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

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]

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

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

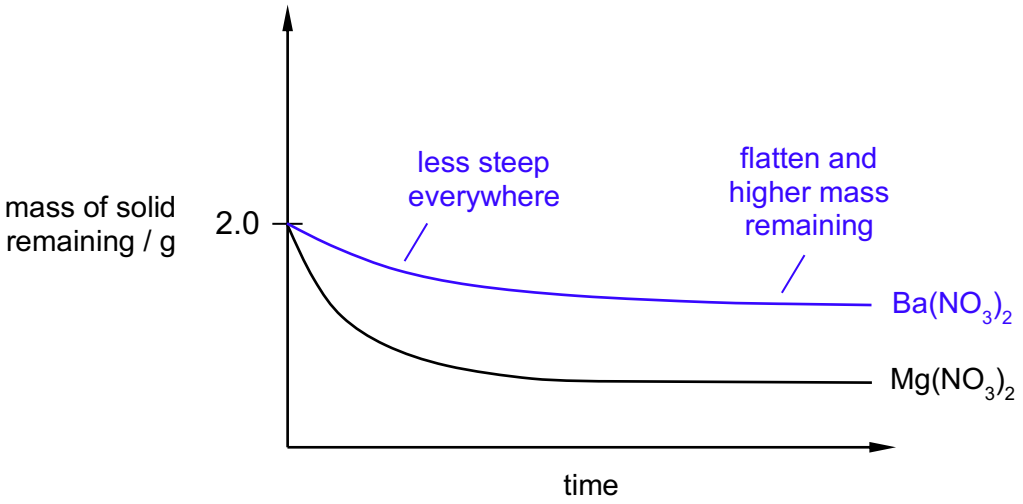
[2]

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]

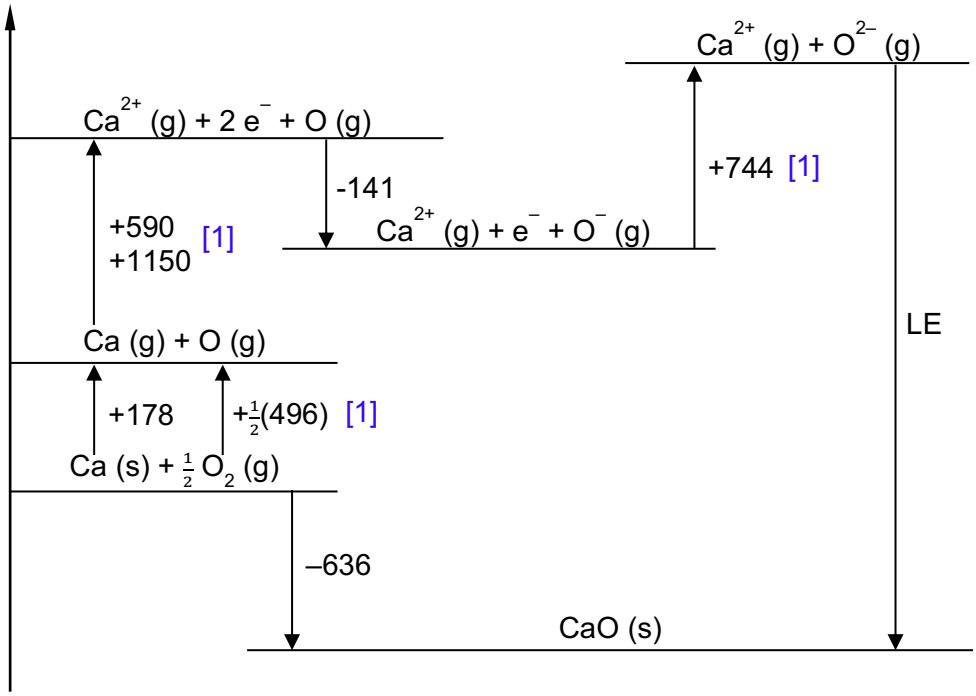
(c) One of the products of the decomposition of Group 2 nitrates is the metal oxide.

