H

NANYANG JUNIOR COLLEGE
JC 2 Preliminary Examinations
Higher 1

CANDIDATE NAME **Answers**

CLASS

TUTOR'S NAME

CHEMISTRY

8872/02

Paper 2

10 September 2012

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A,
Answer **all** the questions.

Section B,
Answer **two** questions on separate answer paper.

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	
1	12
2	4
3	5
4	6
5	13
Total	40

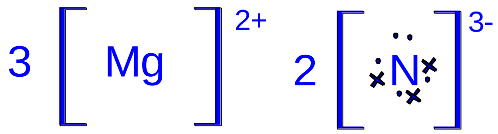
This paper consists of **13** printed pages and **0** blank page

Section A

Answer **all** the questions.
Write your answers on the spaces provided.

1 Nitrides are a large class of compounds with a wide range of properties and applications. They are often used as refractory materials. Two examples are magnesium nitride, Mg_3N_2 and boron nitride, BN.

(a) Draw a dot-and-cross diagram to show the bonding in magnesium nitride. [2]



(b) Suggest the electrical conductivity of magnesium nitride in liquid state. [2]

In liquid state, there is presence of free mobile ions of Mg^{2+} and N^{3-} to carry charges.

Hence Mg_3N_2 can conduct electricity.

(c) Boron nitride is a good lubricant like graphite. Explain, in terms of structure and bonding, this property of boron nitride. [2]

Boron nitride has giant covalent/molecular structure consisting of B and N atoms held by strong covalent bonds.

In between the layers, they are held by weak dispersion/van der Waals' forces.

(d) Suggest one reason why magnesium gives the nitride, Mg_3N_2, in addition to its oxide when burned in air. Construct a balanced equation for the combustion of magnesium in air. [2]

Magnesium burns in air to produce an oxide layer.

The unreacted magnesium below the oxide layer could therefore only reacts with nitrogen.

$4Mg + \frac{1}{2}O_2 + N_2 \rightarrow MgO + Mg_3N_2$

(e) A 2.00 g sample of the powder obtained from burning magnesium in air was boiled with water. The ammonia that was evolved neutralised 12.0 cm^3 of 0.500 mol dm^{-3} hydrochloric acid.

(i) Construct a balanced equation for the reaction with water. [1]

MgO is only slightly soluble in water.
$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

(ii) Calculate the percentage of magnesium nitride in the 2.00 g sample. [3]

