H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME								
CLASS	1	9			TUTOR'S NAME			
CENTRE NUMBER	S					INDEX NUMBER		

CHEMISTRY

9729/02

Paper 2 Structured

31 August 2020

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/25
2	/10
3	/14
4	/11
5	/15
Total	/75

This document consists of **23** printed pages and **1** blank page.

[Turn over

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

1 Heavy metals can leach into water from taps inside older buildings due to the stagnation of water in tanks and water pipes inside the buildings.

A study of the tap water from a building showed that it contained small amounts of lead(II) ions, when consumed past a certain limit, have toxicological effects on human beings.

World Health Organisation (WHO) issues guidelines on the limits of various heavy metal ions in drinkable water. The WHO limit for lead(II) ions concentration is 5.0×10^{-8} mol dm^{-3}.

An environment agency wants to determine if the tap water from the building is within the WHO limits. Through a precipitation titration, the concentration of Pb^{2+} in the water sample can be determined.

You may find the following information useful:

- A titration was conducted where 1.00 dm^3 of sample water was titrated against aqueous sodium hydroxide.
- 1.00×10^{-5} mol of iron(II) nitrate was used as the indicator.
- At the end-point, the solid was filtered and the mass of lead(II) hydroxide precipitate was found to be 1.20×10^{-5} g.
- The water sample only contains lead ions as contaminants.

Precipitate	M_r	Colour of precipitate	value of K_{sp}	solubility / mol dm^{-3}
$Pb(OH)_2$	241.2	white	1.4×10^{-20}	**X**
$Fe(OH)_2$	89.8	green	4.9×10^{-17}	2.30×10^{-6}

(a) **(i)** Explain the term *solubility*.

The solubility of a salt refers to the maximum amount or mass that can dissolve in 1 dm^3 of solvent at a given temperature to form a saturated solution. [1]

.....

..... [1]

(ii) Determine the solubility of lead(II) hydroxide, **X** in mol dm^{-3}.

$Pb(OH)_2$ (s) $\rightleftharpoons$ Pb^{2+}(aq) + $2OH^-$(aq)
$(X)(2X)^2 = 1.4 \times 10^{-20}$
X = solubility of lead hydroxide $= 1.518 \times 10^{-7}$ mol dm^{-3}
$= 1.52 \times 10^{-7}$ mol dm^{-3} [1]

[1]

(iii) Using the data given, state what you would observe

at the beginning of the titration white ppt [1] .....

at the end-point of the titration green ppt [1] ..... [2]

(iv) Determine the amount of lead(II) hydroxide precipitated from the water sample.

$$n(Pb^{2+}) = \frac{\mathbf{1.20 \times 10^{-5}}}{\mathbf{241.2}} = 4.98 \times 10^{-8} \text{ mol}$$

[1]

(v) Determine the maximum concentration of Pb^{2+} left in the mixture at the end-point.

At the end-point, 1st trace of $Fe(OH)_2$, (Ionic product = K_{sp})
where $[Fe^{2+}] = 0.00001$ mol dm^{-3}

$$[OH^-] = \sqrt{\frac{\mathbf{4.9 \times 10^{-17}}}{\mathbf{0.00001}}} = 2.213 \times 10^{-6} \text{ mol dm}^{-3} \quad [1]$$

$$[Pb^{2+}] = \frac{\mathbf{1.4 \times 10^{-20}}}{(\mathbf{2.213 \times 10^{-6}})^2} = 2.857 \times 10^{-9} \text{ mol dm}^{-3}$$

$$= 2.86 \times 10^{-9} \text{ mol dm}^{-3} \quad [1]$$

[2]

(vi) Hence, using your answers in **(iv)** and **(v)**, determine the initial concentration of Pb^{2+} in the water sample and deduce if the concentration is within the WHO limit.

Initial $n(Pb^{2+}) = 4.975 \times 10^{-8} + (\mathbf{2.857 \times 10^{-9} \times 1.00})$

$= 5.260 \times 10^{-8}$ mol

Initial $[Pb^{2+}] = \dfrac{\mathbf{5.260 \times 10^{-8}}}{\mathbf{1\ dm^3}} = 5.26 \times 10^{-8}$ mol dm^{-3} [1]

($> 5.0 \times 10^{-8}$ mol dm^{-3})

The lead concentration is over the limit. [1]

[2]

(vii) To deduce whether Fe^{2+} is a good indicator in this titration, most of the lead(II) ions needs to be precipitated at the end-point.

Show that more than 90% of the lead(II) ions in the water sample has been precipitated when the end-point was reached.

At first trace of $Fe(OH)_2$, most of the Pb^{2+} has precipitated.

$$\%n(Pb^{2+}) \text{ ppted} = \frac{\mathbf{5.260 \times 10^{-8} - 2.857 \times 10^{-9}}}{\mathbf{5.260 \times 10^{-8}}} \times \mathbf{100}\% = \mathbf{94.6}\% \quad [1]$$

OR

Only a small amount of Pb^{2+} remained in solution.

$$\%n(Pb^{2+}) \text{ left in solution} = \frac{\mathbf{2.857 \times 10^{-9}}}{\mathbf{5.260 \times 10^{-8}}} \times \mathbf{100}\% = \mathbf{5.430}\%$$

$\%n(Pb^{2+})$ ppted = 100% - 5.430% = 94.6%

[1]

(viii) Suggest another reason why Fe^{2+} ions are a good indicator for this titration.

The colour change from white to green is distinct. [1]

.....

.....[1]

(ix) When excess sodium hydroxide was added after the end-point, it was observed that the white precipitate dissolved.
With the aid of relevant equations, explain the observations.

- $Pb(OH)_2$ (s) ⇌ Pb^{2+}(aq) + $2OH^-$(aq) ---------- (1)
- $Pb(OH)_2$ (s) + $2OH^-$(aq) ⇌ $[Pb(OH)_4]^{2-}$(aq) ---------- (2)
- When excess OH^- is added, Pb^{2+} reacts to form a soluble complex formed.
- As $[Pb^{2+}]$ decreases, Ionic product of $Pb(OH)_2$ < K_{sp}
- POE (1) shifts to the right.

