



HWA CHONG INSTITUTION
Preliminary Examination
Higher 1

CANDIDATE
NAME

CT GROUP

14S

CHEMISTRY

Paper 2

8872/02

2 Sept 2015

2 hours

Candidates answer **Section A** on the Question Paper.

Additional Materials: Data Booklet

Writing paper

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.

Write in dark blue or black pen.

You may use a pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue, correction fluid or tapes.

Section A

Answer **all** 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.

FOR EXAMINERS' USE ONLY

Paper 1	Paper 2		TOTAL
Multiple Choice	Section A (Structured)	Section B (Free Response)	
	Q1 /18	Q4 / 20	
	Q2 /10	Q5 / 20	
	Q3 /12	Q6 / 20	
/ 30	Subtotal / 40	Subtotal / 40	110

This question booklet consists of **14** printed pages.

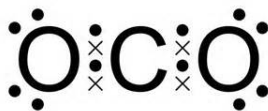
Section A

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

- 1 There is concern over the way the oceans are becoming more acidic as more carbon dioxide dissolves in them

(a) (i) Draw a “dot-and –cross” diagram for carbon dioxide

[1]



- (ii) Use your diagram to state and explain the shape and bond angle of a carbon dioxide molecule.

Linear and 180° ✓

Two areas of electron density (bonding pairs) around central C atom ✓

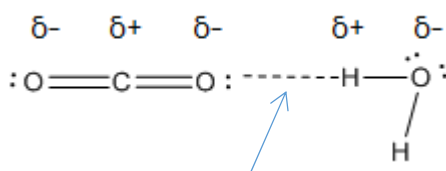
Bonding pairs / electron pairs repel each other; get as far away from each other as possible to minimize repulsion. ✓

..... [3]

- (iii) Carbon dioxide forms hydrogen bonds with water.

Draw a diagram to illustrate this.

Partial charges ; lone pairs ;



Hydrogen bond

- (iv) Carbon dioxide is not very soluble in water. [2]

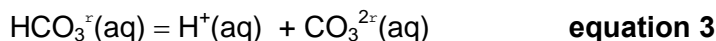
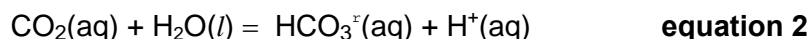
Suggest an explanation for this in terms of hydrogen bonding.

Hydrogen bonds in water ✓

Fewer hydrogen bonds between CO₂ and water. ✓

..... [2]

(b) When carbon dioxide dissolves in water of the ocean, the following reactions occur.



- (i) The reaction in **equation 3** can reach a state of dynamic equilibrium.
Explain what is meant by the term *dynamic equilibrium*.

Rate of forward = rate of backward reaction
Concentrations of reactants and products remain constant (formed at same rate)

[2]

- (ii) Suggest why the balance of $\text{CO}_2(\text{g})$ in the atmosphere and $\text{CO}_2(\text{aq})$ in the oceans cannot be regarded as a dynamic equilibrium.

System is not close / CO_2 moves away from the surface.

.....

[1]

- (iii) Explain why an increase in the concentration of dissolved carbon dioxide leads to an increase in the acidity of the water.

Equilibrium position in equation 2 moves to right, increased H^+ concentration

.....

.....

[1]

- (iv) The pH of the oceans is buffered by the reaction in **equation 2**.

Explain the meaning of buffered.

pH remains almost constant
buffered solution resists pH change when small amounts of acid or alkali added.

[1]

- (v) Give the important condition necessary for this equilibrium to result in buffering, in terms of concentration of species present.

Large HCO_3^- concentration. (reservoir)

Or HCO_3^- concentration similar to the large CO_2 concentration

..... [1]

- (vi) Reference books states that the pH of the oceans has changed from 8.179 in pre-industrial times to 8.069 today.

Calculate the percentage increase in $[H^+]$

$$10^{-8.179} = 6.62 \times 10^{-9}$$

$$10^{-8.069} = 8.53 \times 10^{-9}$$

$$1.91/6.62 \times 100 = 29\%$$

% increase in $[H^+]$ =[1]

- (c) The shells of some sea creatures are made of calcium carbonate.

Use the equations below to explain a possible effect of increased acidity on the shells of these sea creatures.



Equilibrium (position) in equation 5 moves to right with increase H^+

Equilibrium in Equation 4 moves to the right✓

$CaCO_3$ dissolves✓

[2]

- (d) The concentration of a saturated solution of carbon dioxide in water is 3.3×10^{-3} mol per 100 g at room temperature and pressure.
1.0 kg of this saturated solution is boiled, releasing all the CO_2 .