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

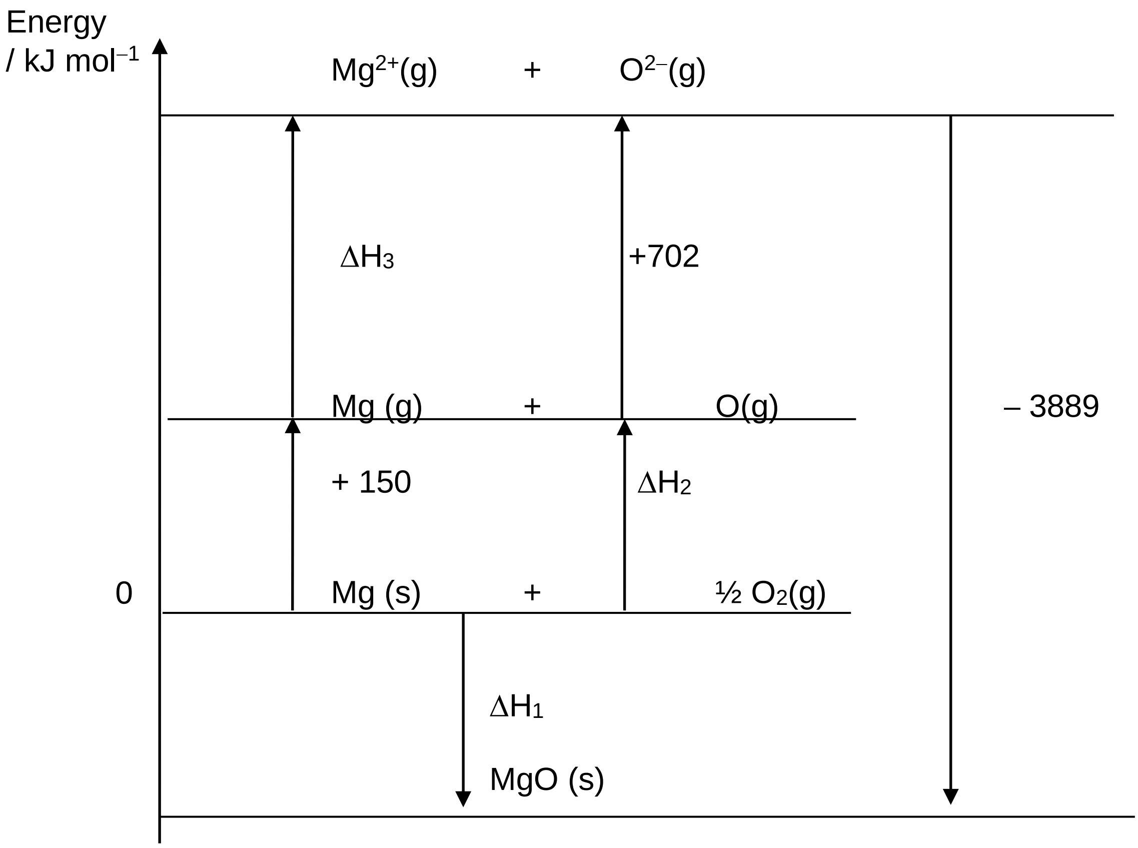
$n(NH_3)$ produced = n(HCl) required = $0.5 \times \frac{12.0}{1000}$ = 6.000×10^{-3} mol dm^{-3}

$n(Mg_3N_2)$ present in sample = $\frac{1}{2}n(NH_3)$ = 3.000×10^{-3} mol dm^{-3}

$m(Mg_3N_2)$ = $3.000 \times 10^{-3} \times 100.9$ = 0.3027 g
% by mass of Mg_3N_2 in sample = 0.3027/2.00 x 100% = 15.1%

[Total:12]

2 The formation of magnesium oxide from its elements may be represented by a Born-Haber cycle as shown below.



(a) Name the enthalpy changes represented by

ΔH_1 **is the enthalpy change of formation of MgO**.

ΔH_2 **is half the bond energy of O_2.**

(b) Using values from the *Data Booklet* and the energy values given in the above cycle, calculate the value of ΔH_1.

ΔH_1 = +150 + 2186 + 248 + 702 + (–3889) = –603 kJ mol^{-1}

[2]

[Total:4]

3 Consider the following reaction where colourless bromide ions react with hydrogen peroxide to form a reddish-brown bromine solution.

$$2Br^- + H_2O_2 + 2H^+ \rightleftharpoons Br_2 + 2H_2O \qquad \Delta H < 0$$

(a) Explain what is meant by the term *dynamic equilibrium*. [2]

A reversible reaction is in dynamic equilibrium when

- the rates of forward and backward reactions are equal, and
- the concentrations of reactants and products remain constant.

(b) Predict and explain the effect on the position of equilibrium when

(i) a catalyst is added, [1]

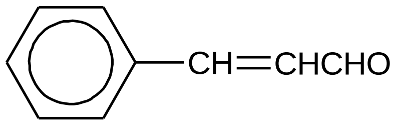
- A catalyst does not affect the position of equilibrium because
- it increases the rate of forward and backward reactions by the same extent.

(ii) temperature is increased. [2]

- By Le Chatelier's Principle, the position of equilibrium will shift to the left
- as the endothermic reaction is favoured more than the exothermic reaction to remove some of the added heat

[Total: 5]

4 Cinnamaldehyde is used in fragrances for its jasmine-like odour.

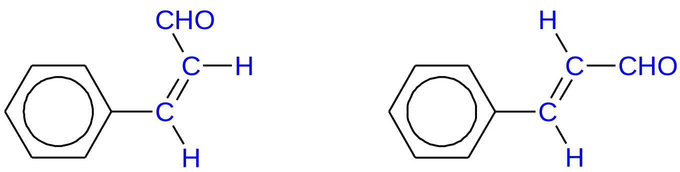


cinnamaldehyde

(a) Name the **two** functional groups, other than the phenyl group, that are present in cinnamaldehyde.