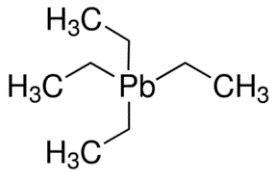
Hence, ppt dissolves.

[2] – 5 points
[1] – 2-4 points

.....

..... [2]

(b) Tetraethyl lead (TEL), an organometallic compound was the main anti-knock agent used in cars in the past. It is a dense, viscous (slow-flowing) liquid which is highly lipophilic - soluble in non-polar solvents such as petrol and hexane.



Tetraethyl lead (TEL)

(i) With reference to the structure and bonding of TEL, suggest a reason for its viscosity.

- TEL has a simple molecular structure with instantaneous dipole-induced dipole forces between TEL molecules.
- TEL has a large number of electrons per molecule OR large electron cloud therefore more easily polarised.
- Hence, significant instantaneous dipole-induced dipole forces between TEL molecules leading to packing more molecules in a given volume/ more energy is required to break the id-id forces between the molecules.

3 pts – [2]
1-2 pts – [1]

.....

.....

.....

..... [2]

(ii) TEL was synthesised industrially by heating a mixture of chloroethane on a powdered metal alloy of lead and sodium atoms according to the following equation.

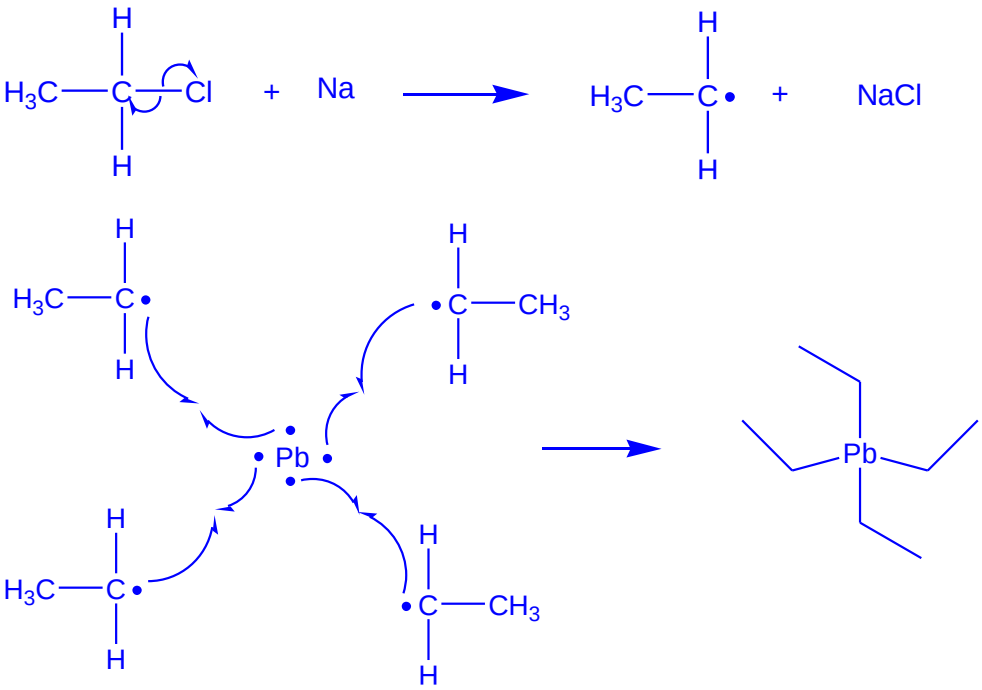
$$4Na + Pb + 4CH_3CH_2Cl \rightarrow (CH_3CH_2)_4Pb + 4NaCl$$

The hypothetical 2-step mechanism involves:

Step 1: Homolytic cleavage of the carbon-chlorine bond in chloroethane to form an ethyl radical. Chlorine radical immediately reacts with sodium atom to form sodium chloride.

Step 2: Four ethyl radicals react with a lead atom from the alloy to form a TEL molecule.

Use the information given above to suggest a simple mechanism for the formation of a TEL molecule, showing clearly the movement of electrons by curly arrows.



- two steps
- curly arrows for homolytic cleavage of C-Cl bond to form ethyl radical
- four electrons around lead atom
- curly arrows clearly shown to form each C-Pb bond

4 points – [2], 2-3 points – [1]

[2]

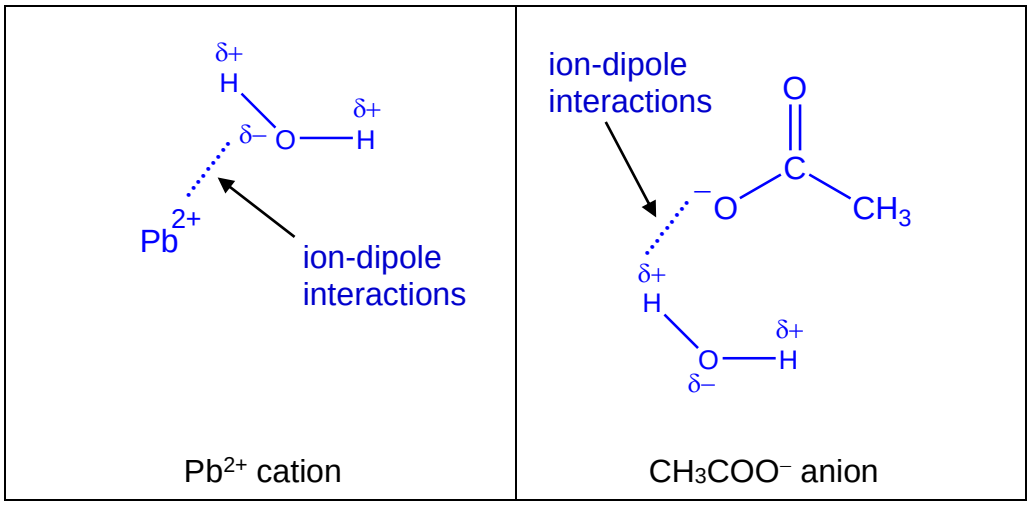
(iii) Deduce the rate determining step.

Step 1. The carbon-chlorine covalent bond requires a higher amount of activation energy to break. [1]
Do not accept: Step 2 is fast due to free radicals being more reactive.

