electrons / size of e-cloud increases from HC*l* < HBr < HI, hence instantaneous dipole-induced dipole forces between molecules become stronger. ;

There is hydrogen bonding between HF molecules, which is stronger than id-id forces. ;

More energy to overcome stronger forces of attraction and hence boiling point increases from HC*l* < HBr < HI < HF. ;

(ii) H**X** molecules dissociate in water, forming acidic solutions.

$$H\mathbf{X}(aq) \rightleftharpoons H^+(aq) + \mathbf{X}^-(aq)$$

State and explain the trend down the Group in the extent of dissociation for the H**X** molecules. [3]

Atomic radius increases down Group 17 and H–**X** bond length increases, ;

so less energy is required / it becomes easier to break the covalent bond. ;

Hence extent of dissociation increases down the Group. ;

(b) To a 90 cm^3 solution containing 0.00100 mol dm^{-3} Cl^- ions, 10 cm^3 of 0.00100 mol dm^{-3} silver nitrate solution was added.

0.001431 g of precipitate was formed.

Calculate the solubility product, K_{sp}, of the precipitate formed.

[3]

$\eta_{Cl^-} = \frac{90}{1000}$ dm^3 × 0.00100 mol dm^{-3} = 9.00 × 10^{-5} mol
$\eta_{Ag^+} = \frac{10}{1000}$ dm^3 × 0.00100 mol dm^{-3} = 1.00 × 10^{-5} mol
new [Cl^-] = $\frac{9.00\times10^{-5}\ mol}{100/1000\ dm^3}$ = **9.00 × 10^{-4} mol dm^{-3}**
new [Ag^+] = $\frac{1.00\times10^{-5}\ mol}{100/1000\ dm^3}$ = **1.00 × 10^{-4} mol dm^{-3}** ;

η_{AgCl} precipitated = $\frac{0.001431\ g}{143.4\ g/mol}$ = **9.979 × 10^{-6} mol** ;

[AgCl] decrease due to precipitation = $\frac{9.979\times10^{-6}\ mol}{100/1000\ dm^3}$ = 9.979 × 10^{-5} mol dm^{-3}
let this value be p
$K_{sp}(AgCl)$ = (9.00 × 10^{-4} − p)(1.00 × 10^{-4} − p) = **1.68 × 10^{-10} mol^2 dm^{-6}** ;

(or calc via amounts first)

[Total: 9]

[Turn over

6 traviolet-visible spectroscopy (UV-VIS) is a technique used to measure differences in energ vels within a compound.

ght of the ultraviolet to visible wavelength range is passed through a sample.

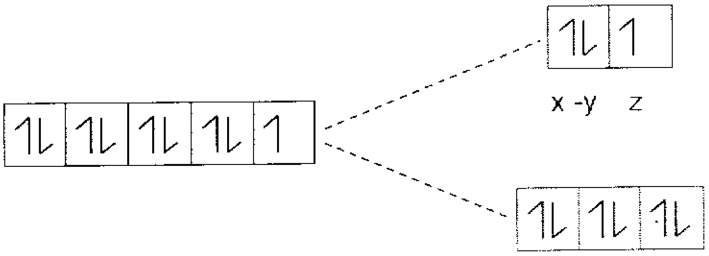
ectrons absorb the incoming light energy to promote to a higher energy level orbital.

e energy of the light absorbed corresponds to the difference in the initial and final energy levels

detecting the wavelengths of light which are not transmitted through the sample, informatio

Copper(II) ions exist as a hexahydrate in aqueous solution, $[Cu(H_2O)_6]^{2+}$.

Due to the approach of the six water molecules, the orbitals in the 3d subshell of th copper(II) ion are split into two separate energy levels.



in why the 3d orbital energy levels are arranged in such a way.

[2

repelling the $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals less, decreasing their energy.

A conjugated system consists of C=C bonds alternating with C–C bonds.

The p orbitals of each carbon atom overlap sideways, forming a π–system.

Lycopene is an example of a molecule containing a conjugated system. It is an intens pigment found in many different types of food.

lycopene

λ_{max} is the wavelength (in nanometres) at which a substance containing conjugated C=(

$$\lambda_{max} = 114 + 5M + n(48 - 1.7n)$$

where M = total number of methyl substituents in the conjugated system
n = number of C=C double bonds in the conjugated system

(i) Calculate the predicted λ_{max} of lycopene. [2]

$M = 6$
$n = 11$;

$\lambda_{max} = 114 + 30 + 11(48 - 1.7(11)) =$ **466 nm** ;

accept 466.3

(ii) Light of different wavelengths correspond to different colours.

When a sample absorbs light of a particular colour, the sample would appear as the complementary colour of the light absorbed.

With reference to the information given in **Table 6.1** and your answer in **(b)(i)**, state the expected colour of lycopene.

Table 6.1

colour	wavelengths / nm	complementary colour
violet	380 – 430	yellow
blue	430 – 490	orange
green	490 – 560	red
yellow	560 – 580	violet
orange	580 – 620	blue
red	620 – 700	green

[1]

Orange (ecf from b(i))

When a pair of atomic orbitals overlap, two new molecular orbitals are formed.

The molecular orbitals – the bonding orbital and the antibonding orbital – are of lower and higher energies than the originating atomic orbitals respectively (**Fig 6.1**).

When multiple atomic orbitals overlap sideways in a π–system, the resulting molecular orbitals will adopt two separate stacks of energy levels – the lower energy bonding orbitals and higher energy antibonding orbitals.

The more of such atomic orbitals overlapping, the more the resultant molecular orbitals will split in energy to form larger stacks (**Fig 6.2**).

The π–overlapping of atomic orbitals also results in a lower energy molecule.

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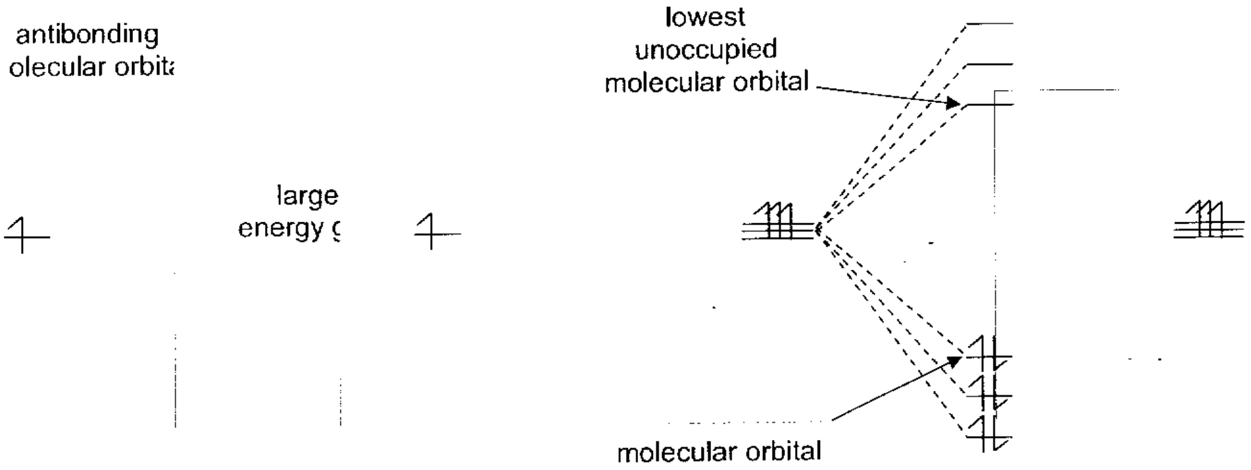


When electrons absorb light energy, they promote to a higher energy antibonding orbital, wit
the energy difference between the antibonding orbital (LUMO) and the starting bonding orbita
(HOMO) equal to the energy of the light.

The higher the light energy, the shorter the wavelength λmax.

in how having more atomic orbitals overlapping will result in

a relatively high λmax. [1

a lower energy molecule. [1

ons are delocalised over the π orbitals / MO / larger volume, decreasing inter
onic repulsion. ;

h is formed by dissolving chlorine in water.