....alkene..
.....aldehyde/alkanal.................... [2]

(b) Cinnamaldehyde can exhibit geometric isomerism.
Draw and label the structure of the geometric isomers and explain how it arises.

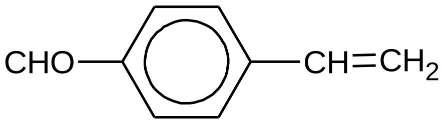


Cis trans

Restricted rotation around C=C bond

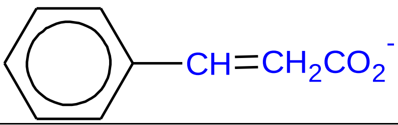
[3]

(c)



is a structural isomer of cinnamaldehyde.

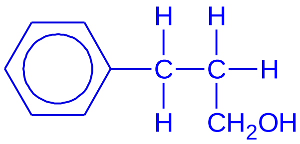
Describe a simple chemical test you could carry out to distinguish the two isomers.

Reagents and conditions	Fehlings solution warm
Observations	Brick red ppt forms for cinnamaldehyde.
Product	

(d) Cinnamaldehyde reacts with hydrogen gas in the presence of nickel catalyst to give a saturated compound **A**.

(i) State the type of reaction taking place.
Reduction OR Addition

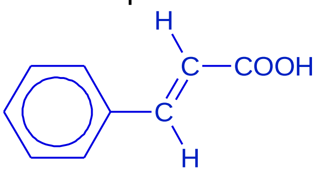
(ii) Draw the structural formula of compound **A**.



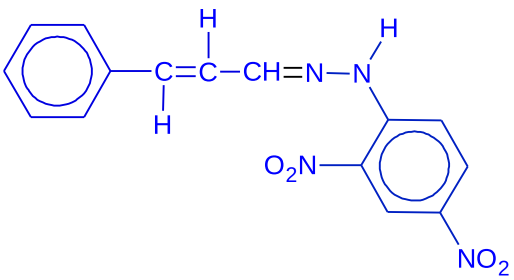
[3]

(e) Draw the structural formula of each of the organic products formed when cinnamaldehyde is treated with the following reagents:

(i) acidified potassium dichromate(VI) when heated under reflux,



(ii) 2,4-dinitrophenylhydrazine.



[2]

[Total: 13]

5 *Use of the Data Booklet is relevant to this question.*
Part of the Periodic Table is shown below.

	Group I	II		III	IV	V	VI	VII	0
Period 2	Li	Be		B	C	N	O	F	Ne
Period 3	Na	Mg		Al	Si	P	S	Cl	Ar

(a) From the elements shown in the table, identify the one which exhibits each of the following property. Write your answers in the table. [4]

(i) It has the highest first ionisation energy.

(ii) It has the largest ionic radius.

(iii) It has an electronegativity similar to that of aluminium.

(iv) It has a hydride that forms the strongest intermolecular hydrogen bonds.

(v) It has a trifluoride with molecules of trigonal shape.

(vi) It has a chloride that neither reacts with nor dissolves in water.

(vii) It has an oxide with a giant structure and a chloride which is readily hydrolysed in water.

(viii) It has an oxide that produces a strong acid when treated with water.

(i) Ne	**(ii)** P	**(iii)** Be	**(iv)** F
(v) B / P / N	**(vi)** C	**(vii)** Al / Si	**(viii)** P / S

(b) Write equations for the reactions in **(vii)** and **(viii)**. [2]

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$
$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H_3O^+$

$SiCl_4(l) + 4H_2O(l) \rightarrow Si(OH)_4(s) + 4HCl(l)$

Either one

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$
$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$
$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

[Total: 6]

Section B

Answer **two** questions from this section on separate answer paper.