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 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]



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

LE(CaO) = **–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]

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

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

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

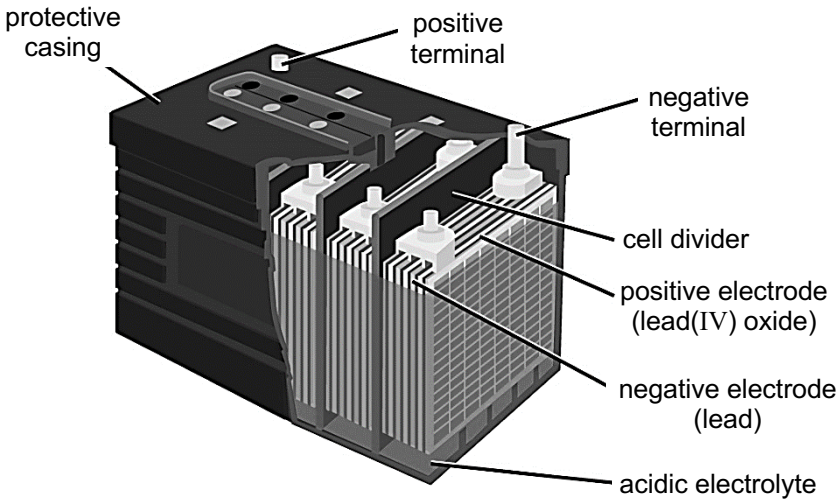
[Total: 13]

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: $PbO_2 + 4\ H^+ + 2\ e^- \longrightarrow Pb^{2+} + 2\ H_2O$ +1.47 ;
anode: $Pb \longrightarrow Pb^{2+} + 2\ e^-$ +0.13 ;
$E_{cell}^{\ominus} = +1.47 + 0.13 =$ **+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
η_{PbO_2} = $\frac{9300\ g}{239.2\ g/mol}$ = 38.8796 mol
since $\frac{\eta_{e^-}}{\eta_{PbO_2}} = \frac{2}{1}$, η_{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 = $k[H_2O_2]$

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

$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{1.44 \times 10^{-5}\ s^{-1}} =$ **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]

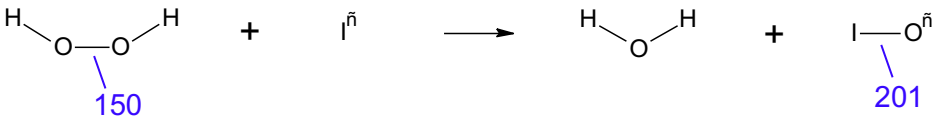
step 1: $H_2O_2 + I^- \longrightarrow H_2O + IO^-$

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]



ΔH_1 = 150 – 201 = **–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

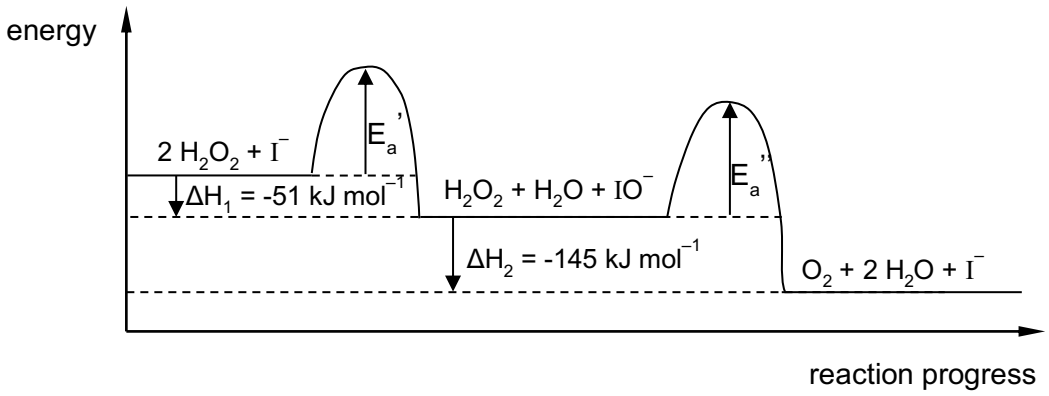
bond energy values are only averages

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]

