Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/02

Paper 2 Structured Questions

26 August 2019
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor’s name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
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	
Question no.	**Marks**
1	**/ 7**
2	**/ 21**
3	**/ 15**
4	**/ 7**
5	**/ 11**
6	**/ 14**
TOTAL	**/ 75**

This document consists of **21** printed pages and **1** blank page.

1 **(a)** The element aluminium and its compounds have some properties characteristic of metals, and some of non-metals. Aluminium hydroxide, for example, is known to be *amphoteric*.

(i) Explain the meaning of the word “amphoteric”. [1]

The ability to react with both acids and bases.

Aluminium sulfate and calcium oxide are sometimes added to water supplies to co-precipitate suspended solids and bacteria. A small amount of aluminium-containing ions remains in solution and its presence in drinking water may contribute to the mental illness known as Alzheimer’s disease.

(ii) Write a balanced equation for the reaction that occurs when aluminium sulfate and calcium oxide are added to water, given that aluminium hydroxide is one of the products formed. [1]

$$Al_2(SO_4)_3 + 3CaO + 3H_2O \rightarrow 2Al(OH)_3 + 3CaSO_4$$

(iii) By considering the nature of calcium oxide, explain why adding too much of it would increase the risk of contracting Alzheimer’s disease.

Write an equation to illustrate how “aluminium-containing ions remains in (drinking water)” as a result of adding too much calcium oxide. [2]

CaO dissolves slightly to form an alkaline solution.
OH^- thus formed reacts with $Al(OH)_3$ to form a soluble complex.

$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$

1 **(b)** Beryllium oxide (BeO) is amphoteric, just like $Al(OH)_3$.

(i) Beryllium oxide reacts with sodium hydroxide according to the equation,

$$2NaOH + BeO \longrightarrow Na_2BeO_2 + H_2O$$

Given the position of beryllium in the Periodic Table, explain how this reaction illustrates the amphoteric nature of beryllium oxide. [2]

BeO: Gp 2 (**metallic**) oxide, expected to form basic oxide and to react with acid.

but here it is reacting with an alkali, illustrating its acidic nature.

(ii) To further illustrate its amphoteric nature, at 500 °C, BeO reacts with Na_2O to form compound **F** as the **sole product**. The molar masses of all three compounds are tabulated below.

compound	molar mass / g mol^{-1}
BeO	25
Na_2O	62
F	149

Write a balanced equation of the above reaction. [1]

$$BeO + 2Na_2O \rightarrow Na_4BeO_3$$

[Total: 7]

2 **(a)** In the laboratory, there are three bottles labelled **X**, **Y** and **Z**. Each bottle contains one of the following reagents:

KI(aq), Cl_2(aq), and NaBr(aq)

Three tests were carried out using the reagents in the bottles. The results are summarised in the table below:

test	procedure	observations
1	mix reagent in bottle **X** with reagent in bottle **Z**	no change in colour
2	mix reagent in bottle **Y** with reagent in bottle **Z**	mixture turns brown
3	mix reagent in bottle **Y** with reagent in bottle **X**	mixture turns reddish-brown

(i) By comparing relevant standard reduction potential values from the Data Booklet, explain how it can be deduced that **Y** is aqueous chlorine. There is **no** need for calculations. [1]

Chlorine has the most positive standard reduction potential (compared to that of bromine and iodine) hence it is able to oxidise both iodide and bromide.

(ii) Tests 2 and 3 were executed to determine the reagents in bottles **X** and **Z**.

Hexane was added to the resulting reaction mixture after the tests were conducted. The bottles were then shaken and allowed to stand.

State the observations that will indicate whether the bottles contained KI(aq) or NaBr(aq) initially. [2]

The bottle with orange-red organic layer contains NaBr (aq) initially.
The bottle with violet / purple organic layer contains KI (aq) initially.

2 **(b)** Sulfur dichloride, SCl_2, is a cherry-red liquid at room temperature and pressure.

SCl_2 is formed from S_8 and Cl_2.

(i) Explain why S_8 exists as a solid while Cl_2 exists as a gas at room temperature. [2]

Both exist as non-polar simple covalent molecules.

The size of the electron cloud of sulfur is so much larger hence the idid interactions amongst sulfur molecules are stronger than the idid amongst chlorine molecules.

Therefore the melting point of sulfur is significantly higher than that of chlorine.

(ii) The formation of SCl_2 from S_8 and Cl_2 takes place in two steps.