.....[1]

(c) Lead(II) ethanoate, $Pb(CH_3COO)_2$, also known as *sugar of lead* is a white crystalline solid which is soluble in water and has a sweet taste. Ancient Romans used sweeteners that contained lead(II) ethanoate to sweeten wine or preserve fruit. Lead(II) ethanoate is no longer used in the production of sweeteners because of its recognised toxicity.

Draw simple diagrams to show how a water molecule can be attached to a lead(II) cation, and to an ethanoate anion. Label each diagram to show the type of interaction involved.



[3]

- structure of ethanoate ion shown
- correct label
- interaction between correct atoms
- dipoles shown

4 pts - [3], 3 pts – [2], 2 pts – [1]

(d) Lead(II) carbonate thermally decomposes according to the equation.

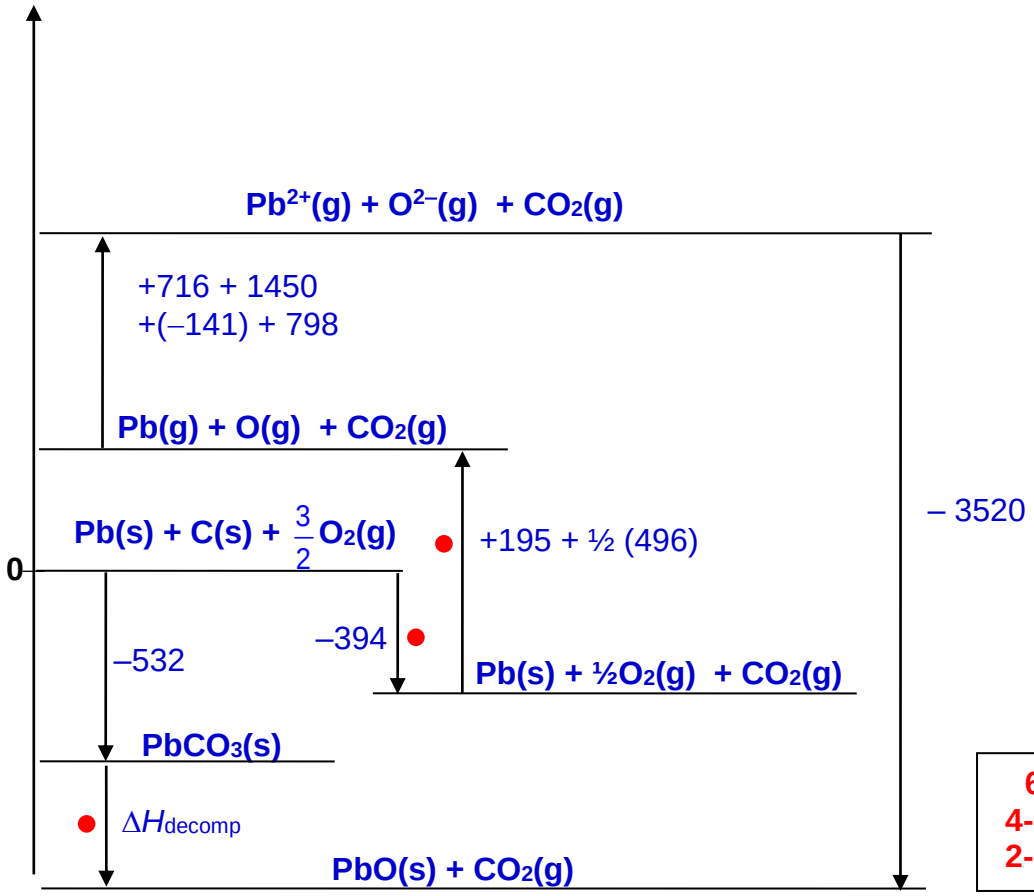
$$PbCO_3(s) \rightarrow PbO(s) + CO_2(g) \qquad \Delta H_{decomp} < 0$$

Some enthalpy changes are listed below.

Enthalpy change of formation of $PbCO_3(s)$	=	–532 kJ mol^{-1}
Enthalpy change of atomisation of lead	=	+195 kJ mol^{-1}
Enthalpy change of combustion of carbon	=	–394 kJ mol^{-1}
Lattice energy of lead(II) oxide	=	–3520 kJ mol^{-1}
First electron affinity of oxygen	=	–141 kJ mol^{-1}
Second electron affinity of oxygen	=	+798 kJ mol^{-1}

By using data in this question and relevant data in the *Data Booklet*, construct a fully-labelled energy level diagram to determine the enthalpy change of decomposition of lead(II) carbonate.

Energy / kJ mol^{-1}



6 pts – [3]
4-5 pts – [2]
2-3 pts – [1]

$\Delta H_{decomp} = -(-532) - 394 + 195 + ½ (496) + 716 + 1450 - 141 + 798 - 3520$

$= -116$ kJ mol^{-1}

[4]

[Total: 25]

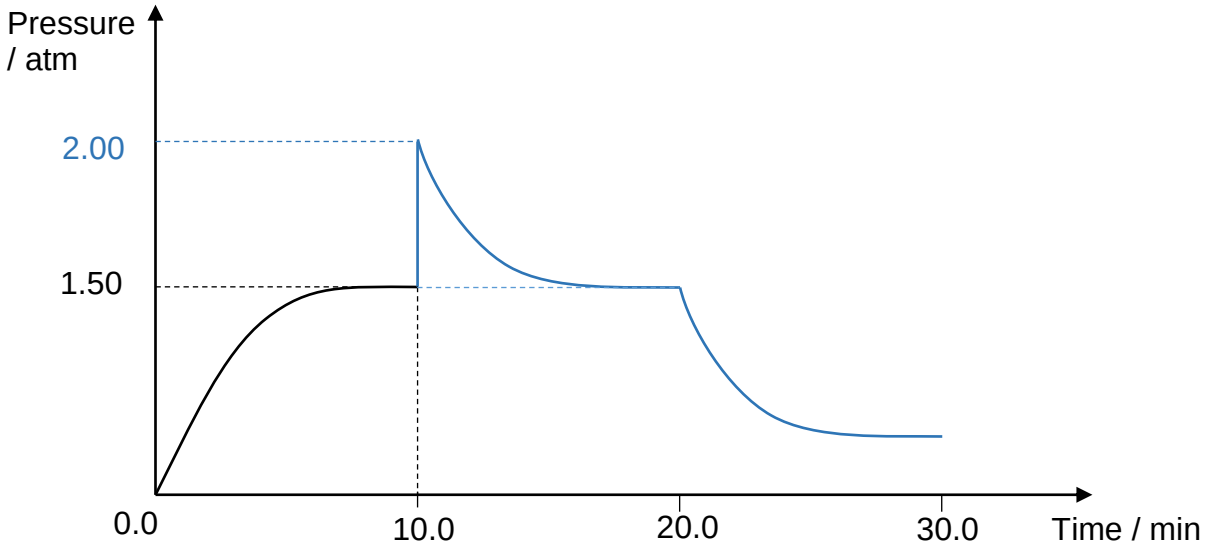
Question 2 starts on the next page.