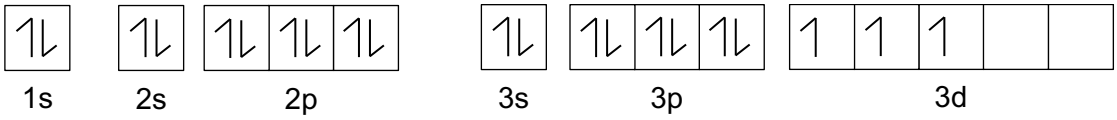


intermediate products and final products [1]
two activation energies with labels [1]
two enthalpy changes with labels [1]

(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]



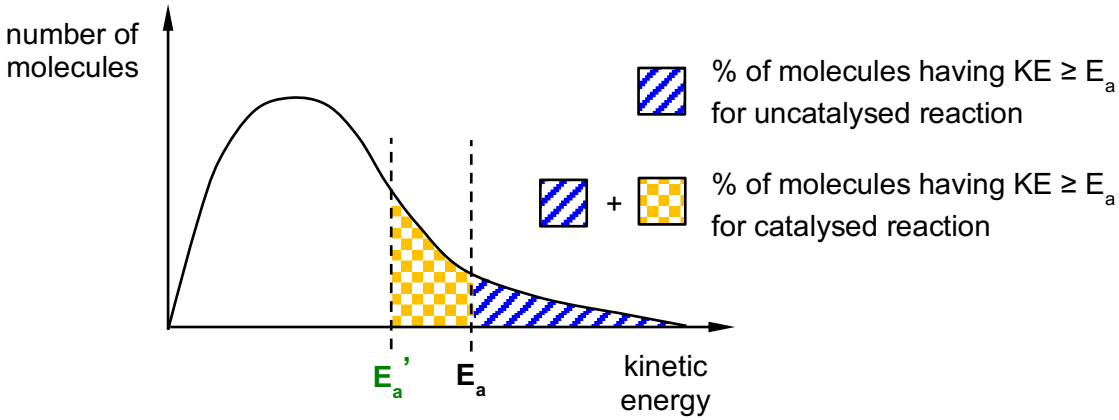
(ii) With reference to the configuration in **(i)**, explain how manganese(IV) oxide allows hydrogen peroxide molecules to interact with it.

[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

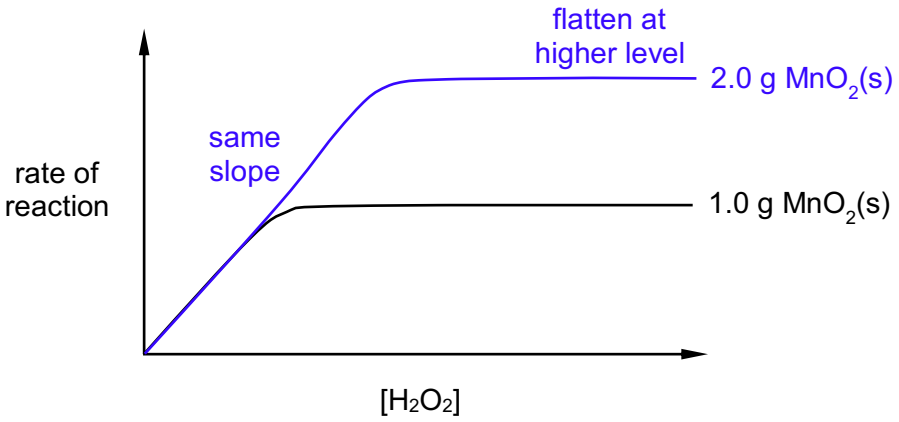
[1]
- label zone for % of molecules having KE ≥ E_a for uncatalysed reaction
- label additional zone for % of molecules having KE ≥ E_a for catalysed reaction

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.