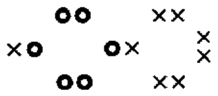
$$Cl_2(g) + H_2O(l) \longrightarrow HCl(aq) + HClO(aq)$$

oxidation numbers, explain why the formation of bleach is a redox reaction. [2

as reduced to HCl as the oxidation state of Cl decreased from 0 (in Cl_2) to −1 (ir
;

the dot-and-cross diagram for a molecule of bleach, HC/O.

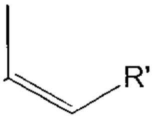
[1



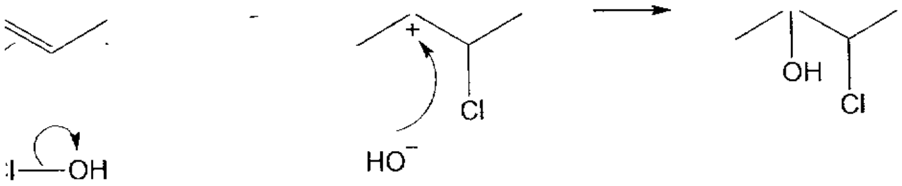
h molecules react with C=C double bonds.

first step, the electron-deficient chlorine atom in the bleach molecule reacts witl =C double bond to form a carbocation.

d on the information given above, outline the mechanism of the reaction betweer h and one C=C double bond in a section of lycopene. You may represent lycopen e structure below.



[2



(vii) in how using bleach removes lycopene stains.

[2

h attacks C=C bond by electrophilic addition, converting it into C–C bond ating the bond, ;

esults in the loss of conjugation / p or π orbital overlap, causing the energy ga rease. Wavelength absorbed decreases to outside of the visible region and n

[Total: 15

END OF PAPER

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Class	Adm No

Candidate Name: ____________________

H

millennia
institute

2021 Preliminary Examinations
Pre-University 3

H2 CHEMISTRY

Paper 3 Free Response

9729/03

17 Sep 2021

2 hours

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.

Section A: Answer **all** questions

Section B: Answer any **1** question

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.

	Section A			Section B		Total
Question	1	2	3	4	5	
Marks	24	20	16	20	20	80

This question paper consists of **24** printed pages and **2** blank pages.

Section A

Answer **all** questions from this section.

1 **(a)** A metallic element, **M**, exists as three isotopes. The relative isotopic masses and their relative abundances are shown in Table 1.1.

Relative Isotopic Mass	Relative Abundance
53.94	3
55.93	46
56.94	1

Table 1.1

(i) Define the term *relative isotopic mass.* [1]

(ii) Using the information in **Table 1.1**, calculate the relative atomic mass of **M**, leaving your answer to 2 decimal places. [1]

A dilute aqueous solution of the chloride salt of **M**, MCl_n, was electrolysed using a current of 0.5 A for 1 hour as shown in the setup in **Fig. 1.1**. The experiment was carried out at 32 °C and 1 atm.

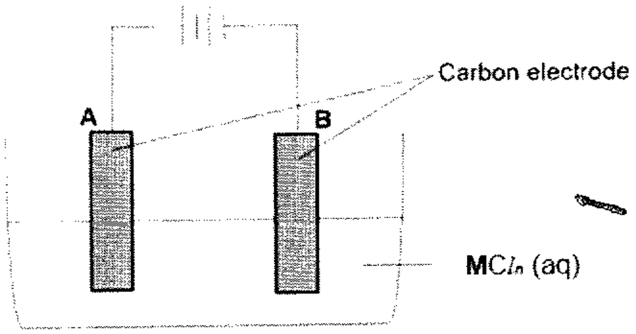

Fig. 1.1

0.3471 g of metal **M** was deposited at electrode **B**.

(iii) Using your answer in **(a)(ii)**, determine *n*. [3]

(iv) A gas is produced at electrode **A**.
Write the ion-electron equation for the reaction taking place at electrode **A**. [1]

(v) Calculate the volume of gas produced at electrode **A**. [2]

(vi) Suggest why electrode **A** will decrease in mass over time. [1]

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(b) Chromium(III) chloride, $CrCl_3$, reacts with water to form a violet complex, $[Cr(H_2O)_6]Cl_3$. This violet complex is isomeric to two other complexes as shown in Table 1.2.

Structural Formula of Complex	Colour of Complex
$[Cr(H_2O)_6]Cl_3$	violet
$[CrCl(H_2O)_5]Cl_2 \cdot H_2O$	pale green
$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$	dark green

Table 1.2

(i) Give one characteristic properties of transition elements as shown by chromium in the isomers in **Table 1.2**. [1]

(ii) Using $[Cr(H_2O)_6]Cl_3$, explain what is meant by the term *ligand*. [1]

(iii) When 2.665 g of one of the complexes in **Table 1.2** was reacted with an excess of aqueous $AgNO_3$, 2.868 g of $AgCl$ was obtained.

Deduce the structural formula of the complex. [2]

(iv) Draw the full structure of the cation in the pale green complex, $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$, showing the shape of the cation. [1]

(c) Potassium dichromate(VI) can be produced from chromium(III) chloride via a 3-step reaction.

Step 1:	Chromium(III) chloride is boiled with hydrogen peroxide in an alkaline medium, forming a bright yellow solution, CrO_4^{2-}.
Step 2:	Boiling is continued until excess hydrogen peroxide is destroyed.
Step 3:	The yellow solution is then cooled and acidified with ethanoic acid, forming the orange dichromate(VI) solution.

(i) Write the ion-electron equation for the oxidation of Cr^{3+} in step 1 and hence the overall balanced equation for the reaction between Cr^{3+} and H_2O_2 under alkaline conditions. [2]

(ii) Suggest how would you know when all the excess hydrogen peroxide has been destroyed in step 2. [1]

(iii) The reaction in step 3 has the following equation:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

State and explain if the reaction in step 3 is a redox reaction. [1]

(iv) The reaction in step 3 is an exothermic reaction.

State and explain the effect of increasing the temperature of the system on the yield of $Cr_2O_7^{2-}(aq)$. [2]

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(d) A solution of sodium dichromate(VI) is acidified with dilute sulfuric acid before adding to an organic compound. The solution slowly turns green. Boiling the green solution with more of the organic compound produces a pale blue solution.

0.10 mol of the pale blue ions was found to require 0.020 mol of acidified potassium manganate(VII) solution to oxidise it back to the green ions.

(i) State the identity of the green ion. [1]

(ii) Deduce the oxidation number of the blue ion. [2]

(iii) State, with a reason, which reagent, acidified H_2O_2 or aqueous Fe^{3+} could be used to convert the green ions back to dichromate(VI) ions. [1]

[Total: 24]

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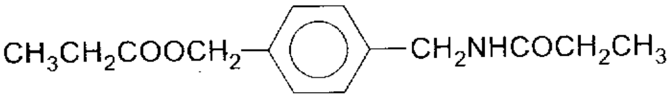
2 **(a)** Compound **P**, C_8H_9NO, can react with Tollen's reagents but not with Fehling's solution. **P** is also soluble in dilute hydrochloric acid.

On reacting **P** with lithium aluminium hydride, **Q**, $C_8H_{11}NO$, is formed. **Q** reacts readily with sodium metal. 1 mole of **Q** reacts with 2 moles of propanoyl chloride to give the following compound.



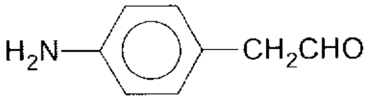
Q also reacts with hot acidified $KMnO_4$ to give **R**, $C_8H_6O_4$. 1 mole of **R** reacts with excess Na_2CO_3(s) to give 1 mole of CO_2(g).

When **P** is heated with excess CH_3Br, a crystalline solid **S**, $C_{11}H_{16}NOBr$, is formed. **S** has very high melting point.

Deduce the structure of compounds **P**, **Q**, **R** and **S**, explaining the chemistry of the reactions described. [10]

[Turn over

(b) **T** is an isomer of **P**.