The first step involves disulfur dichloride, S_2Cl_2, as an intermediate.

$$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

Write the equation of the second step. [1]

$$S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$$

Some chemists speculate that the intermediate is not disulfur dichloride but **K**.
K shares the same elemental mass percentages as sulfur dichloride and has a molar mass of 206.2 g mol^{-1}.

(iii) State the molecular formula of **K**. [1]

S_2Cl_4

(iv) All the chlorine atoms in **K** are terminal.
There are only two central atoms in **K**.
The bond angles about each central atom are different.

State the shape around each central atom and the respective bond angles. [2]

See-saw (90^0 and/or 120^o). (88^0 and/or 118^0)

and

bent (105^0 or 104.5^0)

2 **(c)** Sulfuryl chloride, SO_2Cl_2, is commonly confused with thionyl chloride, $SOCl_2$.

The properties of these two sulfur oxychlorides are quite different. SO_2Cl_2 is a source of chlorine while $SOCl_2$ is a source of chloride ions for various organic reactions.

When heated, sulfuryl chloride decomposes endothermically as follows:

$$SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$$

In an experiment, 1.00 mol of SO_2Cl_2 vapour was heated in a closed 4.00 dm^3 flask at 500 K until equilibrium was established. The flask was then rapidly cooled to liquefy SO_2Cl_2.

After removing gaseous SO_2 and Cl_2, excess water was then carefully added to the liquid SO_2Cl_2, causing the following reaction to occur.

$$SO_2Cl_2\,(l) + 2H_2O\,(l) \rightarrow H_2SO_4\,(aq) + 2HCl\,(aq)$$

The resulting solution was made up to 250 cm^3 in a standard graduated flask.

20.0 cm^3 of this solution was titrated with 1.00 mol dm^{-3} NaOH. 40.00 cm^3 of NaOH was required for complete neutralisation.

(i) Write an expression for K_c for the equilibrium above and state its units. [2]

$$K_c = [SO_2][Cl_2] / [SO_2Cl_2]$$

mol dm^{-3}

(ii) Calculate the equilibrium amount of SO_2Cl_2, SO_2, and Cl_2 in the original equilibrium at 500 K. Hence calculate a value for the K_c for the equilibrium. [4]

$n(H_2SO_4) = \frac{1}{4}\,(40.00/1000)(250/20.0) = 0.125$

$n(SO_2Cl_2)$ at eqm = 0.125

$n(SO_2)$ and $n(Cl_2)$ at eqm are 1.00 – 0.125 = 0.875 each

$K_c = (0.875)^2 / (0.125 \times 4) = 1.53$ mol dm^{-3}

2 **(c)** **(iii)** A student suggested to carry out the decomposition process at a higher temperature and high pressure to decrease the time required for the process. Discuss the effects of the proposed changes on the rate and the yield. [2]

At a higher temperature, both rate and yield would increase.

However, at high pressures, the rate (but not the yield) would increase as the position of equilibrium will be shifted to the LHS

2 **(d)** SO_2Cl_2 is widely used as a reagent in chlorination of the hydrocarbons. Such reactions occur under free radical conditions using H_2O_2 as an initiator.

For example, methylbenzene undergoes free radical substitution with SO_2Cl_2 to give benzyl chloride, $C_6H_5CH_2Cl$.

The mechanism of this reaction involves three stages:

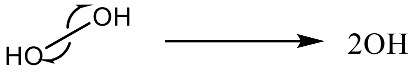
I. Initiation
II. Propagation
III. Termination

- The **initiation** stage is unique as it involves two successive steps.

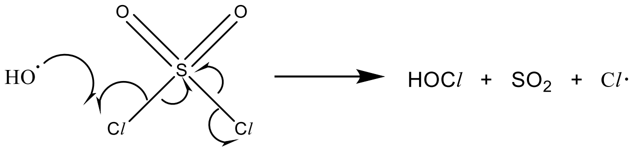
(i) In the first step, there is an initial homolytic breaking of the peroxide bond in hydrogen peroxide forming two hydroxyl radicals.

Using curly arrows, show the mechanism for this step.

[1]



The second initiation step involves the reaction between the hydroxyl radical and SO_2Cl_2 to give SO_2, $HOCl$ and a chlorine radical. It has been drawn for you below.