Calculate the volume that this CO_2 would occupy at room temperature and pressure.
One mole of gas at room temperature and pressure occupies 24 dm^3 .

$$3.3 \times 10^{-3} \times 10 \times 24000 = 790 \text{ or } 792 \text{ cm}^3$$

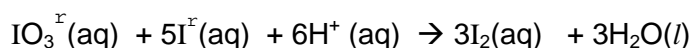
Volume of CO_2 : [1]

Total [18]

- 2 (a) E300 is an oxidant used in white wines. The maximum allowed concentration of E300 in drinks is 150 mg dm^{-3} .

A student performed the following redox titration procedure to find out if a 250.0 cm^3 sample of a drink containing E300 was within this limit.

The sample was acidified followed by the addition of 25.0 cm^3 of $0.00500 \text{ mol dm}^{-3}$ $\text{KIO}_3(\text{aq})$. Excess $\text{KI}(\text{aq})$ was then added to form I_2 in solution.



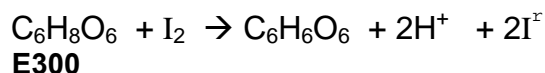
- (i) Calculate the amount, in moles, of iodine, I_2 , formed in this reaction.

$$n \text{ KIO}_3 = 0.00500 \times 25.0 \times 10^{-3} = 0.000125 \text{ mol}$$

$$n \text{ I}_2 = 3 \times 0.000125 = 3.75 \times 10^{-4} \text{ mol}$$

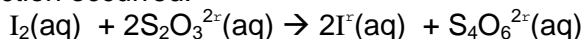
[1]

- (ii) Some of the I_2 formed reacted with the E300 in the 250.0 cm^3 sample of the drink.



The amount of unreacted I_2 was found by titrating with sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$, using starch indicator. At the end point, 20.4 cm^3 of $0.00500 \text{ mol dm}^{-3}$ $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$, had been added.

The following reaction occurred:



Calculate the amount, in moles, of iodine, I_2 , remaining after the E300 had reacted.

$$n \text{ S}_2\text{O}_3^{2-} = 0.00500 \times 20.4 \times 10^{-3} = 0.000102 \text{ mol}$$

$$n \text{ I}_2 = 0.5 \times 0.000102 = 0.000051 \text{ mol} = 5.10 \times 10^{-5} \text{ mol}$$

[1]

- (iii) Determine the concentration of the E300 in the 250.0 cm^3 sample of the drink and hence whether the drink is within the limit allowed.

$$M_r (\text{E300}) = 176$$

$$n \text{ E300} = n \text{ I}_2 - n \text{ I}_2 = 0.000375 - 0.000051 = 0.000324 \text{ mol}$$

a(i) a(ii)

$$\text{conc E300} = 0.000324 \times 1000/250.0 = 0.001296 \text{ mol dm}^{-3}$$

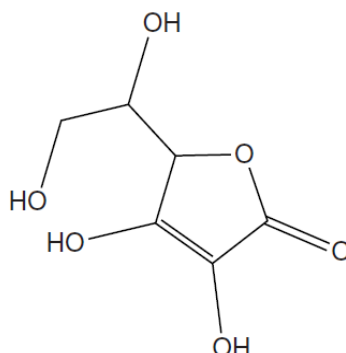
$$0.001296 \times 176 = 0.228 \text{ g dm}^{-3} = 228 \text{ mg dm}^{-3} > 150 \text{ mg dm}^{-3}$$

$$\text{Concentration} = 228 \text{ mg dm}^{-3} \quad \text{units: } \text{mg dm}^{-3}$$

Is the drink within the allowed limit for E300? No

[3]

- (b) E300 has a C=C bond with two different groups on each carbon. It does not, however, show geometrical isomerism whereas 1,2-dichloroethene does.



E300

Explain why 1,2-dichloroethene shows geometrical isomerism **and** suggest a reason why E300 does not.

Restricted rotation around C=C bond

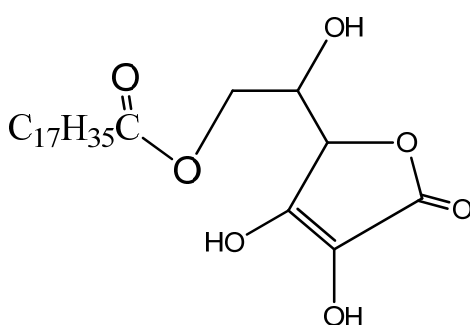
each carbon atom has two different groups/atoms attached to it

The two –OH groups in E300 can only be on the same side of C=C; ring structure will not allow them to be on opposite side/ ring cannot rotate.