For Examiner's Use

2 When heated in a 5.0 dm^3 closed vessel at 450 °C, a 50.0 g sample of calcium carbonate decomposes according to the following equation:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad \Delta H > 0$$

The pressure changes in the vessel are shown in the following graph:



(a) Calculate the K_c of the reaction at 450 °C.

$K_c = [CO_2]$

$pV = nRT$

$$n(CO_2) = \frac{1.50 \times 101325 \times 5 \times 10^{-3}}{8.31 \times (450 + 273)}$$

$$= 0.1264 \text{ mol}$$

$$K_c = [CO_2]$$

$$= \frac{0.1264}{5.0}$$

$$= 0.0253 \text{ mol dm}^{-3}$$

1 mark for $n(CO_2)$
1 mark for K_c

[2]

(b) Calculate the percentage change in mass of solid at 10.0 min after equilibrium was reached.

$$\% \text{ change in mass of solid} = \% \text{ loss in mass} = \frac{0.1264 \times 44.0}{50.0} \times 100 = 11.0\%$$

[1]

(c) At time = 10.0 min, the pressure of CO_2 was increased to 2.00 atm. Equilibrium was achieved again at 20.0 min at the same temperature.

Sketch and label the pressure changes that occurred from 10.0 min to 20.0 min. [1]

(d) At time = 20.0 min, the temperature was decreased to 200 °C. A new equilibrium was achieved at 30.0 min.

Sketch the pressure changes that occurred from 20.0 min to 30 min. Explain your answer below.

1 mark for graph

By Le Chatelier's principle, when temperature was decreased,

- the position of equilibrium shifts left to
- compensate the reduced heat,
- hence favouring the backward exothermic reaction. Hence pressure of CO_2 decreases. [2 pts 1 mark, 3 pts 2 marks]

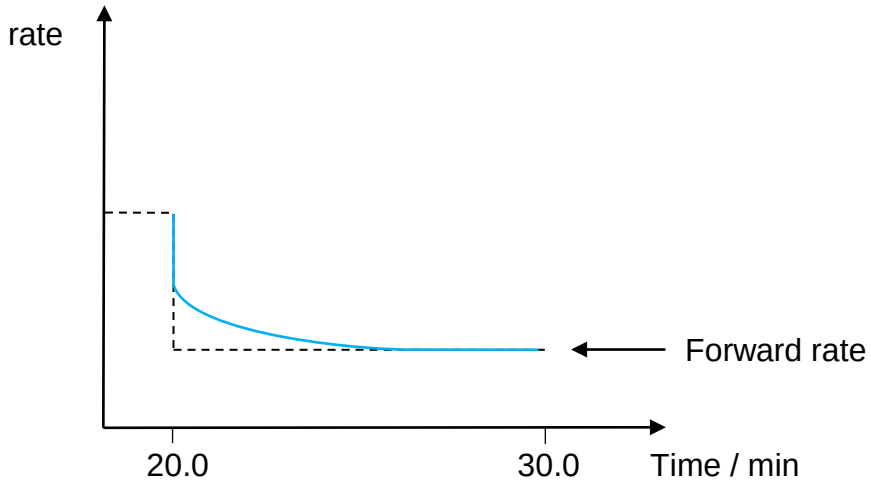
.....[3]

(e) When dynamic equilibrium is reached, the forward rate will be equal to the backward rate.

The graph below shows the change in **forward rate** (shown by dotted line - - - - -) of the decomposition reaction when temperature was decreased at 20.0 min.

Sketch the change in the backward rate of the reaction from 20.0 min to 30.0 min. Use a smooth line (——) to represent the backward rate on the graph.

Explain your answer below.



- When temperature decreased, both the forward and backward rates dropped instantly, but dropped less for the backward exothermic reaction. (since exothermic reactions are favoured by temperature decrease)
- As position of equilibrium shifts left, product concentrations decrease, and the backward rate decreases until it becomes equal to the forward rate.
  (The forward rate does not change as the concentration of the solid reactant did not change.)

1 mark for graph. 2 mark for explanation [3]

[Total: 10]

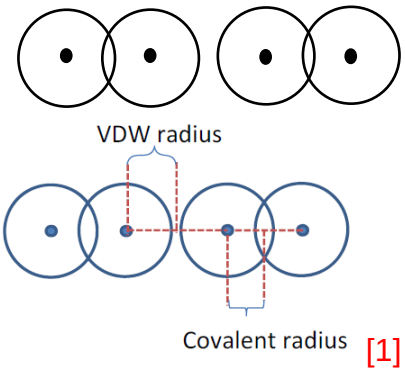
3(a) There are three types of atomic radii listed in the *Data Booklet*: metallic, covalent and van der Waals.

(i) Explain what is meant by 'covalent radius of chlorine'.

The covalent radius of chlorine is defined to be half the distance between the nuclei of two adjacent chlorine atoms. **[1]**

.....[1]

(ii) The diagram below represents two chlorine molecules. Label on the diagram the covalent radius **and** van der Waals radius of chlorine.



[1]

Legend:  represents a chlorine atom

d

[1]

(iii) The atomic radius of argon is described in the *Data Booklet* as the van der Waals radius. Suggest, with a reason, how the van der Waals radius of chlorine might compare with the van der Waals radius of argon.