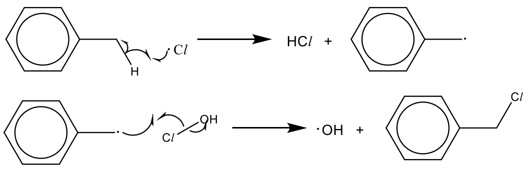
After these two initiation steps,

- The chlorine radical then reacts with methylbenzene in two **propagation** steps to form benzyl chloride and regenerating the hydroxyl radicals.
- The chain reaction **terminates** when two radicals combine to give stable compounds.

(ii) Complete the mechanism by writing the steps for the **propagation** and **termination** stages.

[3]

Propagation



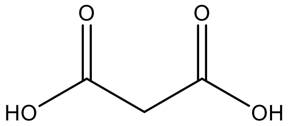
Termination

$2OH \rightarrow H_2O_2$

$HO + Cl \rightarrow HOCl$

[Total: 21]

3 Malonic acid is an important precursor to some polyesters.



(a) Malonic acid can be synthesised in more than one way.

(i) Suggest a three-step synthetic route from ethene to malonic acid. [5]

1) aqueous bromine
2) KCN (ethanolic) heat
3) acidified $KMnO_4$ (or $K_2Cr_2O_7$), heat with reflux

Intermediates: 2-bromoethanol; 3-hydroxypropanenitrile.

(ii) Malonic acid can be made by reacting two moles of **L** with a mole of carbon suboxide. [1]

$$O=C=C=C=O$$

carbon suboxide

Identify **L**.

H_2O

(b) Malonic acid behaves as a diprotic acid. The values of its K_{a1} and K_{a2} are 1.51×10^{-3} mol dm^{-3} and 2.00×10^{-6} mol dm^{-3} respectively.

In an experiment, 15.0 cm^3 of a 0.100 mol dm^{-3} solution of malonic acid was titrated against 0.100 mol dm^{-3} NaOH.

(i) Calculate the initial pH. [1]

$pH = -\log(1.51 \times 10^{-2}) = 1.91$

(ii) Calculate the volume of NaOH required for the first equivalence point. [1]

15.0 times 0.100 / 0.100 = 15.00 cm^3

(iii) Write an equation to explain why the second equivalence point is above 7. [1]

$${}^{-}O_2CCH_2CO_2^{-} + H_2O \rightleftharpoons HO_2CCH_2CO_2^{-} + HO^{-}$$

(iv) Calculate the second equivalence pH. [2]

2nd equivalence volume = 30.0 cm^3
$[{}^{-}OOCCH_2COO^{-}]$ at 2nd equivalence point = 15/(30+15) X 0.100
= 0.0333 mol dm^{-3}

$K_b = 10^{-14} / K_{a2} = 5.00 \times 10^{-9}$ mol dm^{-3}
$pOH = -\frac{1}{2}\log(5.00 \times 10^{-9} \times 0.0333) = 4.89$
$pH = 14 - pOH = 9.11$

3 **(b)** A buffer is obtained after the addition of 12.00 cm^3 of NaOH solution.

(v) Write an equation for the reaction that occurs when a drop of HNO_3 is added to this buffer. [1]

$$HO_2CCH_2CO_2^- + H^+ \rightarrow HO_2CCH_2CO_2H$$

(vi) Calculate the pH of this buffer. [2]

n(malonic acid) remaining = $[(15.0)(0.100)-(12.00)(0.100)] / 1000$
$= 3.00 \text{ X } 10^{-4}$

n($HO_2CCH_2CO_2^-$) = $(12.00)(0.100) / 1000$
$= 1.20 \text{ X } 10^{-3}$

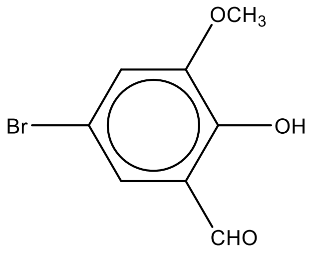
$\text{pH} = – \log (1.51 \times 10^{-3}) + \log (12.0/3.00) = 3 + \log (4/1.51) = 3.42$

(vii) Another buffer is obtained after the addition of 22.50 cm^3 of NaOH solution. Calculate its pH. [1]

$\text{pH} = \text{p}K_{a2} = - \log (2.00 \times 10^{-6}) = 6 – \lg 2.00 = 5.70$

[Total: 15]

4 **V** is a mono-brominated derivative of *ortho*-vanillin. *Ortho*-vanillins are used in the study of mutagenesis and as a synthetic precursor for pharmaceuticals.