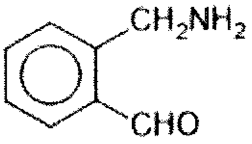
T

(i) State the type of reaction when **T** reacts with 2,4-dinitrophenylhydrazine. Write a balanced equation for the reaction. [2]

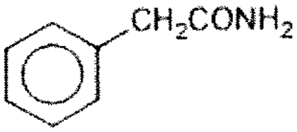
(ii) Draw the structure of the organic product formed when **T** reacts with $Br_2(aq)$. [1]

(iii) Outline the mechanism for the reaction of **T** with cold alkaline HCN. [3]

(c) Compounds **U** and **W** are constitutional isomers of **T**.



U



W

(i) Explain why **U** has a lower boiling point compared to **W**. [2]

(ii) State and explain the relative basicity of **U** and **W**. [2]

[Total: 20]

3 This question involves sulfur and its compounds.

(a) (i) State the full electronic configuration of S^{3+}. [1]

(ii) Write an equation to represent the fourth ionisation energy of sulfur. [1]

(iii) The fourth ionisation energy of sulfur and phosphorus is 4540 kJ mol^{-1} and 4960 kJ mol^{-1} respectively.

Explain why the fourth ionisation energy of sulfur is lower than that of phosphorus. [2]

(iv) A sample of S contains 2 isotopes. In order to identify the mass of these two isotopes, they were first ionised to form singly-charged positive ions and passed through an electric field of constant strength. Their angles of deflection, along with a reference sample of helium nucleus, ${}^{4}_{2}\mathrm{He}$, were recorded in **Table 3.1**.

Species	**Angle of deflection**
Isotope **X**	1.60 °
Isotope **Y**	1.51 °
Helium nucleus, ${}^{4}_{2}\mathrm{He}$	25.6 °

Table 3.1

Calculate the relative mass of each isotope of sulfur, giving your answer to the nearest whole number. [3]

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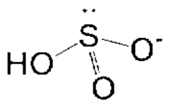
(b) Hydrogen sulfite ion, HSO_3^-, has the following structure:



Hydrogen sulfite ion reacts with carbonate ion according to the following equation:

$$2HSO_3^- + CO_3^{2-} \rightarrow 2SO_3^{2-} + H_2O + CO_2$$

(i) Define the term *Brønsted-Lowry acid.* [1]

(ii) State which species in the reaction between hydrogen sulfite ion and carbonate ion acts as a Brønsted-Lowry acid. [1]

(iii) The carbon dioxide gas produced from the reaction is a non-ideal gas. **Fig. 3.1** shows the experimental values of the compressibility factor (Z) plot for 1 mole of carbon dioxide gas at 298 K. (Z = pV/RT)

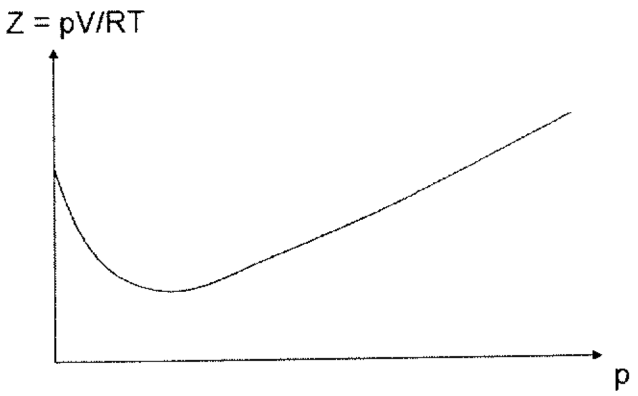


Fig. 3.1

On the plot given in **Fig. 3.1**, sketch the graph to illustrate the behaviour of

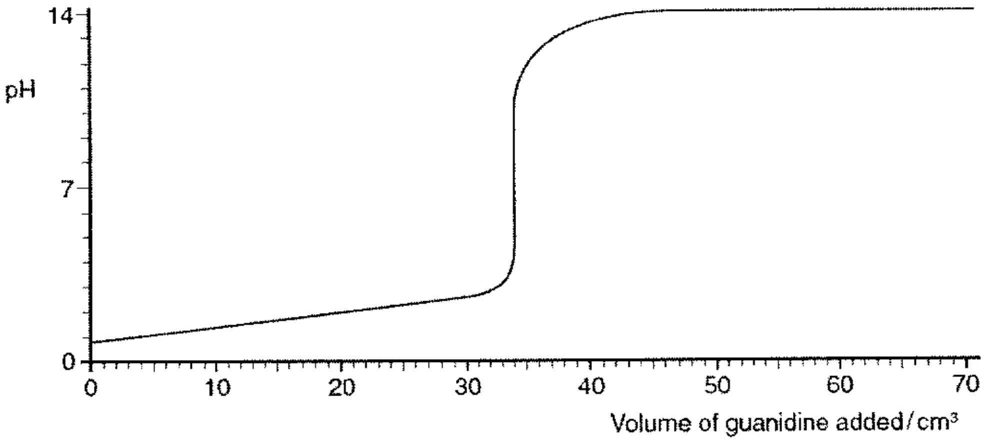
- I. 1 mole of an ideal gas at 298 K,
- II. 1 mole of carbon dioxide gas at 398 K.

Label your answer clearly. [2]

(c) Sulfuric acid reacts with guanidine, $(H_2N)_2CNH_2$, as follows:

$$H_2SO_4 + 2(H_2N)_2CNH \rightarrow SO_4^{2-} + 2(H_2N)_2CNH_2^+$$

When a 25.0 cm^3 sample of dilute sulfuric acid was titrated against a solution of guanidine, the following titration curve was obtained.



(i) Deduce if guanidine is a strong or a weak base. [1]

(ii) The initial pH of the sulfuric acid is 0.61.

Calculate [H^+], and hence the initial concentration of sulfuric acid. [2]

(iii) Calculate the concentration, in mol dm^{-3}, of guanidine in the solution. [2]

[Total: 16]

Section B

Answer **one** question from this section.

4 In the stratosphere, there is an equilibrium established between O_2 and O_3:

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

When UV radiation from the sun breaks up O_3 into an oxygen atom and an oxygen molecule, the oxygen atom quickly recombines with an oxygen molecule to form back ozone. However, this equilibrium is disrupted by the radicals produced from the chlorofluorocarbons (CFCs) due to human activities.

(a) One such CFC is CF_2Cl_2.

Write two equations to illustrate how CF_2Cl_2, in the presence of UV light, causes the decomposition of ozone layer. [2]

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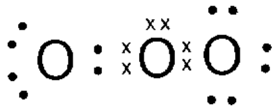
(b) The dot-and-cross diagram of O_3 is shown below.



With the aid of suitable diagram, explain why the two oxygen-oxygen bonds in the ozone molecule have the same bond strength. [2]

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(c) One method to determine the concentration of the ozone layer is to pass air through acidified potassium iodide and to measure the amount of iodine liberated. The following reaction takes place:

$$O_3 + 2H^+ + 2I^- \rightarrow O_2 + H_2O + I_2$$

The concentration of iodine liberated, in mol dm^{-3}, is measured using platinum / iodine electrode against standard silver / silver chloride reference electrode. The E_{cell} of the system, in volts, is given by the following equation:

$$E_{cell} = 0.32 + 0.029 \log_{10}[I_2]$$

To determine concentration of ozone in the atmosphere, a balloon was used to carry a sampling device. A 1.00 m^3 sample of air, measured at 25 °C and 0.24 atm was passed through 10 cm^3 of acidified potassium iodide. The E_{cell} of the platinum electrode dipping into the solution against the standard silver / silver chloride electrode was 0.21 V.