6(a) Propan-2-ol is a clear colourless volatile liquid. It is often used as a solvent and an antiseptic. It can be formed from the reaction between propene and steam.

(i) Name the type of reaction and state the condition required for the reaction to occur.

Addition
Concentrated H_3PO_4 , 300 °C, 60 atm.

(ii) Write a balanced equation for the complete combustion of propan-2-ol.

$$CH_3CH(OH)CH_3\,(l) + \frac{9}{2}O_2\,(g) \rightarrow 3CO_2\,(g) + 4H_2O\,(l)$$

(iii) When 1.00 g of propan-2-ol was burned under a container of water, it was found that 100 g of water was heated from 20 °C to 80 °C. The process was known to be only 75% efficient.

Calculate the enthalpy change of combustion of propan-2-ol.

Heat absorbed, Q = mcΔT
= (100) 4.18 (80 – 20)
= 25.08 kJ
Heat evolved from the combustion of propanol = (100/75) x 25.08
= 33.44 kJ
n(propanol) = 1.00/(36.0+8.0+16.0) = 0.01666 mol

$$\Delta Hc\ (\text{propanol}) = -\frac{33.44}{0.01666}$$

= –2006 kJ mol^{-1}
= –2006 kJ mol^{-1} (to 3 sf)

[6]

(b) (i) Use bond energy values from the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of propan-2-ol.

Bonds broken	kJ mol^{-1}	Bonds formed	kJ mol^{-1}
3(C-C)	3(+350)	6(C=O)	6(+740)
7(C-H)	7(+410)	8(O-H)	8(+460)
1(O-H) + 1(C-O)	+460 +360		
$\frac{9}{2}$ O=O	$\frac{9}{2}$(+496)		

ΔHr = ∑Bonds broken – ∑Bonds formed

$$= [3(+350) + 7(+410) + (+460) + (+360) + \frac{9}{2}(+496)] - [6(+740) + 8(+460)]$$

= 6972 – 8120
= – 1,148 kJ mol^{-1}
= – 1,150 kJ mol^{-1} (to 3 sf)

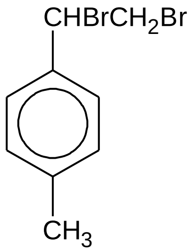
(ii) Suggest a reason for the discrepancy between this value and the value calculated in **b(i)**.

Bond energies quoted in the *Data Booklet* are average values from many different molecules. Hence calculations done by applying the bond energies to specific compounds only give approximate answers.

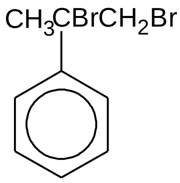
[4]

(c) **R** and **S** are aromatic compounds with the molecular formula $C_9H_{12}O$. Both **R** and **S** react with sodium metal. When heated with acidified $K_2Cr_2O_7$, the reagent does not change colour with **S** but turns green with compound **R** to produce compound **T**, $C_9H_{10}O$. Both **R** and **T** form a pale yellow precipitate with warm alkaline aqueous iodine.

In the presence of concentrated H_2SO_4, **R** and **S** form hydrocarbons **U** and **V** respectively. Both **U** and **V** react with bromine to give **W** and **X** with the following structural formula:



W



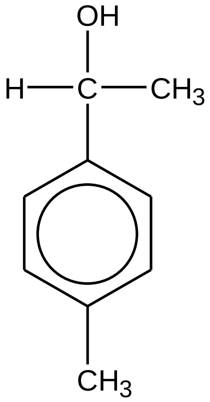
X

Identify and suggest structures for **R**, **S**, **T**, **U** and **V**.

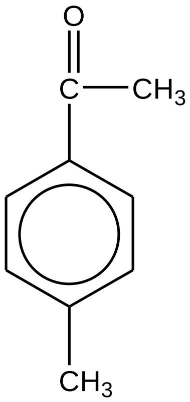
Show how you deduce these structures and suggest the types of reaction that are occurring.