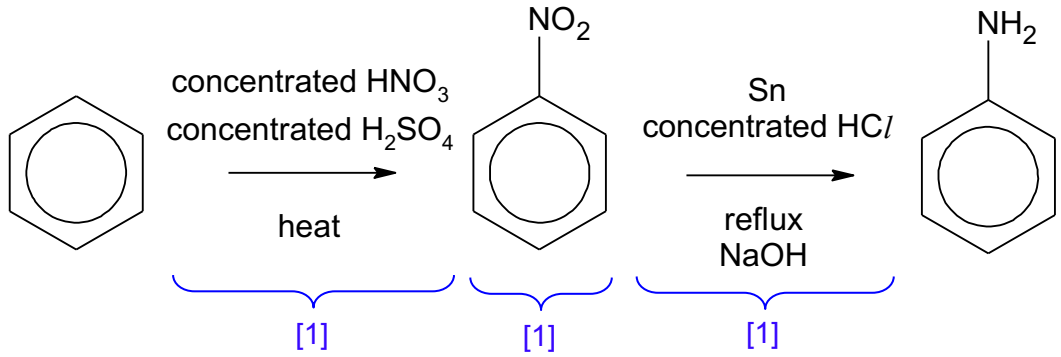
[1]

[Total: 18]

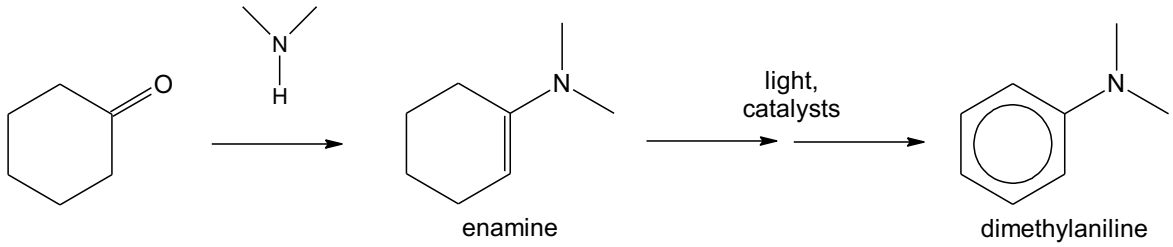
4 Aniline is conventionally synthesised with benzene as the starting organic material.

(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 ;
$CH_3Br + CH_3NH_2 \longrightarrow (CH_3)_2NH + HBr$;