Chlorine molecules have **more electrons** per molecule, hence are **more polarisable**. Instantaneous dipole-induced dipole forces/ van der Waals forces are **stronger** between the Cl_2 molecules, pulling them closer to each other. Hence, van der Waals radius of chlorine is **smaller** than that of argon. [1]

.....[1]

(iv) Suggest why argon does not have a covalent radius.

Ar atoms have a complete outer shell of electrons and exist as single atoms. [1]

.....[1]

(b) **X**, **Y** and **Z** are elements in Period 3. Data about the reactions of the oxides of **X**, **Y** and **Z** are given in the table below.

Reaction	Reagent added to oxide	Observation
1	HCl(aq)	Only oxide of **X** dissolves.
2	NaOH(aq)	Only oxides of **X** and **Z** dissolve.
3	$H_2O(l)$	Oxides **X** and **Y** do not dissolve. Green solution obtained when Universal Indicator is added.

(i) Based on the observation for each reaction, complete the following blanks by stating all the possible identities of the relevant element(s).

Reaction	Deduction
1	**X** can be Na, Mg or Al [1]
2	**X** and **Z** can be Al, P or S [1] do not penalize if Cl is stated.
3	**X** and **Y** can be Al or Si [1]

[3]

(ii) Identify **X** and **Y**, and hence explain the observation for reaction 3.

- **X** is Al and **Y** is Si. Both Al_2O_3 and SiO_2 do not react with water/remains insoluble in water, and gives neutral solutions at pH 7, with universal indicator remaining green.
- Al_2O_3 is insoluble as the (hydration) energy evolved from ion-dipole interactions between Al^{3+} ions with water and O^{2-} ions with water is not enough to overcome the strong ionic bonds between Al^{3+} and O^{2-} ions.
- SiO_2 is insoluble as the weak instantaneous dipoles-induced dipoles with water molecules do not evolve enough energy to break the strong covalent bonds between Si and O atoms.

1 pt 1 mk; total 3 mks

.....

.....[3]

(c) The chlorides of the elements, sodium to phosphorus, dissolve or react with water.

(i) In the table below, state the variation in pH of the solutions obtained when one mole of each of these chlorides is separately added to 1 dm^3 of water.

	NaCl	$MgCl_2$	$AlCl_3$	PCl_5
pH of a 1 mol dm^{-3} solution	7	6.5	3	2

[1]

[1] for all correct values

(ii) Explain the pH of the resultant solutions when $MgCl_2$ and PCl_5 are added to excess water separately. Support your answer with relevant equations, showing state symbols.

- $MgCl_2$ undergoes hydration followed by slight hydrolysis because Mg^{2+} has a relatively high charge density, and is able to polarise the water molecules, resulting in breakage of O–H bond to form H_3O^+.
- $MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$
- $[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$
- PCl_5 undergoes complete hydrolysis to give a strongly acidic solution (and white fumes.)
- $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)/(g)$

5 pts 3mks; 4pts 2mks; 3 pts 2mks; 1 or 2 pts 1 mk
Minus 1 mk for any wrong state symbols in the 3 eqns

.....

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.....

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.....

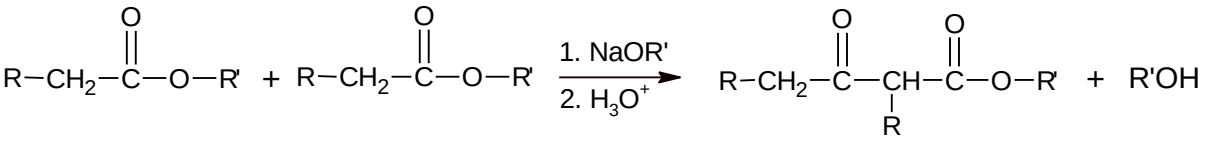
.....

.....[3]

[Total: 14]

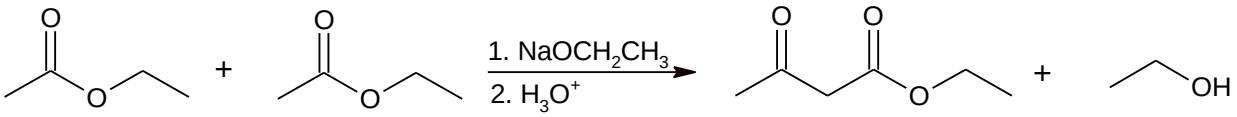
Question 4 starts on the next page.

4 The Claisen condensation occurs between two esters in the presence of a strong base to produce a keto ester and an alcohol.



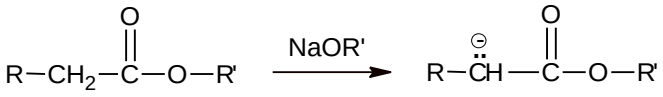
ester 1 ester 2 keto ester alcohol

An example of this reaction involving two ethyl ethanoate, with sodium ethoxide as the base, is shown below.



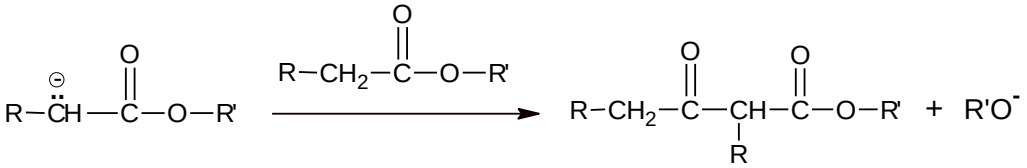
(a) For this reaction to occur, at least one of the reactants must have an α-hydrogen atom. The α-hydrogen atom is the hydrogen atom attached to the first carbon atom beside the carbonyl carbon atom. In the first step, this α-hydrogen atom is removed by a strong base, such as an alkoxide, resulting in the formation of an enolate anion.

step I



enolate anion

step II



enolate anion keto ester

(i) Suggest a reason why the α-hydrogen atom of the ester is acidic.