[10]

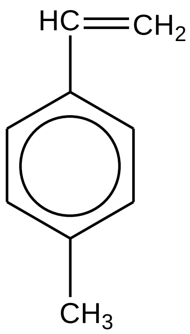
[Total: 20]



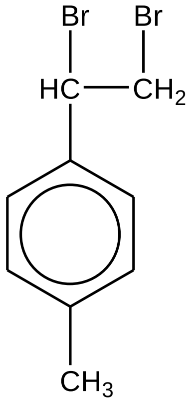
R



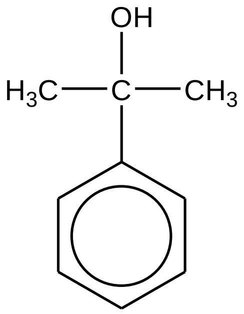
T



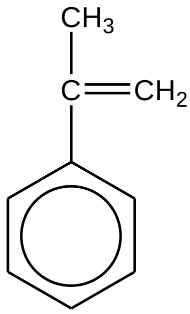
U



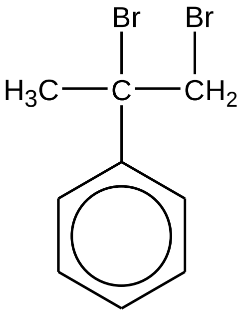
W



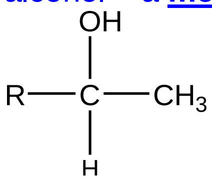
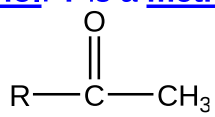
S

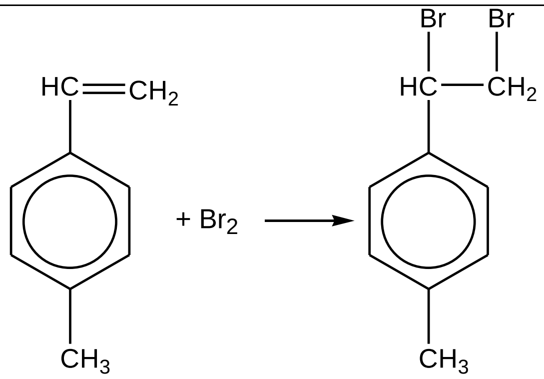


V

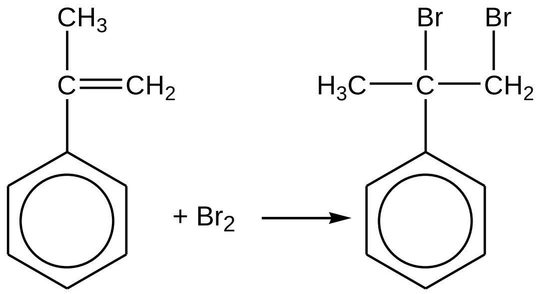


X

Observation	Deductions
R and **S** are aromatic compounds with molecular formula $C_9H_{12}O$. Both **R** and **S** react with sodium metal.	A benzene ring exists in the compound. **An alcohol** functional group exists in compounds **R** and **S**.
When heated with acidified $K_2Cr_2O_7$, the reagent does not change colour with S but turns green with compound **R** to produce compound **T**($C_9H_{10}O$).	**R** undergoes an **oxidation** reaction to give **T** with 1 O atom. **T** is likely to be a ketone.
Both **R** and **T** form a pale yellow precipitate with warm alkaline aqueous iodine.	**R** is a 2° alcohol – a **methyl alcohol**. **T** is a **methyl ketone**.  **R**  **T**
In the presence of concentrated H_2SO_4, **R** and **S** form hydrocarbons **U** and **V** respectively. Both **U** and **V** react with bromine to give **W**, (1,2-Dibromoethyl)-4-methylbenzene and **X**, (1,2-dibromo-1-methyl-ethyl)benzene.	Alcohol **R** and **S** undergo an **elimination** reaction to give alkenes **U** and **V.** **U** and **V** undergo an **addition** reaction with bromine to give a halogenated alkane.