(i) Calculate the amount of ozone present in the sample. [3]

(ii) Hence calculate the volume of O_3 present in the 1.00 m^3 sample of air. [2]

(iii) The actual volume of O_3 present in the 1.00 m^3 sample of air would be less than the calculated value in **(c)(ii)**. Suggest a reason for this discrepancy. [1]

(iv) Explain why O_2 is a gas but I_2 is a solid at room temperature. [2]

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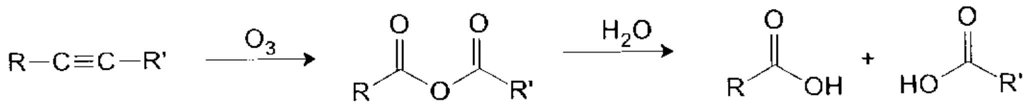
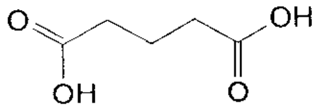
(d) Ozone reacts with alkynes to form carboxylic acids in a two-step reaction as shown below.



When alkyne **E** undergoes the same two-step reaction, only compound **F** is formed.



F

Suggest the structure of **E**. [1]

[Turn over

(e) Nitrogen monoxide in the air can be converted to nitric acid, which results in acid rain. Both nitrogen monoxide and nitrogen dioxide also cause ozone layer depletion. One way of forming nitrogen monoxide is through the dissociation of nitrogen dioxide.

$$2NO_2\ (g) \rightleftharpoons 2NO\ (g) + O_2\ (g) \qquad \Delta H = +114.2\ \text{kJ mol}^{-1}$$

At 494 °C, the value of K_p for the above reaction is 36.9 kPa.

When a certain partial pressure of nitrogen dioxide is put into an empty vessel at 494 °C, equilibrium is reached when 40% of the original nitrogen dioxide has dissociated.

(i) Write an expression for the equilibrium constant, K_p, for the reaction. [1]

(ii) Calculate the initial partial pressure of nitrogen dioxide before any dissociation occurred. [2]

(iii) Given that the standard enthalpy change of formation of NO(g) is +90.3 kJ mol^{-1}, determine the standard enthalpy change of formation of NO_2(g). [2]

(iv) With reference to the equation given in **(e)**, state and explain the sign of entropy change, ΔS, for the dissociation of NO_2(g). [1]

(v) Using your answer in **(e)(iv)**, state whether the reaction would be spontaneous at high or low temperatures. [1]

[Total: 20]

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[Turn over

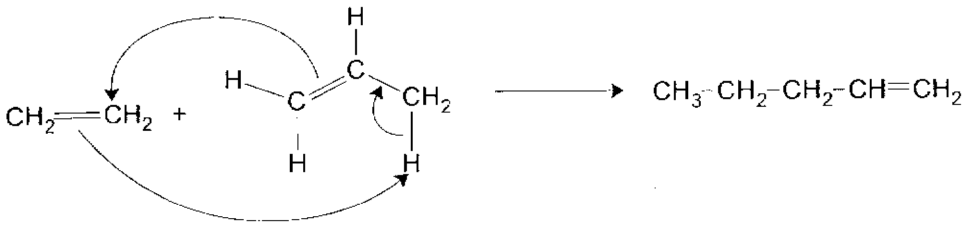
5 **(a)** Aluminium chloride is used in the production of chlorobenzene from the reaction between benzene and chlorine.

(i) Outline the mechanism for the reaction above. [3]

(ii) Explain, with the aid of relevant equations, why the aluminium chloride used in the above reaction must be anhydrous. [2]

(iii) Aluminium chloride can also act as a catalyst for the Alder-ene reaction.

One example of Alder-ene reaction is illustrated below using propene and ethene.



Suggest the structure of the organic product formed when cyclohexene reacts with ethene in an Alder-ene reaction. [1]

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(b) Aluminium chloride reacts with CH_3NH_2 to form an adduct $AlCl_3{\cdot}CH_3NH_2$.

Explain how this adduct is formed. [2]

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[Turn over

(c) Describe the reaction, if any, of aluminium oxide with water, and sodium oxide with water. Write equations, with state symbols, where appropriate and predict the pH of the resultant solution. [3]

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(d) 100 cm^3 of 0.100 mol dm^{-3} of aqueous magnesium nitrate was mixed with 100 cm^3 of aqueous sodium hydroxide and the reaction mixture was filtered. Solid magnesium hydroxide was collected as residue, and the filtrate contained a saturated solution of magnesium hydroxide, $Mg(OH)_2$, at 298 K and pH 9.5.

$$Mg(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Mg(OH)_2(s) + 2NaNO_3(aq)$$

The value of K_{sp} of magnesium hydroxide is 1.5×10^{-11}.

(i) Write an expression for the K_{sp} of magnesium hydroxide, stating its units. [2]

(ii) Calculate the concentration of hydroxide ions that remained in the **filtrate**. [2]

(iii) Calculate the concentration of magnesium ions that remained in the **filtrate**. [1]

(iv) Hence, calculate the mass of solid magnesium hydroxide formed. [2]

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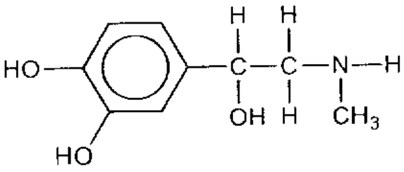
(e) The structure of compound **L** is shown below.



Compound **L**

Draw the structure of the organic product formed when compound **L** reacts with the following reagents.

(i) $SOCl_2$ [1]

(ii) Bromine water [1]

[Total: 20]

END OF PAPER

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	Class	Adm No
Candidate Name: ____________________		

millennia
institute

2021 Preliminary Examinations
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **17 Sep 2021**

2 hours

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.

Section A: Answer **all** questions

Section B: Answer any **1** question

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.

	Section A			**Section B**		Total
Question	**1**	**2**	**3**	**4**	**5**	
Marks	**24**	**20**	**16**	**20**	**20**	**80**

This question paper consists of **28** printed pages and **2** blank page.

Section A

Answer **all** questions from this section.

1 **(a)** A metallic element, **M**, exists as three isotopes. The relative isotopic masses and their relative abundances are shown in Table 1.1.

Relative Isotopic Mass	**Relative Abundance**
53.94	3
55.93	46
56.94	1

Table 1.1

(i) Define the term *relative isotopic mass*. [1]

Relative isotopic mass is defined as the mass of one atom of an isotope compared to $\frac{1}{12}$ of the mass of one atom of ^{12}C.

(ii) Using the information in Table 1.1, calculate the relative atomic mass of **M**, leaving your answer to 2 decimal places. [1]

Relative atomic mass = $\frac{(53.94\times3)+(55.93\times46)+(56.94\times1)}{(3+46+1)} = 55.83$

A dilute aqueous solution of the chloride salt of **M**, **M**Cl_n, was electrolysed using a current of 0.5 A for 1 hour as shown in the setup in Fig. 1.1. The experiment was carried out at 32 °C and 1 atm.

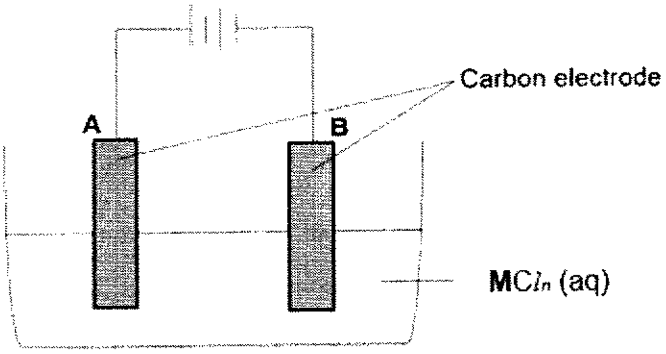


Fig. 1.1

0.3471 g of metal **M** was deposited at electrode **B**.

(iii) Using your answer in **(a)(ii)**, determine *n*. [3]

Amount of **M** deposited = $\frac{0.3471}{55.83} = 0.006217\ mol$;

Q = 0.5 × 1 × 60 × 60 = 1800 C

Amount of electrons = $\frac{1800}{96500} = 0.01865\ mol$;

$\mathbf{M}^{n+} + ne^{-} \rightarrow \mathbf{M}$

n = $\frac{0.01865}{0.006217} = 3$;

(iv) A gas is produced at electrode **A**.
Write the ion-electron equation for the reaction taking place at electrode **A**. [1]

$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-}$

(v) Calculate the volume of gas produced at electrode **A**. [2]

Amount of O_2 = 0.01865 ÷ 4 = 0.004663 mol ;

V = $\frac{nRT}{p} = \frac{0.004663 \times 8.31 \times (32+273)}{101325} = 1.166 \times 10^{-4}\ m^3 = 117\ cm^3$;

(vi) Suggest why electrode **A** will decrease in mass over time. [1]

The oxygen gas produced from the electrolysis reacts with the carbon electrode to form carbon dioxide.