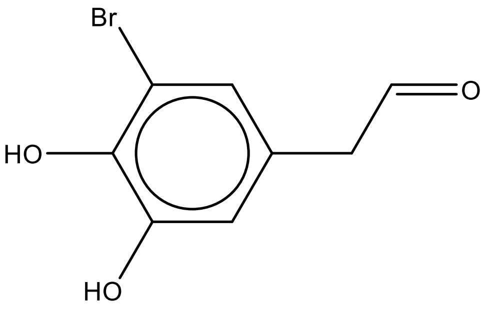


V

(a) Define the term "constitutional isomerism". [1]

Compounds having the same molecular formula but different structural formulae/different structures.

(b) **U** is a constitutional isomer of **V**.



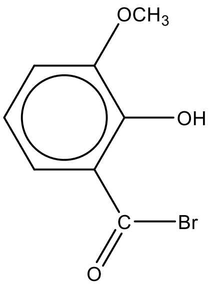
U

State a simple chemical test to distinguish between **U** and **V**. State the observations. [2]

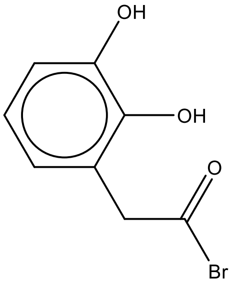
Fehling’s test.
No ppt for V. brick-red/brown/reddish-brown ppt for U.

The structures you draw from 4(c) to 4(e) must contain one benzene ring.

(c) Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself by cold $AgNO_3$ solution. State the observations. [2]



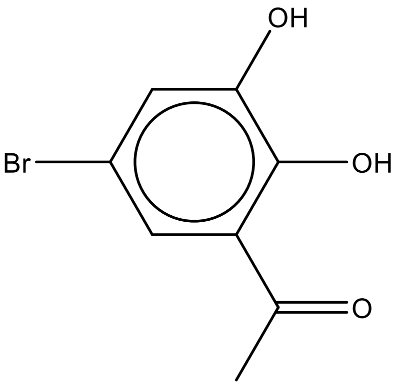
or

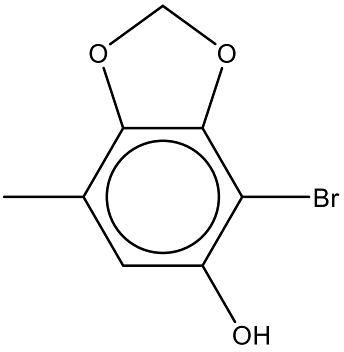


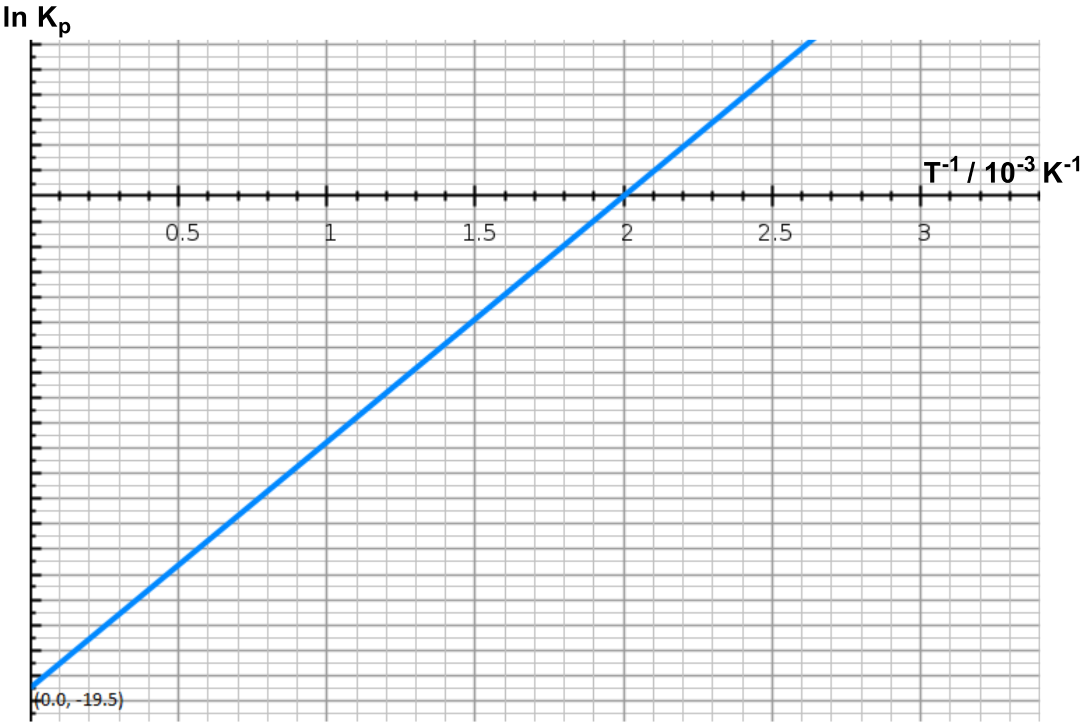
No ppt for X.
Cream/off-white ppt for this constitutional isomer.