U **W**



V **X**

7 This question is about hydroxyacids.

One of the simplest hydroxyacids is lactic acid, 2-hydroxypropanoic acid. It can be synthesised in the laboratory by the following route.

$$CH_3CHO \xrightarrow{\text{I}} CH_3CH(OH)CN \xrightarrow{\text{II}} CH_3CH(OH)CO_2H$$

lactic acid

(a) State the reagents and conditions needed for reaction **I** and reaction **II**.

[3]

Reaction I: HCN, trace amount of NaOH, 10 – 20 °C
Reaction II: aq HCl, heat

(b) Lactic acid is used to treat warts which are viral growths on dead skin. The value of its acid dissociation constant, K_a, is just high enough for the acid to kill the infection without damaging the live skin underneath.

(i) Write an equation for the reaction between lactic acid and water.
Indicate which species are the acid, the base and their conjugate pairs in the reaction.

$$CH_3CH(OH)CO_2H + H_2O \rightleftharpoons CH_3CH(OH)CO_2^- + H_3O^+$$

acid 1 base 2 base 1 acid 2

(ii) Explain what is meant by the term *acid dissociation constant*, K_a.

$$K_a = \frac{[CH_3CH(OH)CO_2^-][H_3O^+]}{[CH_3CH(OH)CO_2H]} \qquad \text{units} = \text{mol dm}^{-3}$$

The K_a value varies only with temperature.

The larger the K_a value, the stronger the acid.

(iii) Lactic acid is described as a *weak Bronsted acid*. What do you understand by the terms in italics?
It is a weak acid because it ionises partially in water to produce H_3O^+.

[7]

(c) After consuming food or drink containing sugar, the pH in the mouth can decrease from pH 6.8 to a pH of about 4.8 as the sugar is broken down into lactic acid. In time, hydrogencarbonate ions in saliva restore the pH to its original value.

(i) How many times greater is the hydrogen ion concentration in the mouth at pH 4.8 compared with that at pH 6.8?

pH = –lg $[H_3O^+]$

$$\frac{10^{-4.8}}{10^{-6.8}} = 100$$

(ii) Write an equation to show how hydrogencarbonate ions decrease the acidity.

Either equation [1]

$HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$

$HCO_3^- + H^+ \rightarrow H_2CO_3$

$HCO_3^- + H^+ \rightarrow H_2O + CO_2$

[3]

(d) When lactic acid reacts with ethanol to form an ester, the following equilibrium is established.

$CH_3CH(OH)CO_2H(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CH(OH)CO_2CH_2CH_3(l) + H_2O(l)$

A student mixed 0.2 mol of lactic acid in a conical flask with 0.3 mol of ethanol and 1.0 mol of water. He then carefully added concentrated sulfuric acid catalyst. The flask was sealed with a bung and cooled rapidly in an ice bath. It was found that 0.05 mol of lactic acid was present at equilibrium.

(i) Explain the purpose of cooling the conical flask rapidly.

To prevent the shift in position of equilibrium so the amounts of reactants & products can be determined.

(ii) Write an expression for the equilibrium constant, K_c, for this reaction. Calculate the value of K_c.

$$K_c = \frac{[CH_3CH(OH)CO_2CH_2CH_3]\,[H_2O]}{[CH_3CH(OH)CO_2H]\,[CH_3CH_2OH]}$$

Let total volume be V dm^3.

$$K_c = \frac{\left(\frac{0.15}{V}\right)\left(\frac{1.15}{V}\right)}{\left(\frac{0.05}{V}\right)\left(\frac{0.15}{V}\right)} = 23$$

(iii) Suggest and explain what would happen to the position of equilibrium if more lactic acid were added to the conical flask.

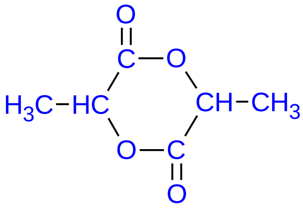
By Le Chatelier's principle, the position of equilibrium shifts right to reduce the concentration of lactic acid.