(b) Chromium(III) chloride, $CrCl_3$, reacts with water to form a violet complex, $[Cr(H_2O)_6]Cl_3$. This violet complex is isomeric to two other complexes as shown in Table 1.2.

Structural Formula of Complex	Colour of Complex
$[Cr(H_2O)_6]Cl_3$	violet
$[CrCl(H_2O)_5]Cl_2 \cdot H_2O$	pale green
$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$	dark green

Table 1.2

(i) Give one characteristic properties of transition elements as shown by chromium in the isomers in Table 1.2. [1]

Can form coloured compounds

[Turn over

(ii) Using $[Cr(H_2O)_6]Cl_3$, explain what is meant by the term *ligand*. [1]

H_2O is a molecule that has lone pairs of electrons on O atom, which can be used to form a dative bond with the central metal ion Cr^{3+}.

(iii) When 2.665 g of one of the complexes in Table 2 was reacted with an excess of aqueous $AgNO_3$, 2.868 g of $AgCl$ was obtained.

Deduce the structural formula of the complex. [2]

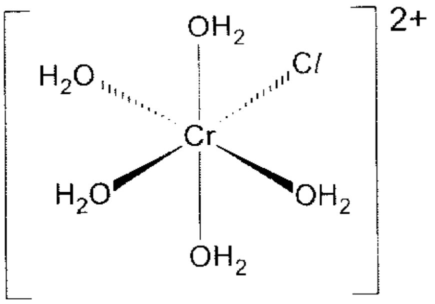
Amount of complex = $\frac{2.665}{52.0+18.0\times6+35.5\times3} = 0.0100\,mol$

Amount of $AgCl$ = $\frac{2.868}{(107.9+35.5)} = 0.0200\,mol$ **both amounts ;**

1 mole of complex contains 2 moles of free chloride ions

Structural formula = $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$;

(iv) Draw the full structure of the cation in the pale green complex, $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$, showing the shape of the cation. [1]



(c) Potassium dichromate(VI) can be produced from chromium(III) chloride via a 3-step reaction.

Step 1:	Chromium(III) chloride is boiled with hydrogen peroxide in an alkaline medium, forming a bright yellow solution, CrO_4^{2-}.
Step 2:	Boiling is continued until excess hydrogen peroxide is destroyed.
Step 3:	The yellow solution is then cooled and acidified with ethanoic acid, forming the orange dichromate(VI) solution.

(i) Write the ion-electron equation for the oxidation of Cr^{3+} in step **1** and hence the overall balanced equation for the reaction between Cr^{3+} and H_2O_2 under alkaline conditions. [2]

$Cr^{3+} + 8OH^- \rightarrow CrO_4^{2-} + 4H_2O + 3e^-$;

$2Cr^{3+} + 10OH^- + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 8H_2O$;

(ii) Suggest how would you know when all the excess hydrogen peroxide has been destroyed in step 2. [1]

No more effervescence

(iii) The reaction in step 3 has the following equation:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

State and explain if the reaction in step 3 is a redox reaction. [1]

No. The oxidation state of chromium remains the same at +6.

(iv) The reaction in step 3 is an exothermic reaction.
State and explain the effect of increasing the temperature of the system on the yield of $Cr_2O_7^{2-}(aq)$. [2]

When temperature is increased, position of equilibrium will shift left to remove the excess heat by favouring the endothermic reaction. ;
Yield of $Cr_2O_7^{2-}$ will decrease. ;

(d) A solution of sodium dichromate(VI) is acidified with dilute sulfuric acid before adding to an organic compound. The solution slowly turns green. Boiling the green solution with more of the organic compound produces a pale blue solution.
0.10 mol of the pale blue ions was found to require 0.020 mol of acidified potassium manganate(VII) solution to oxidise it back to the green ions.

(i) State the identity of the green ion. [1]

Cr^{3+} or $[Cr(H_2O)_6]^{3+}$

(ii) Deduce the oxidation number of the blue ion. [2]

$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$
$Cr^{n+} \rightarrow Cr^{3+} + (3-n)e$
Amount of electrons = 5 x 0.020 = 0.100 mol ;
Ratio of blue ion : e = 0.10 : 0.100 = 1:1
n = 3 – 1 = +2 ;

(iii) State, with a reason, which reagent, acidified H_2O_2 or aqueous Fe^{3+} could be used to convert the green ions back to dichromate(VI) ions. [1]

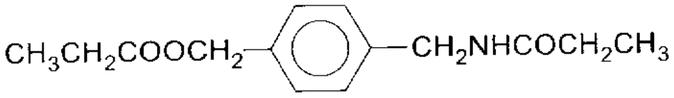
Acidified H_2O_2
Only $E^\circ(H_2O_2/H_2O)$ is more positive than $E^\circ(Cr_2O_7^{2-}/Cr^{3+})$ OR calculate E°_{cell}

[Total: 24]

[Turn over

2 (a) Compound **P**, C_8H_9NO, can react with Tollen's reagents but not with Fehling's solution. **P** is also soluble in dilute hydrochloric acid.

On reacting **P** with lithium aluminium hydride, **Q**, $C_8H_{11}NO$, is formed. **Q** reacts readily with sodium metal. 1 mole of **Q** reacts with 2 moles of propanoyl chloride to give the following compound.

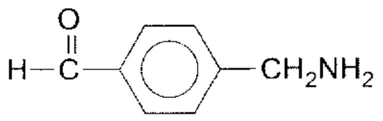


Q also reacts with hot acidified $KMnO_4$ to give **R**, $C_8H_6O_4$. 1 mole of **R** reacts with excess $Na_2CO_3(s)$ to give 1 mole of $CO_2(g)$.

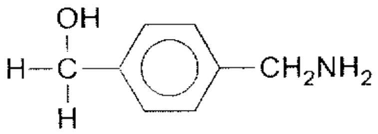
When **P** is heated with excess CH_3Br, a crystalline solid **S**, $C_{11}H_{16}NOBr$, is formed. **S** has very high melting point.

Deduce the structure of compounds **P**, **Q**, **R** and **S**, explaining the chemistry of the reactions described. [10]

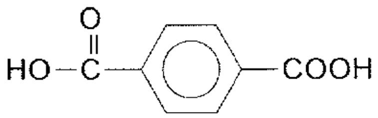
Information	**Deductions**
P, C_8H_9NO, can react with Tollen's reagents but not with Fehling's solution.	**P** is a benzaldehyde ; Oxidation reaction with Tollen's reagents ;
P is also soluble in dilute hydrochloric acid.	**P** has an alkaline amine group ; Acid-base reaction ;
On reacting **P** with lithium aluminium hydride, **Q**, $C_8H_{11}NO$, is formed.	Reduction reaction ; **Q** contains primary alcohol ;
Q reacts readily with sodium metal.	Acid-metal (or redox) reaction; **Q** contains –OH group ;
1 mole of **Q** reacts with 2 moles of propanoyl chloride to give the following compound.	Condensation reaction;
Q also reacts with hot acidified $KMnO_4$ to give **R**, $C_8H_6O_4$.	Side chain oxidation ;
1 mole of **R** reacts with excess $Na_2CO_3(s)$ to give 1 mole of $CO_2(g)$.	**R** contains 2 carboxylic acid group ; Acid-carbonate reaction ;
When **P** is heated with excess CH_3Br, a crystalline solid **S**, $C_{11}H_{16}NOBr$, is formed. **S** has very high melting point.	Nucleophilic substitution ; **S** has a giant ionic lattice structure ;



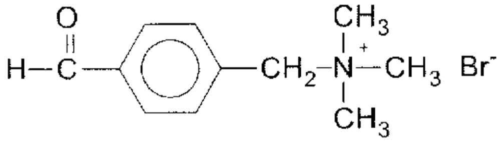
P



Q



R

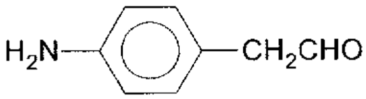


S

Each structure 1m ;;;;

Every 2 deductions 1m, capped at 6m ;;;;;;

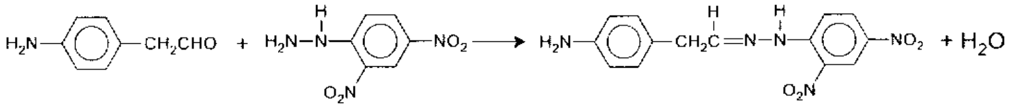
(b) **T** is an isomer of **P**.