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

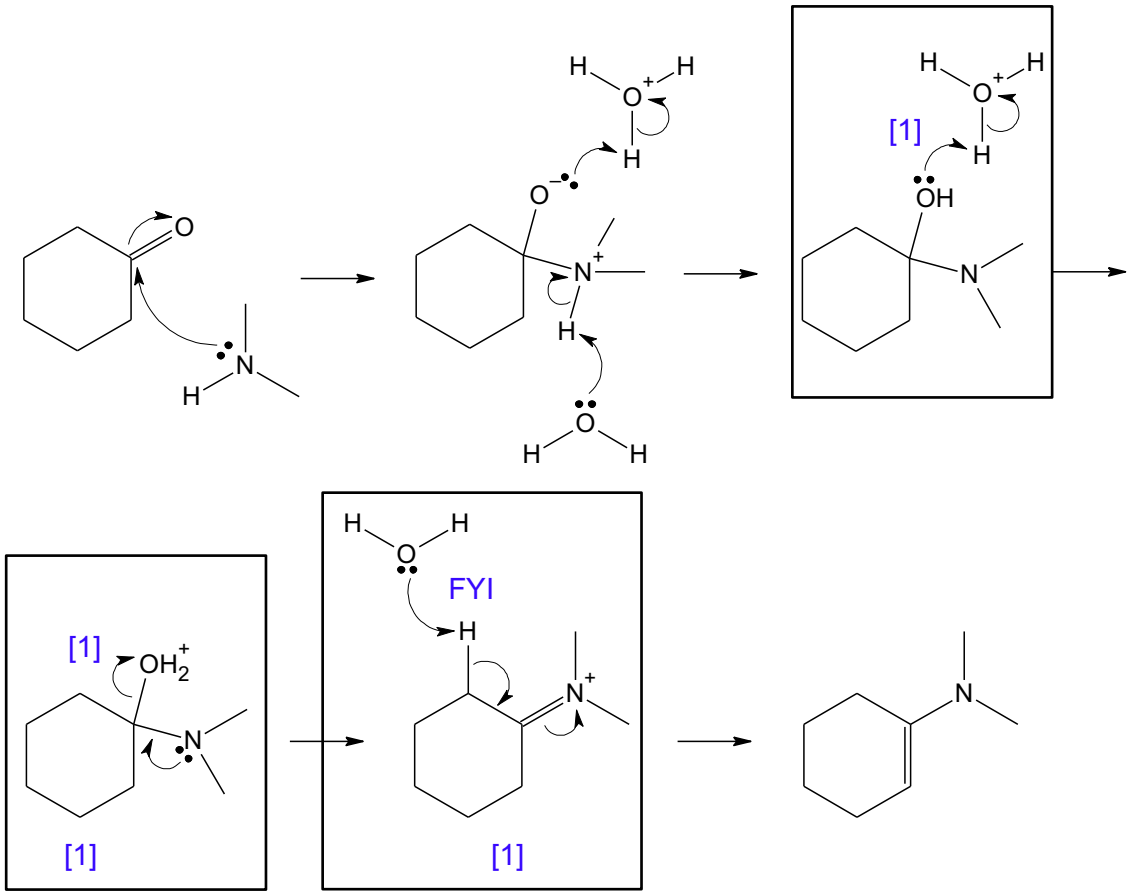
Enamines contain a carbon-carbon double bond (C=C) next to a nitrogen atom.

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]

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]

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.

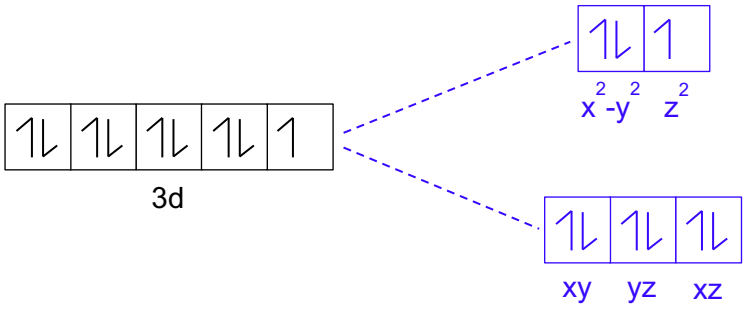
Electrons absorb the incoming light energy to promote to a higher energy level orbital.

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]

Water molecules approach the Cu^{2+} ion along the x, y and z axes, repelling the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals more, increasing their energy, ;

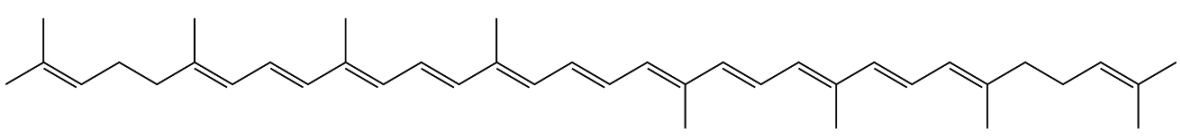
while repelling the $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals less, decreasing their energy. ;

(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]

$\boldsymbol{M}$ = 6
$\boldsymbol{n}$ = 11 ;

λ_{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.