[5]

(e) On heating in the absence of air, lactic acid loses water to give a single compound **Z**, $C_6H_8O_4$. Compound **Z** is a neutral compound that does not react with both sodium and 2,4-dinitrophenylhydrazine.

Suggest the identity of compound **Z**.

[2]



Two lactic acid molecules can be dehydrated to produce a cyclic ester.

[Total: 20]

8(a)(i) Using the chlorides of magnesium, aluminium and phosphorus as examples, describe the reactions of the chlorides of the third period of the Periodic Table with water. Write equations where appropriate.

$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$

$Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$

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

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

Either $PCl_3(l) + 4H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(l)$

Or $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(l)$

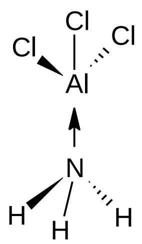
(ii) Suggest what influences the type of bonding present in these three chlorides has on their reaction with water.

Ionic chlorides hydrates in water.

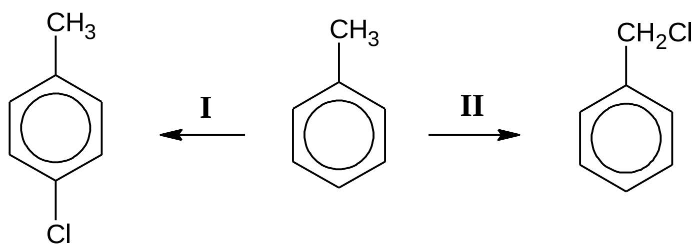
Covalent chlorides hydrolyses in water to give a strongly acidic solution.

(iii) Aluminium chloride forms a compound with ammonia. State the type of bond that is formed during this reaction. Draw a diagram to illustrate the shape of and bonding in the product.

Dative bond.



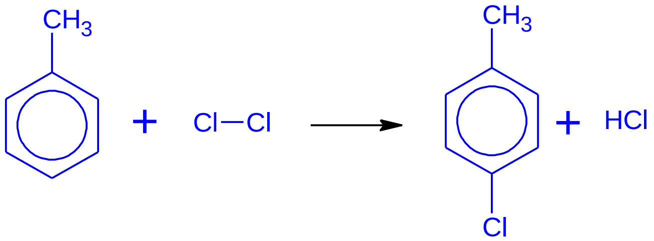
(b) Methylbenzene can undergo halogenation with chlorine as follows:



(i) State the reagents and conditions needed for

- reaction **I**: anhydrous $AlCl_3$, Cl_2
- reaction **II**: UV or heat, Cl_2

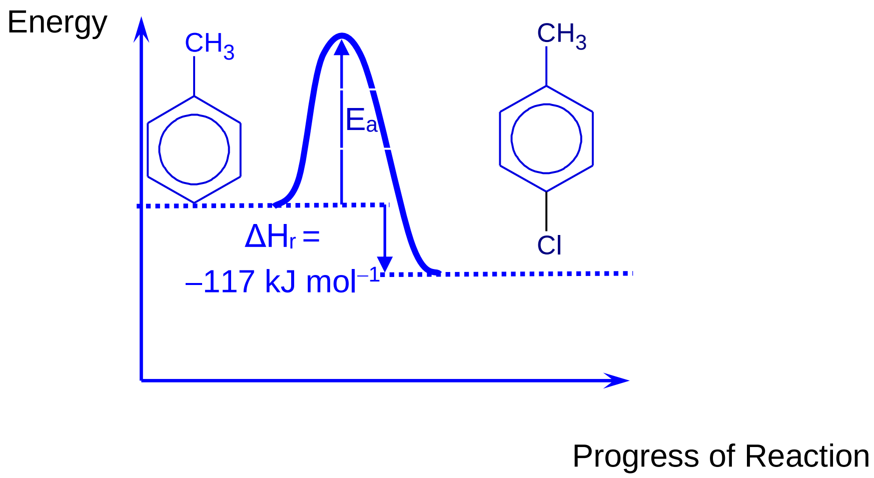
(ii) Use bond energy values from the *Data Booklet* to calculate the enthalpy change for reaction **I**.