In the conjugate base, orbital of C atom overlaps with π orbital of C=O resulting in the delocalisation of lone pair of electrons into C=O. The negative charge is dispersed, hence stabilising the conjugate base. The position of equilibrium of the acid dissociation lies to the right and the α-hydrogen atom can be donated readily. [1]

OR

In the conjugate base, the presence of electron-withdrawing ester group disperses the negative charge on the C atom, hence stabilising the conjugate base. The position of equilibrium of the acid dissociation lies to the right and the α-hydrogen atom can be donated readily. [1]

.....[1]

(ii) NaOH(aq) is not used as a strong base in step I to remove the α-hydrogen atom because it will react with the ester instead.

Explain how NaOH reacts with the ester.

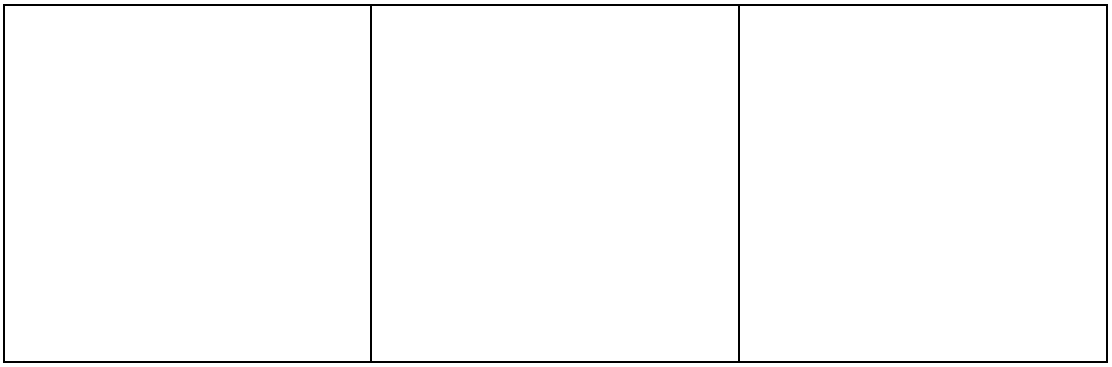
OH^- is a strong nucleophile that can attack the electron deficient carbonyl carbon atom. [1] .....[1]

(iii) State the type of reaction between the ester and the enolate anion in the second step.

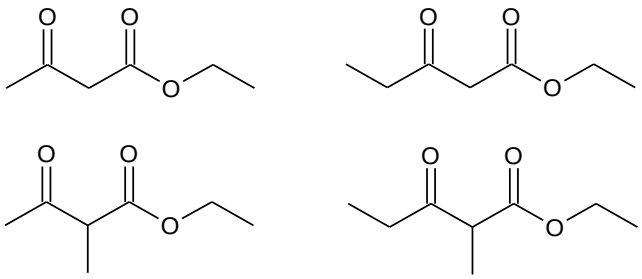
Nucleophilic (acyl) substitution [1] .....[1]

(iv) When two different esters are used as reactants in the Claisen condensation, a mixture of four different keto esters can be formed.

Suggest the structures of three possible keto esters produced when a mixture of ethyl ethanoate, $CH_3CO_2CH_2CH_3$, and ethyl propanoate, $CH_3CH_2CO_2CH_2CH_3$, is used.

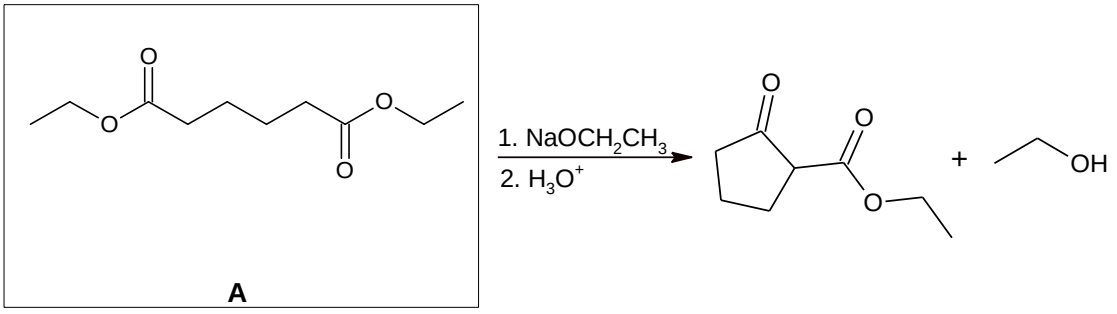


[2]



3 structures – 2 marks; 1 structure – 1 mark

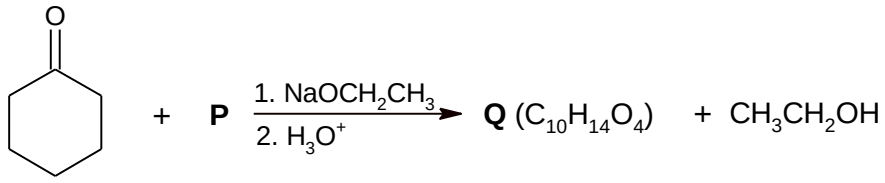
(v) Suggest the structure of compound **A**.



[1]

(b) The Claisen condensation can also occur between a ketone and an ester. An α-hydrogen atom in the ketone is first removed by the strong base, and the subsequent reaction with the ester can then take place with the same mechanism described in part **(a)**.

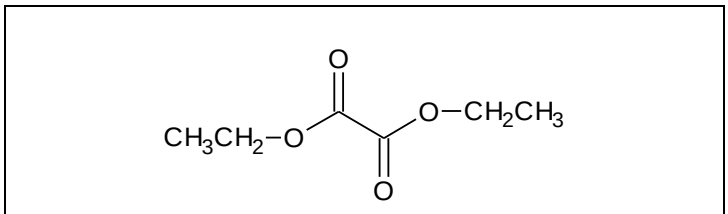
Cyclohexanone reacts with one mole of compound **P** to produce compound **Q** and ethanol in the Claisen condensation.