The structures you draw from 4(c) to 4(e) must contain one benzene ring.

4 **(d)** Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself by warm alkaline iodine. [1]



	(e)	Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself via 2,4-dinitrophenylhydrazine but not neutral iron(III) chloride solution not sodium metal. [1] 
		[Total: 7]

5	Space-suits need to be designed in such a way to supply oxygen to astronauts and to remove the carbon dioxide exhaled by them.		
	(a)	Metal oxides like silver oxide, Ag_2O, are used to get rid of the carbon dioxide. Ag_2O reacts reversibly with carbon dioxide, as described in the equilibrium equation, $Ag_2O (s) + CO_2 (g) \rightleftharpoons Ag_2CO_3 (s)$ The van't Hoff plot shows how the equilibrium constant, K_p, of this reaction varies with temperature. 	
		(i)	From the above graph, deduce the relationship between K_p and T. [1] When one increases, the other decreases/inversely related/inverse relationship.
		(ii)	Hence, explain whether the reaction between silver oxide and carbon dioxide is exothermic or endothermic. [2] The reaction is exothermic. Explanation: as the T increases/decreases, K_p decreases/increases, implying that PoE shifted left/right, which further implies that the backward reaction is endothermic/forward reaction is exothermic.

5 **(a)** **(iii)** Given that the straight line graph for ln K_p versus T^{-1} is described by the equation

$$\ln K_p = \left(\frac{-\Delta H^0}{R}\right)\frac{1}{T} + \frac{\Delta S^0}{R}$$

Calculate the standard entropy change of this reaction and explain the significance of its sign with respect to the reaction. [2]

y-intercept = -19.5

$\Delta S = (-19.5) \times 8.31 = -162\ \text{J mol}^{-1}\ \text{K}^{-1}$

The sign is negative because there is a decrease in the amount of gas. [

After absorbing carbon dioxide for some time, most if not all of the silver oxide would have been depleted. To **recharge** the system, heat is applied into the system to form Ag_2O again.

(iv) ΔG^0 and K_p are mathematically related by the equation

$$\Delta G^0 = -RT \ln K_p$$

Using the graph, estimate the minimum temperature at which the **recharging** of this system becomes spontaneous. [1]

x-intercept = $2 \times 10^{-3}\ \text{K}^{-1}$

minimum temperature = $1 / (2 \times 10^{-3}\ \text{K}^{-1}) = 500$ K

5 **(b)** Silver carbonate (relative formula mass = 275.8) is a sparingly soluble salt. At 25 °C, its solubility is 0.032 g dm^{-3} of water.

(i) Show that the value of the K_{sp} of silver carbonate at 25 °C is 6.25×10^{-12}. [1]

$4(0.032 / 275.8)^3 = 6.25 \times 10^{-12}\ \text{mol}^3\ \text{dm}^{-9}$

(ii) Calculate the solubility of silver carbonate in 0.100 mol dm^{-3} silver nitrate at 25 °C. [1]

$6.25 \times 10^{-12} = (0.100 + 2x)^2 x$

$x = 6.25 \times 10^{-10}\ \text{mol dm}^{-3}$

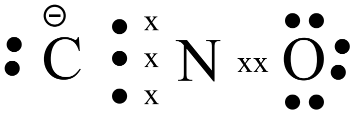
(iii) 1.00 cm^3 of a 1.20×10^{-5} mol dm^{-3} silver nitrate solution was mixed with 3.00 cm^3 of a 7.45×10^{-5} mol dm^{-3} sodium carbonate solution.