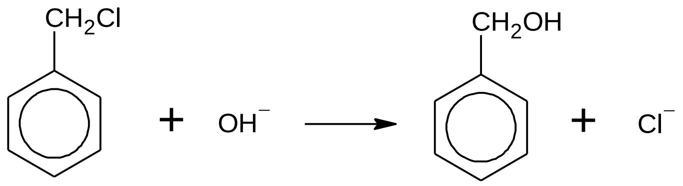
ΔH_r = [BE (C—H) + BE(Cl—Cl)] –[BE(C—Cl) + BE (H—Cl)]

= –117 kJ mol^{-1}

(iii) Using your answer from **b(ii)**, construct a reaction pathway diagram for reaction **I**.



(c) The hydrolysis of $C_6H_5CH_2Cl$ in alkaline solution is represented by the equation below:



In investigations of this reaction, the following results were obtained.

Experiment	Initial concentration of reactants / mol dm^{-3}		Initial rate / mol dm^{-3} s^{-1}
	$[C_6H_5CH_2Cl]$	$[OH^-]$	
I	0.10	0.10	0.024
II	0.10	0.15	0.036
III	0.20	0.10	0.048

(i) Deduce the order of reaction with respect to

- $C_6H_5CH_2Cl$
- OH^-

Hence construct a rate equation for the reaction.

Comparing Expt I and II

- As $[OH^-]$ increases by 1.5 times, initial rate increases by 0.036/0.024 = 1.5 times as well.
- First order wrt OH^-

Comparing Expt I and III

- As $[OH^-]$ increases by 2 times, initial rate increases by 0.048/0.024 = 2 times as well.
- First order wrt $C_6H_5CH_2Cl$

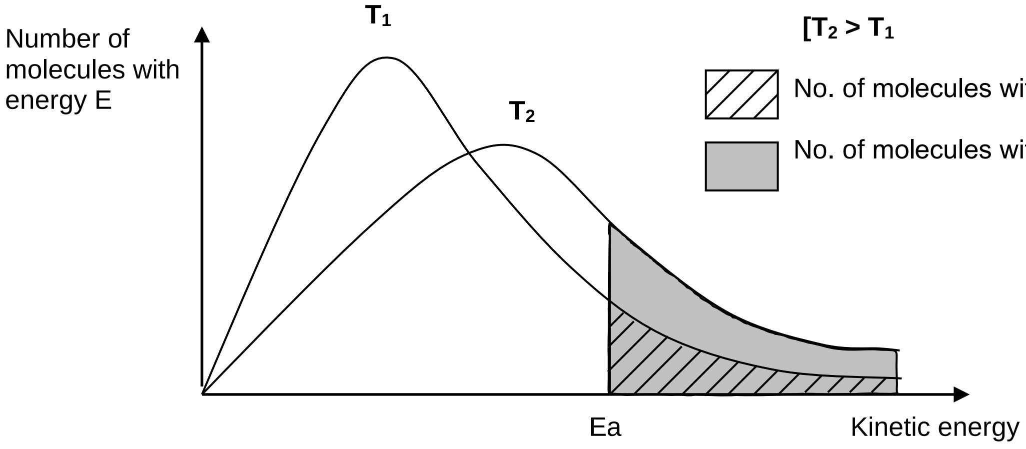
Rate = k $[C_6H_5CH_2Cl]$ $[OH^-]$

(ii) Predict how you would expect the rate of reaction to change if the total volume of the reaction mixture is doubled.

Total volume doubled means concentration of reactant is halved.

Rate = (1/2)2 = ¼ of the original rate.

(iii) With the aid of a suitable diagram, explain why a relative small increase in temperature can cause a large increase in the rate of reaction between $C_6H_5CH_2Cl$ and OH^-.



- An increase in temperature will lead to increase in the average kinetic energy of reactant molecules.

- More molecules will have energy larger than Ea resulting in more collisions with energy greater than Ea.

- Hence frequency of activated collisions will increase. Rate increases.

[7]
[Total: 20]