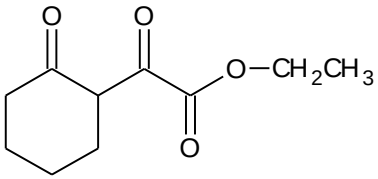
cyclohexanone

Upon heating compound **Q** with dilute sulfuric acid, compound **R** ($C_8H_{10}O_4$) is obtained. Compound **R** gives an orange precipitate with 2,4-DNPH, but no silver mirror was observed with Tollen's reagent. When compound **R** is heated with acidified $K_2Cr_2O_7$, the orange solution remained. Effervescence was observed when solid Na_2CO_3 was added to compound **R**.

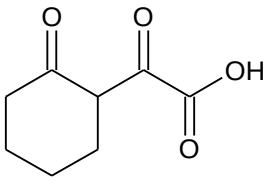
Suggest the structures of **P**, **Q** and **R** and explain the chemistry of the reactions occurred.



P



Q



R

1 mark for each structure

For Q and R, no need to mark for α-hydrogen concept. Accept side chain on any position.
For P, can be any R group on the other ester since the molecular formula is not given.

- Ester in **Q** undergoes acidic hydrolysis with dilute H_2SO_4 to produce carboxylic acid in **R**.
- Ketone in **R** undergoes condensation with 2,4-DNPH.
- Carboxylic acid in **R** undergoes acid-base reaction with Na_2CO_3 to produce effervescence of CO_2.
- (Aldehyde not present in **R** to undergo oxidation with Tollen's reagent.)
- (Primary/secondary alcohol and aldehyde not present in **R** to undergo oxidation with $K_2Cr_2O_7$.)

3 points – 2 marks; 2 points – 1 mark

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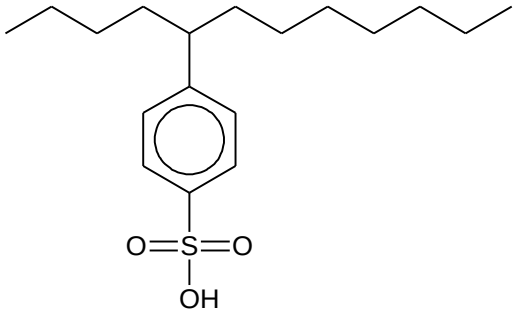
.....[5]

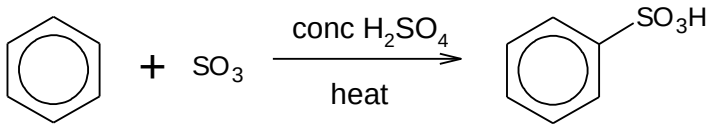
[Total: 11]

5 Alkyl benzenesulfonic acid is a class of organic compounds used in detergent formulations.



alkyl benzenesulfonic acid

(a) In the presence of sulfur trioxide, concentrated sulfuric acid and heat, benzene undergoes sulfonation to produce benzenesulfonic acid.



benzene benzenesulfonic acid

The mechanism of this reaction is similar to that of the nitration of benzene. Concentrated sulfuric acid is used in an initial step to generate the electrophile.

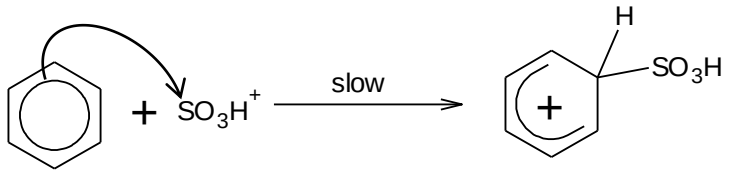
(i) State and explain the role of concentrated sulfuric acid in the initial step to generate the electrophile.

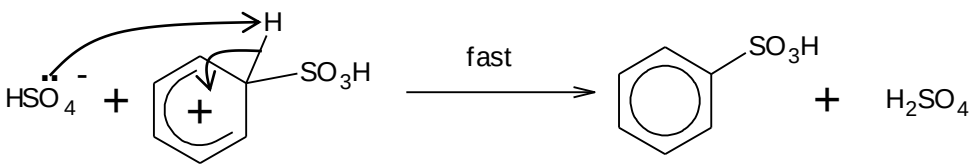
Concentrated sulfuric acid behaves as a Brønsted-Lowry acid by donating a proton to nitric acid (or sulfur trioxide) . [1].....[1]

(ii) Suggest a mechanism for the reaction between benzene and sulfur trioxide. Indicate clearly any intermediates that may be formed. Show all charges and relevant lone pairs and the movement of electron pairs by using curly arrows.

Electrophilic substitution

$SO_3 + H_2SO_4 \rightleftharpoons SO_3H^+ + HSO_4^-$





[1] for balanced equations and rate of reaction
[1] for correctly drawn intermediate and type of reaction
[1] for arrows, lone pairs and charges

[3]

(iii) Describe how the structure and bonding of the six-membered ring intermediate of the mechanism in **(ii)** differ from those in benzene. In your answer refer to the hybridisation, the π bonding and the bond angles in the ring system.

The delocalised π system (or bonding) extends over only five carbons in the intermediate while it extends over all six carbons in benzene.
or
There are only four π electrons in the delocalised system of the intermediate while there are six π electrons in the delocalised system of the benzene. [1]

In the intermediate, the carbon which undergoes substitution is sp^3 hybridised (or only five carbon are sp^2 hybridised). In benzene, all the six carbon are sp^2 hybridised. [1]

In the intermediate, the carbon which undergoes substitution has a bond angle of 109.5°. In benzene, all the bond angles are 120°.[1]

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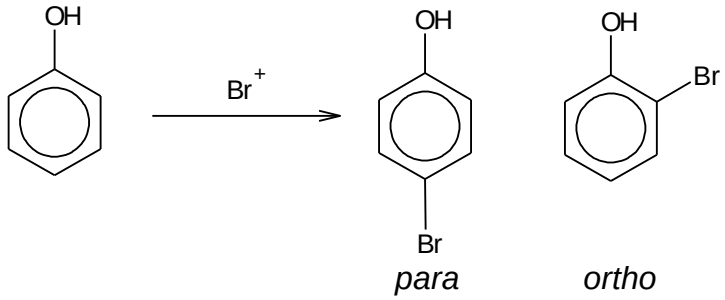
.....[3]

(b) In electrophilic substitution of *ortho*-, *para*-directors, a mixture of products slightly favouring *para* over *ortho* with a 60: 40 ratio is usually obtained.



para *ortho*

60 : 40

(i) Suggest why the *ortho*- products are less favoured over the *para*- products.