T

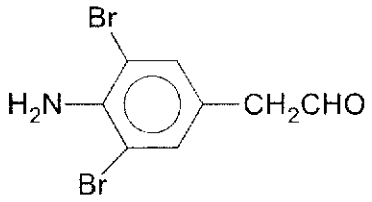
(i) State the type of reaction when **T** reacts with 2,4-dinitrophenylhydrazine. Write a balanced equation for the reaction. [2]

Condensation ;



;

(ii) Draw the structure of the organic product formed when **T** reacts with $Br_2(aq)$. [1]



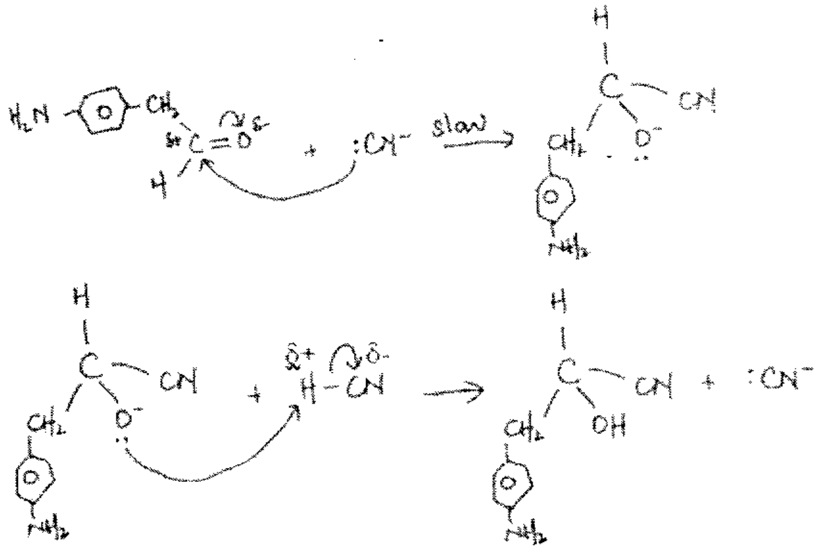
;

(iii) Outline the mechanism for the reaction of **T** with cold alkaline HCN. [3]

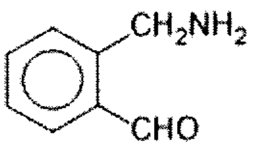
Nucleophilic Addition ;

$HCN \rightleftharpoons H^+ + CN^-$

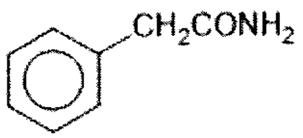
$NaOH + HCN \rightarrow NaCN + H_2O$



(c) Compounds **U** and **W** are constitutional isomers of **T**.



U



W

(i) Explain why **U** has a lower boiling point compared to **W**. [2]

U can form intramolecular hydrogen bond due to the proximity of the $-NH_2$ and the $-CHO$ groups hence its intermolecular forces of attraction is predominantly instantaneous dipole-induced dipole interactions or it forms less extensive intermolecular hydrogen bonds ;

Less energy is required to overcome the weaker id-id between **U** molecules than the stronger hydrogen bond between **W** molecules ;

(ii) State and explain the relative basicity of **U** and **W**. [2]

U is a stronger base than **W** ;

The lone pair on N of **W** is delocalised into the π electron cloud of the C=O bond causing it unavailable for protonation ;

[Total: 20]

[Turn over

3 This question involves sulfur and its compounds.

(a) **(i)** State the full electronic configuration of S^{3+}. [1]

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

(ii) Write an equation to represent the fourth ionisation energy of sulfur. [1]

$S^{3+}(g) \rightarrow S^{4+}(g) + e^-$;

(iii) The fourth ionisation energy of sulfur and phosphorus is 4540 kJ mol^{-1} and 4960 kJ mol^{-1} respectively.

Explain why the fourth ionisation energy of sulfur is lower than that of phosphorus. [2]

Less energy is required to remove an electron from the **3p orbital in S^{3+} than to remove an electron from the 3s orbital in P^{3+}** ; as the **3p electron is further away from the nucleus** and experiences **greater shielding** than 3s electron. ;

(iv) A sample of S contains 2 isotopes. In order to identify the mass of these two isotopes, they were first ionised to form singly-charged positive ions and passed through an electric field of constant strength. Their angles of deflection, along with a reference sample of helium nucleus, ${}^{4}_{2}\mathrm{He}$, were recorded in Table 3.1.

Species	**Angle of deflection**
Isotope **X**	1.60 °
Isotope **Y**	1.51 °
Helium nucleus, ${}^{4}_{2}\mathrm{He}$	25.6 °

Table 3.1

Calculate the relative mass of each isotope of sulfur, giving your answer to the nearest whole number. [3]

$25.6 = k\frac{2}{4}$

$k = 51.2$;

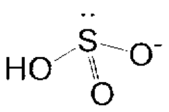
$1.60 = 51.2\left(\frac{1}{mass\ of\ X}\right)$

Mass of X = 32 ;

$1.51 = 51.2\left(\frac{1}{mass\ of\ Y}\right)$

Mass of Y = 34 ;

(b) Hydrogen sulfite ion, HSO_3^-, has the following structure:



Hydrogen sulfite ion reacts with carbonate ion according to the following equation:

$$2HSO_3^- + CO_3^{2-} \rightarrow 2SO_3^{2-} + H_2O + CO_2$$

(i) Define the term *Brønsted-Lowry acid.* [1]

Species which donate a proton ;

(ii) State which species in the reaction between hydrogen sulfite ion and carbonate ion acts as a Brønsted-Lowry acid. [1]

HSO_3^-

(iii) The carbon dioxide gas produced from the reaction is a non-ideal gas. Fig. 3.1 shows the experimental values of the compressibility factor (Z) plot for 1 mole of carbon dioxide gas at 298 K. (Z = pV/RT)

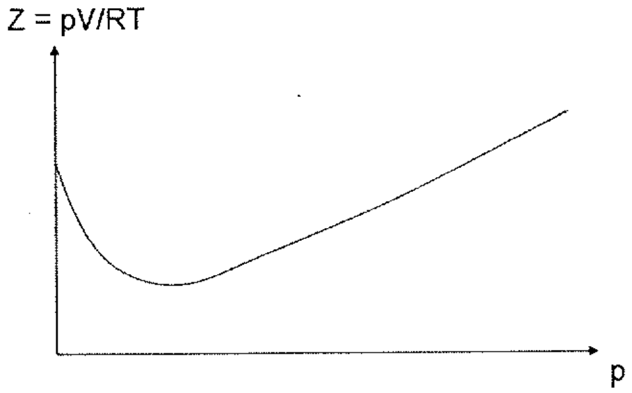


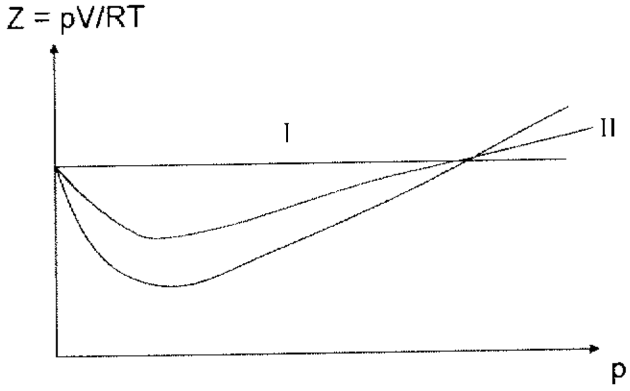
Fig. 3.1

On the plot given in Fig. 3.1, sketch the graph to illustrate the behavior of

I. 1 mole of an ideal gas at 298 K,
II. 1 mole of carbon dioxide gas at 398 K.

Label your answer clearly. [2]