Determine whether there would be precipitation of silver carbonate. [2]

Ionic Product = $(0.25 \times 1.20 \times 10^{-5})^2(0.75 \times 7.45 \times 10^{-5})$

$= 5.03 \times 10^{-16}\ \text{mol}^3\ \text{dm}^{-9}$

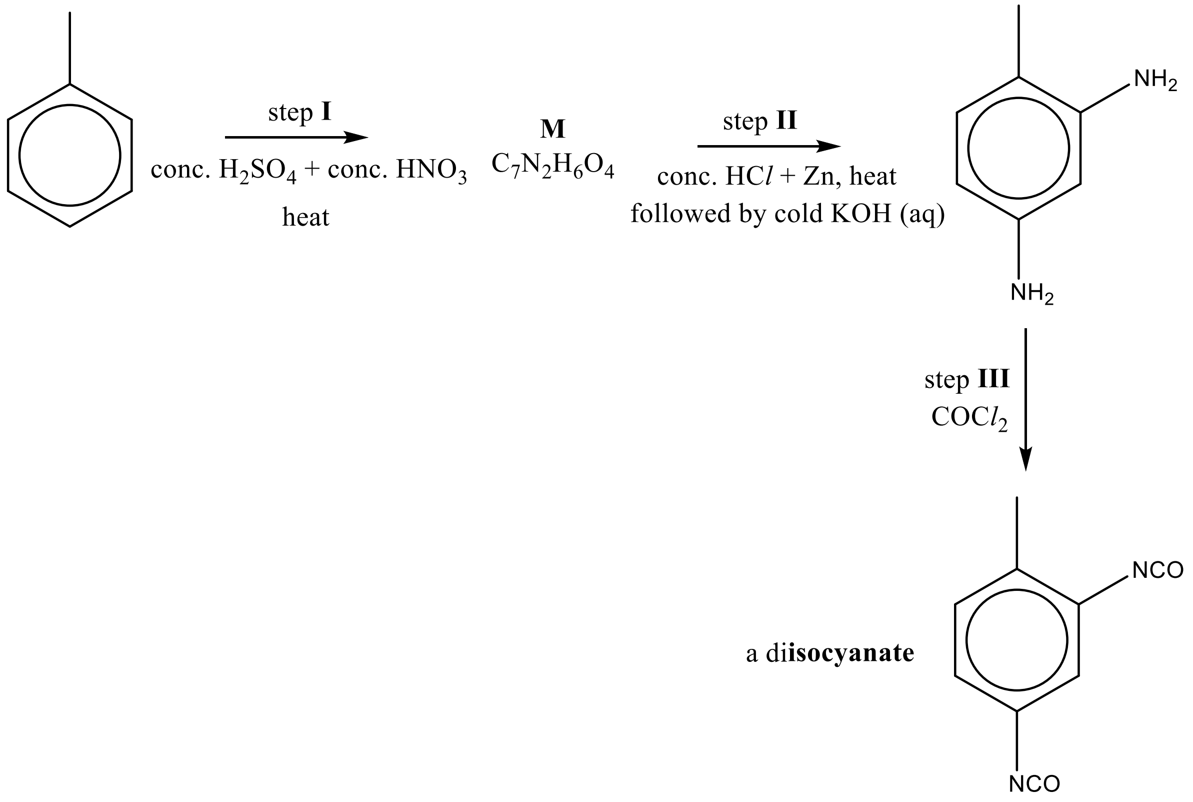
As IP < K_{sp}, there will not be precipitate of silver carbonate.

5	**(c)**	Silver carbonate can be reacted with ammonia to form silver fulminate, AgCNO, a powerful primary explosive. $4\ Ag_2CO_3 + 4\ NH_3 \rightarrow 4\ AgCNO + 6\ H_2O + 4\ Ag + O_2$
		Draw the dot-and-cross diagram of the fulminate ion given that the N is the central atom and the negative charge is on the carbon. [1] 
		[Total: 11]

6 The isocyanate functional group is a constitutional isomer of the fulminate, which was mentioned in question **5(c)**. The isocyanate has the carbon atom instead of nitrogen atom as the central atom.

Isocyanates are important industrial chemicals; they react with alcohols to produce polyurethane polymers, which are components of polyurethane foams, thermoplastic elastomers and polyurethane paints.

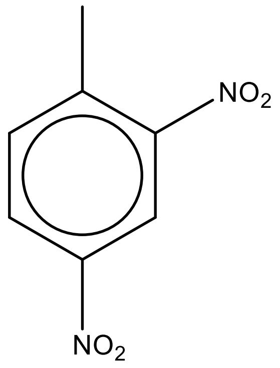
(a) This part is about the synthesis of a diisocyanate from methylbenzene.