Fig 6.1

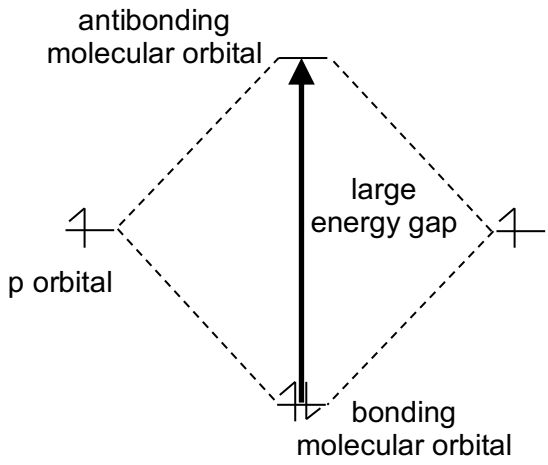
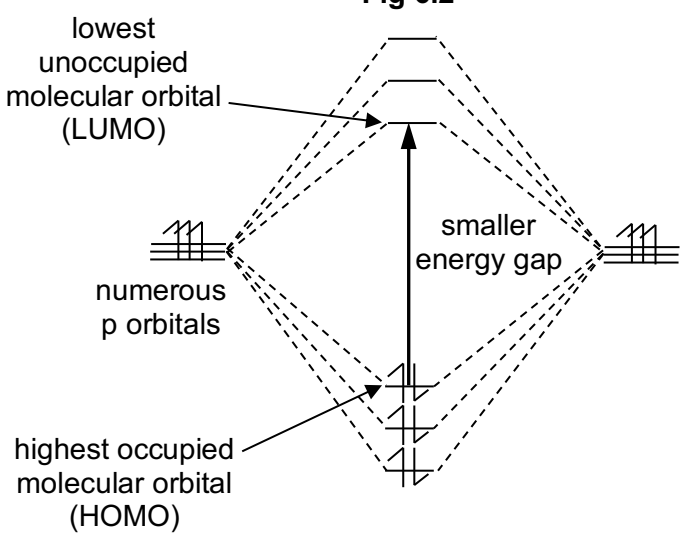


Fig 6.2



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]

MO energies split and energy gap / LUMO-HOMO gap decreases. ;

Electrons are delocalised over the π orbitals / MO / larger volume, decreasing inter-electronic repulsion. ;

(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.

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

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

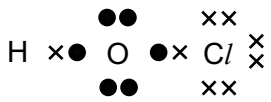
[2]

Cl_2 was oxidised to HClO as the oxidation state of Cl increased from 0 (in Cl_2) to +1 (in HClO) ;

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

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

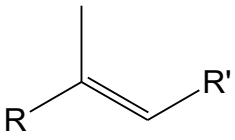
[1]



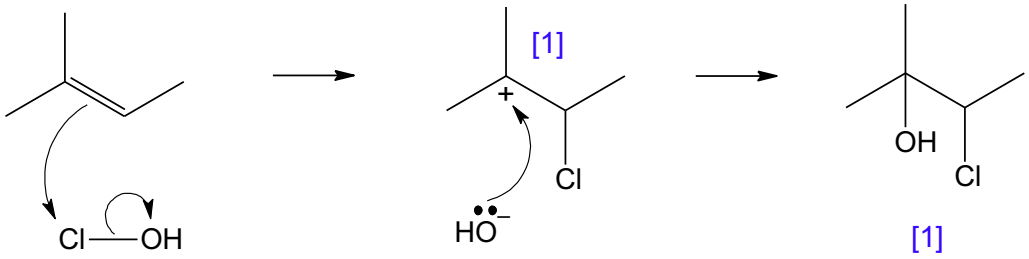
(vi) Bleach molecules react with C=C double bonds.

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.

[2]

Bleach attacks C=C bond by electrophilic addition, converting it into C–C bond / saturating the bond, ;

This results in the loss of conjugation / p or π orbital overlap, causing the energy gap to increase. Wavelength absorbed decreases to outside of the visible region and no colour is observed. ;

[Total: 15]

END OF PAPER