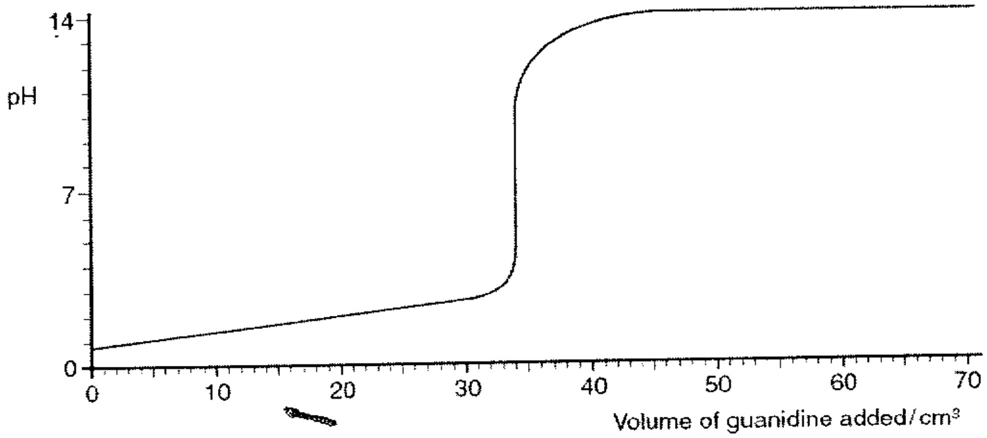
[Turn over



(c) Sulfuric acid reacts with guanidine, $(H_2N)_2CNH_2$, as follows:

$$H_2SO_4 + 2(H_2N)_2CNH \rightarrow SO_4^{2-} + 2(H_2N)_2CNH_2^+$$

When a 25.0 cm^3 sample of dilute sulfuric acid was titrated against a solution of guanidine, the following titration curve was obtained.



(i) Deduce if guanidine is a strong or a weak base. [1]

Guanidine is a strong base.

For the titration of H_2SO_4 (a strong acid) against guanidine, the pH of equivalence point is about 7. (also accept pH is approaching 14 when guanidine is in excess)

Will not accept no inflexion point, no buffer region.

(ii) The initial pH of the sulfuric acid is 0.61.

Calculate [H$^+$], and hence the initial concentration of sulfuric acid. [2]

$[H^+] = 10^{-0.61} = \mathbf{0.245\ mol\ dm^{-3}}$

$[H_2SO_4] = \mathbf{0.123\ mol\ dm^{-3}}$

(iii) Calculate the concentration, in mol dm^{-3}, of guanidine in the solution. [2]

Amount of guanidine = 2 × amount of H_2SO_4 = $2 \times \frac{25}{1000} \times 0.123 = 0.00614\,mol$;

[guanidine] = $\frac{0.00614}{\left(\frac{34}{1000}\right)} = 0.180\,mol\,dm^{-3}$;

Accept between 33.5 to 34.5 cm^3 as end point (same numerical answer)

[Total: 16]

Section B

Answer **one** question from this section.

4 In the stratosphere, there is an equilibrium established between O_2 and O_3:

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

When UV radiation from the sun breaks up O_3 into an oxygen atom and an oxygen molecule, the oxygen atom quickly recombines with an oxygen molecule to form back ozone. However, this equilibrium is disrupted by the radicals produced from the chlorofluorocarbons (CFCs) due to human activities.

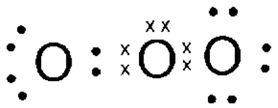
(a) One such CFC is CF_2Cl_2.

Write two equations to illustrate how CF_2Cl_2, in the presence of UV light, causes the decomposition of ozone layer. [2]

$CF_2Cl_2 \xrightarrow{UV} CF_2Cl\bullet + Cl\bullet$

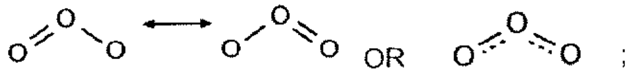
$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$

(b) The dot-and-cross diagram of O_3 is shown below.



With the aid of suitable diagram, explain why the two oxygen-oxygen bonds in the ozone molecule have the same bond strength. [2]

O_3 forms resonance structures as shown below. ;



(dative bonds acceptable)

Thus, the two oxygen-oxygen bonds are equivalent in length and strength

(c) One method to determine the concentration of the ozone layer is to pass air through acidified potassium iodide and to measure the amount of iodine liberated. The following reaction takes place:

$$O_3 + 2H^+ + 2I^- \rightarrow O_2 + H_2O + I_2$$

The concentration of iodine liberated, in mol dm^{-3}, is measured using platinum / iodine electrode against standard silver / silver chloride reference electrode. The E_{cell} of the system, in volts, is given by the following equation:

$$E_{cell} = 0.32 + 0.029 \log_{10}[I_2]$$

To determine concentration of ozone in the atmosphere, a balloon was used to carry a sampling device. A 1.00 m^3 sample of air, measured at 25 °C and 0.24 atm was passed through 10 cm^3 of acidified potassium iodide. The E_{cell} of the platinum electrode dipping into the solution against the standard silver / silver chloride electrode was 0.21 V.

(i) Calculate the amount of ozone present in the sample. [3]

$0.21 = 0.32 + 0.029 \log_{10}[I_2]$

$[I_2] = 0.0001610 \text{ mol dm}^{-3}$;

amount of $I_2 = 0.0001610 \times 0.0100 = 1.61 \times 10^{-6}$ mol ;

Amount of $O_3 = 1.61 \times 10^{-6}$ mol ;

(ii) Hence calculate the volume of O_3 present in the 1.00 m^3 sample of air. [2]

pV = nRT

$$V = \frac{nRT}{p} = \frac{1.61\times10^{-6}\times8.31\times(25+273)}{0.24\times101325} = 1.64 \times 10^{-7} m^3 = 0.164\, cm^3$$

Correct conversion of units;

Correct substitution of values using ideal gas equation ;

(iii) The actual volume of O_3 present in the 1.00 m^3 sample of air would be less than the calculated value in **(c)(ii)**. Suggest a reason for this discrepancy. [1]

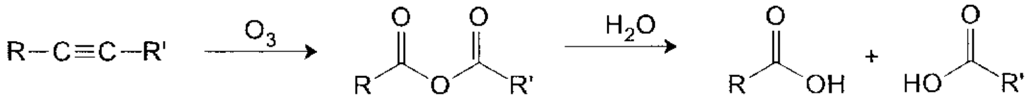
O_3 has significant intermolecular forces of attraction, which causes the molecule to be closer together, hence the volume decreases. ;

(iv) Explain why O_2 is a gas but I_2 is a solid at room temperature. [2]

Both are simple molecular structures ;

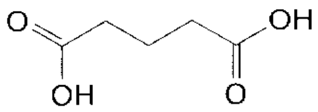
However I_2 has stronger instantaneous dipole-induced dipole interactions due to its larger electron cloud size ; hence requiring more energy to overcome its IMF.

(d) Ozone reacts with alkynes to form carboxylic acids in a two-step reaction as shown below.



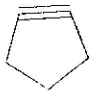
When alkyne **E** undergoes the same two-step reaction, only compound **F** is formed.