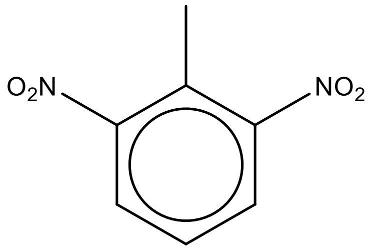
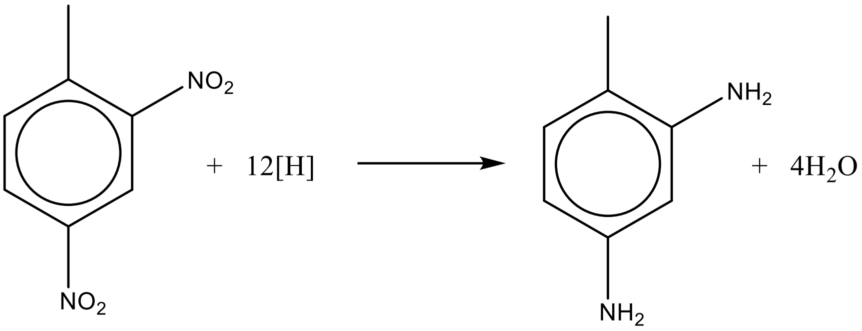


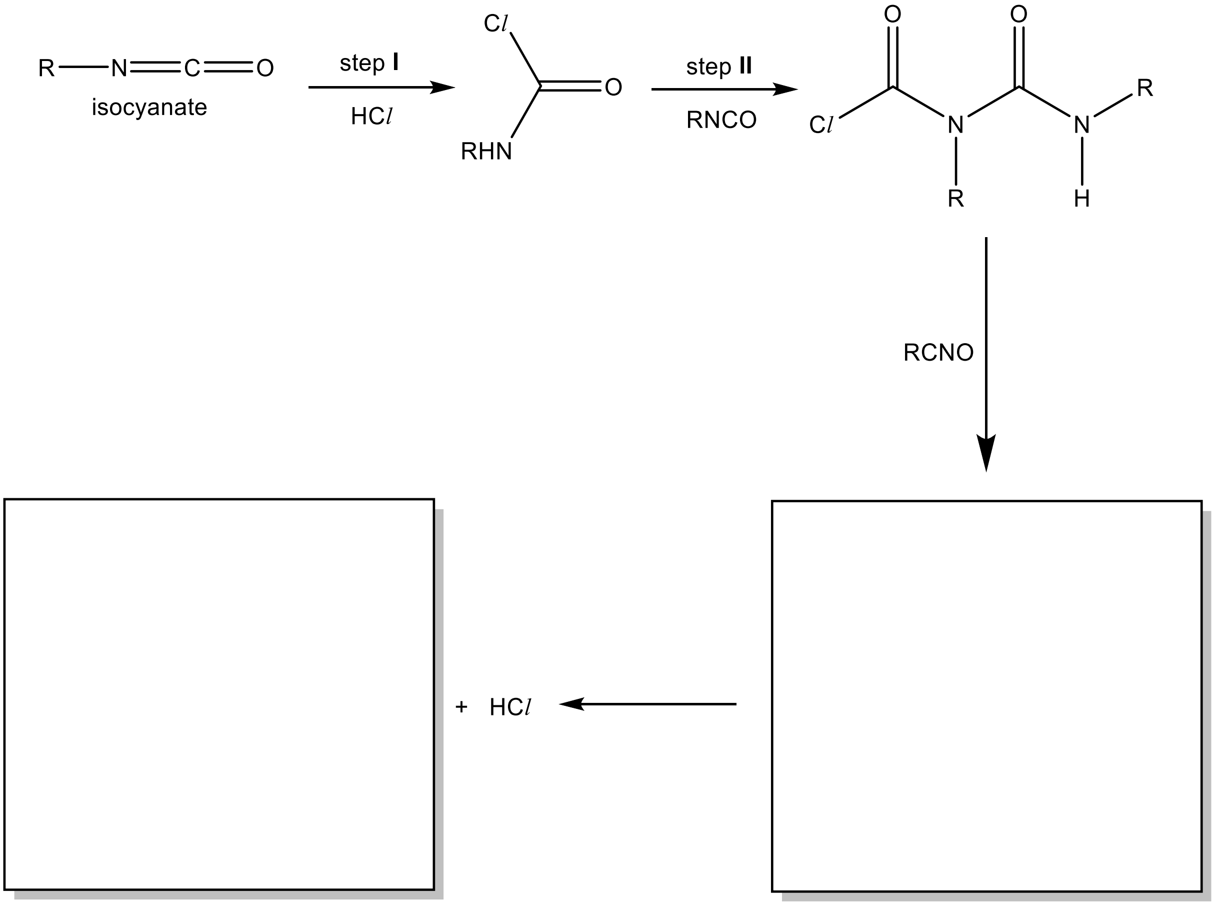
(i) State the type of reaction in step **I**. [1]

Electrophilic substitution.