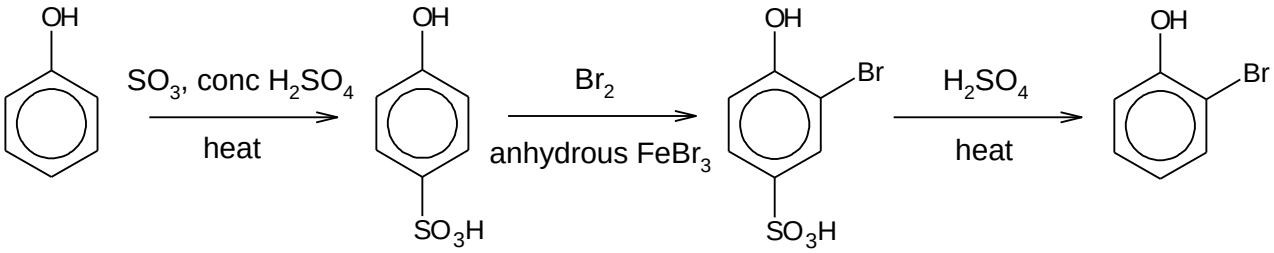
The *ortho*-positions are adjacent to the substituent which cause steric effects and block the path of incoming electrophile. [1] The *para*-position is more accessible for the incoming electrophile to attack.

.....

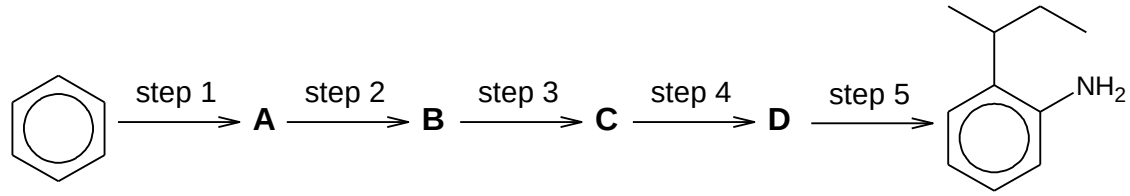
.....

.....[1]

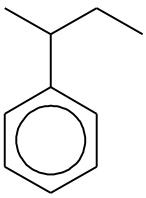
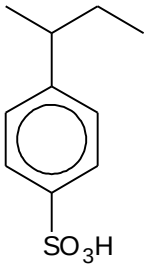
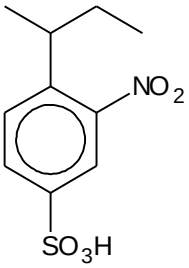
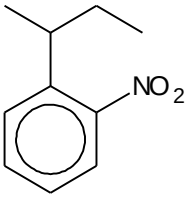
One way to get the *ortho*- products exclusively is to use the sulfonyl as a "blocking group". The *para*- position is first blocked with SO_3H, followed by performing the desired reaction at the *ortho*- position (e.g. bromination). As sulfonation is reversible, heating with strong acid will remove SO_3H, giving the *ortho*- substituted product.

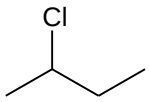


(ii) 2-(butan-2-yl)aniline can be formed via a 5-step synthesis with benzene as the starting material. Draw the structures of the reaction intermediates and state the reagents and conditions for each step. One of your steps should include the use of sulfonyl as a "blocking group".



benzene 2-(butan-2-yl)aniline

 **A**	 **B**
 **C**	 **D**

Step 1  , anhydrous $AlCl_3$, room temperature .....

Step 2 SO_3, conc H_2SO_4, heat.....

Step 3 conc HNO_3, conc H_2SO_4, heat.....

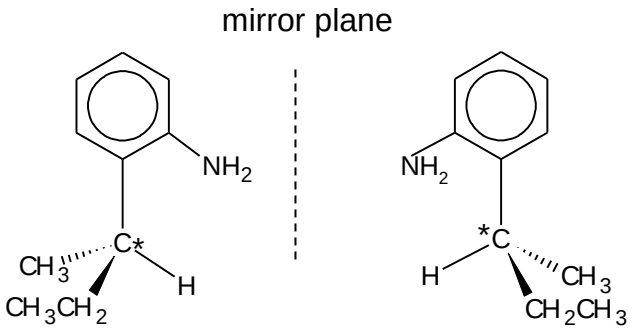
Step 4 H_2SO_4, heat.....

Step 5 Sn, conc HCl, heat, followed by NaOH(aq), room temperature..... [4]

[2] for 4 correct intermediates, [1] for 2 correct intermediates
[1] for reagent and condition for alkylation and nitration
[1] for reagent and condition for reduction
Minus 1 for alternative method that involves unintended neutralisation of phenylamine and sulfonic acid

(iii) 2-(butan-2-yl)aniline exists as two stereoisomers.

Draw 3-dimensional diagrams to show the stereoisomers of 2-(butan-2-yl)aniline and state the type of stereoisomerism shown.



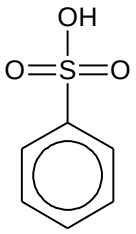
(+) 2-(butan-2-yl)aniline (–) 2-(butan-2-yl)aniline

[1] for drawing & name

type of stereoisomerism enantiomerism .....

[1]

(c) Explain why benzenesulfonic acid is more acidic than ethanol.



benzenesulfonic acid

CH_3CH_2OH

ethanol

The benzenesulfonate ion is more stable. p orbital of S atom and two O atoms overlaps with π orbital of benzene ring, resulting in the delocalisation of lone pair of electrons on the O atom into S=O and benzene ring.

The negative charge on oxygen is equally dispersed over three electronegative oxygen atoms and the benzene ring, hence stabilising the conjugate base. [1]

The position of equilibrium for the acid dissociation lies more to the right. Hence, benzenesulfonic acid is more acidic.

The ethoxide ion is less stable. The negative charge on O atom is intensified by the electron donating alkyl group, hence destabilising the conjugate base. [1]

The position of equilibrium for the acid dissociation lies most to the left. Hence, ethanol is less acidic.

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.....[2]

[Total: 15]

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