[Turn over



F

Suggest the structure of **E**. [1]



(e) Nitrogen monoxide in the air can be converted to nitric acid, which results in acid rain. Both nitrogen monoxide and nitrogen dioxide also cause ozone layer depletion. One way of forming nitrogen monoxide is through the dissociation of nitrogen dioxide.

$$2NO_2\,(g) \rightleftharpoons 2NO\,(g) + O_2\,(g) \qquad \Delta H = +114.2 \text{ kJ mol}^{-1}$$

At 494 °C, the value of K_p for the above reaction is 36.9 kPa.

When a certain partial pressure of nitrogen dioxide is put into an empty vessel at 494 °C, equilibrium is reached when 40% of the original nitrogen dioxide has dissociated.

(i) Write an expression for the equilibrium constant, K_p, for the reaction. [1]

$K_p = \frac{p_{NO}{}^2 p_{O_2}}{p_{NO_2}{}^2}$;

(ii) Calculate the initial partial pressure of nitrogen dioxide before any dissociation occurred. [2]

Let the initial pressure of NO_2 be ***x*** mol.

	$2\,NO_2\,(g) \rightleftharpoons$	$2\,NO\,(g)\;+$	$O_2\,(g)$
Initial pressure (kPa)	***x***	0	0
Change in Pressure	-0.40***x***	+0.40***x***	+0.20***x***
Equilibrium pressure (kPa)	0.60***x***	0.40***x***	0.20***x***

$$K_p = \frac{(0.40x)^2(0.20x)}{(0.60x)^2} = 36.9 \quad ;$$

x = 415 kPa

Hence, initial pressure of NO_2 = 415 kPa ;

(iii) Given that the standard enthalpy change of formation of NO(g) is +90.3 kJ mol^{-1}, determine the standard enthalpy change of formation of NO_2(g). [2]

$\Delta H = \Delta H_f$ (products) – ΔH_f (reactants)

$114.2 = 2(90.3) + 0 - (2 \times \Delta H_f\, NO_2)$;

$\Delta H_f\, NO_2 = +33.2$ kJ mol^{-1} ;

(iv) With reference to the equation given in **(e)**, state and explain the sign of entropy change, ΔS, for the dissociation of $NO_2(g)$. [1]

ΔS is positive since there is an increase in disorderliness due to increase in amount of gas particles. ;

(v) Using your answer in **(e)(iv)**, state whether the reaction would be spontaneous at high or low temperatures. [1]

[Total: 20]

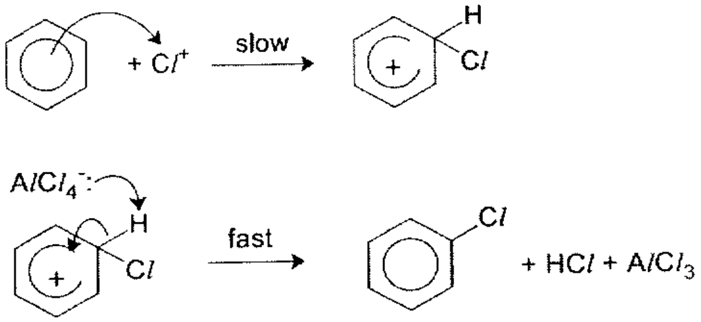
High temperature ;

5 **(a)** Aluminium chloride is used in the production of chlorobenzene from the reaction between benzene and chlorine.

(i) Outline the mechanism for the reaction above. [3]

Electrophilic substitution ;

$AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$



(ii) Explain, with the aid of relevant equations, why the aluminium chloride used in the above reaction must be anhydrous. [2]

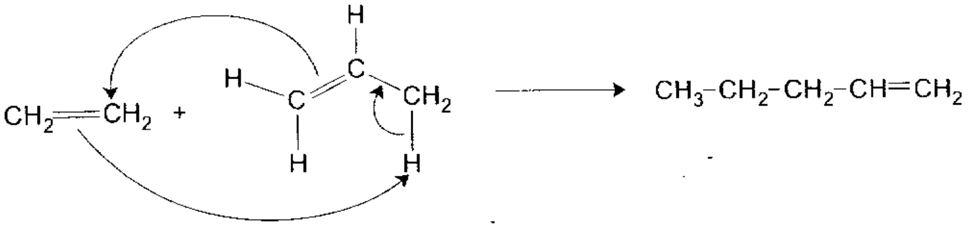
In the presence of water, Al^{3+}, having a high charge density is able to hydrolyse in water, causing $AlCl_3$ unable to act as a halogen carrier. ;

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

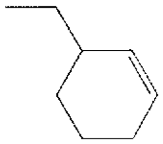
$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$;

(iii) Aluminium chloride can also act as a catalyst for the Alder-ene reaction.

One example of Alder-ene reaction is illustrated below using propene and ethene.



Suggest the structure of the organic product formed when cyclohexene reacts with ethene in an Alder-ene reaction. [1]



(b) Aluminium chloride reacts with CH_3NH_2 to form an adduct $AlCl_3{\cdot}CH_3NH_2$.
Explain how this adduct is formed. [2]

Al in $AlCl_3$ is electron-deficient and is able to accept the lone pair on N of CH_3NH_2, ;
forming a dative bond. ;

(c) Describe the reaction, if any, of aluminium oxide with water, and sodium oxide with water. Write equations, with state symbols, where appropriate and predict the pH of the resultant solution. [3]

Aluminium oxide cannot dissolve in water;

Sodium oxide dissolves in water to form an alkaline solution of pH 13 ;

$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$;

(d) 100 cm^3 of 0.100 mol dm^{-3} of aqueous magnesium nitrate was mixed with 100 cm^3 of aqueous sodium hydroxide and the reaction mixture was filtered. Solid magnesium hydroxide was collected as residue, and the filtrate contained a saturated solution of magnesium hydroxide, $Mg(OH)_2$, at 298 K and pH 9.5.

$$Mg(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Mg(OH)_2(s) + 2NaNO_3(aq)$$

The value of K_{sp} of magnesium hydroxide is 1.5×10^{-11}.

(i) Write an expression for the K_{sp} of magnesium hydroxide, stating its units. [2]

$K_{sp} = [Mg^{2+}][OH^-]^2$;

$mol^3\ dm^{-9}$;

(ii) Calculate the concentration of hydroxide ions that remained in the **filtrate**. [2]

$pOH = pK_w - pH = 14 - 9.5 = 4.5$

$[OH^-] = 10^{-pOH} = 10^{-4.5} = 0.0000316\ mol\ dm^{-3}$

(iii) Calculate the concentration of magnesium ions that remained in the **filtrate**. [1]

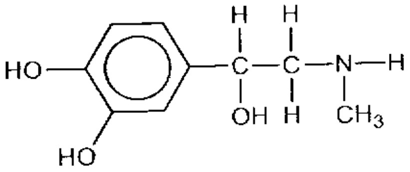
$[Mg^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.5\times10^{-11}}{(0.0000316)^2} = 0.0150\ mol\ dm^{-3}$;

(iv) Hence, calculate the mass of solid magnesium hydroxide formed. [2]

Amount of Mg^{2+} in solid = $(0.100 \times \frac{100}{1000}) - (0.0150 \times \frac{200}{1000}) = 7.00 \times 10^{-3}$ mol ;

Mass of $Mg(OH)_2$ formed = $7.00 \times 10^{-3} \times [24.3+2(1.0 + 16.0)] = 0.408$ g ;

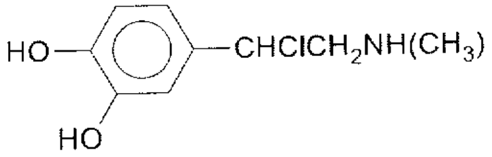
(e) The structure of compound **L** is shown below.



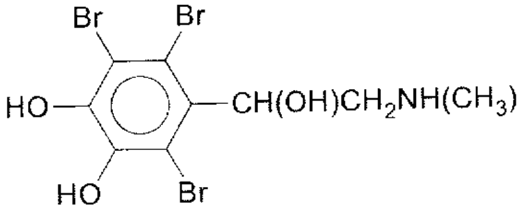
Compound **L**

Draw the structure of the organic product formed when compound **L** reacts with the following reagents.

(i) $SOCl_2$ [1]



(ii) Bromine water [1]



[Total: 20]