(ii) Draw the structure of **M**. [1]



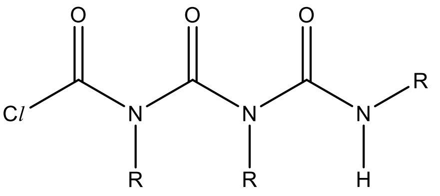
6	**(a)**	**(iii)**	Draw the structure of the isomer of **M** which is formed as a side-product in step **I**. [1] 
		(iv)	Explain the purpose of KOH in step **II**. [1] It is to liberate the amine from its protonated form. It is to form the amine from its protonated form.
		(v)	Write a balanced equation for the overall reaction in step **II**. You are to use [H] to balance the equation. [1] 
		(vi)	State the type of reaction in step **III**. [1] Condensation / addition-elimination
6	**(b)**	Examine the synthetic route below.	

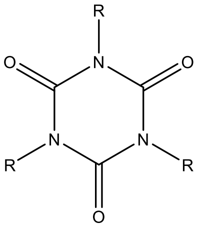


cyclic trimer **T**
$R_3C_3N_3O_3$

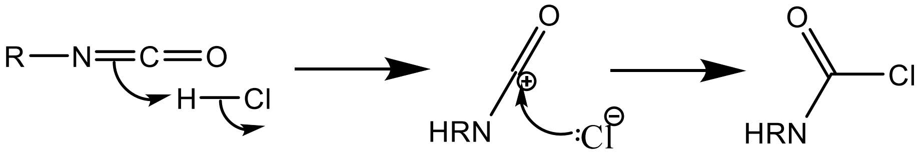
Q
$R_3C_3N_3O_3HCl$

(i) Draw the skeletal formulae of **Q** and the cyclic trimer **T** in the boxes provided. [2]





(ii) Step **I** is an electrophilic addition reaction. Draw the mechanism of step **I**. [3]



6 **(c)** When heated with HC*l* (aq), organic isocyanates (RNCO) are hydrolysed to the amine salt ($RNH_3^+Cl^-$) and carbon dioxide.

$$RNCO + HCl + H_2O \rightarrow RNH_3^+Cl^- + CO_2$$

A 1.13 g sample of an organic isocyanate was treated in this way, and the carbon dioxide produced was absorbed in an excess of aqueous $Ba(OH)_2$, according to the equation shown.

$$Ba(OH)_2\,(aq) + CO_2\,(g) \longrightarrow H_2O\,(l) + BaCO_3\,(s)$$

The mixture was filtered and the residue $BaCO_3$ washed and dried thoroughly. The mass of the residue was 1.97 g.

(i) Show that the molecular mass of the organic isocyanate is 113 g mol^{-1}. [1]

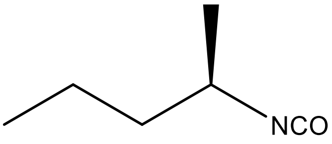
n(org. isocyanate) = $1.97 / 197.3 = 1.00 \times 10^{-2}$
molecular mass of org. isocyanate = $1.13 / (1.00 \times 10^{-2}) = 113.2$ g mol^{-1}

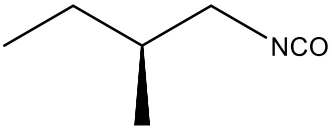
(ii) The R group in RNCO and $RNH_3^+Cl^-$ contains only carbon and hydrogen.

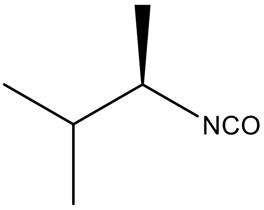
Use the molecular mass mentioned in **(i)** to suggest the molecular formula of the organic isocyanate. [1]

$C_6H_{11}NO$

(iii) Given that a pure sample of this organic isocyanate rotates plane-polarised light, draw a possible stereochemical formula of it. [1]







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