[3]

- (c) The **primary** alcohol group in E300 reacts with $C_{17}H_{35}COOH$ to form another antioxidant.

- (i) Draw the structural formula of the compound formed in this reaction.



[1]

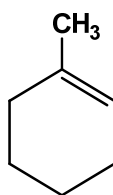
- (ii) What else must be added to a mixture of E300 and $C_{17}H_{35}COOH$, to make the new antioxidant?

Conc H_2SO_4

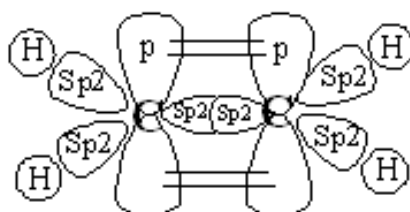
[1]

Total [10]

- 3 1-methylcyclohexene is a naturally occurring hydrocarbon that can be used as a starting material to make other chemicals.



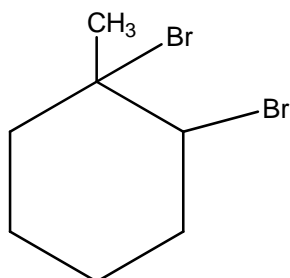
- (a) Draw a labeled diagram to show the orbitals that form the C=C bond in an alkene.



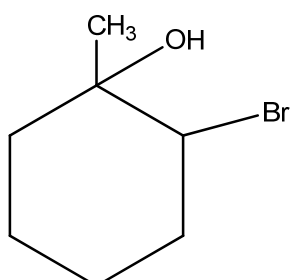
Each carbon consists of three sp^2 hybrid orbitals ; the sigma bond between C-C is due to $sp^2 - sp^2$ orbitals overlap. The pi bond is due to side-way overlap of p orbitals.

- (b) When 1-methylcyclohexene is added to bromine in an inert organic solvent, there is a fast reaction that decolourises the bromine. [1]

Suggest the structure of the organic compound formed.



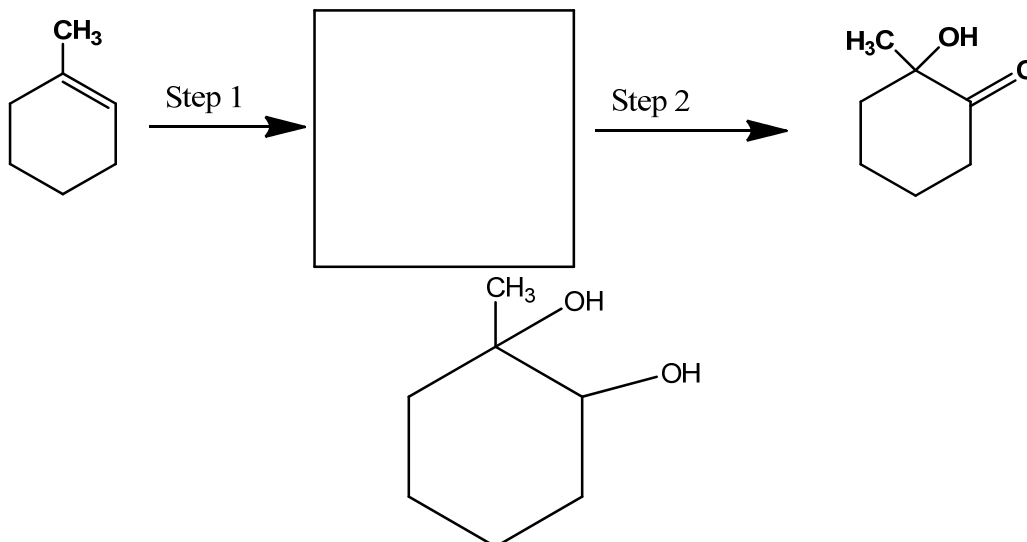
- (c) 1-methylcyclohexene also decolourises aqueous bromine. [1]
When water is present, a different organic compound with molecular formula $C_7H_{13}OBr$ can be formed.
Suggest the structure of this organic compound.



[1]

- (d) State the reagents and conditions needed to convert 1-methylcyclohexene into each of the three organic compounds shown below in two steps. Show the structure of the intermediate organic compound in each case.

(i)

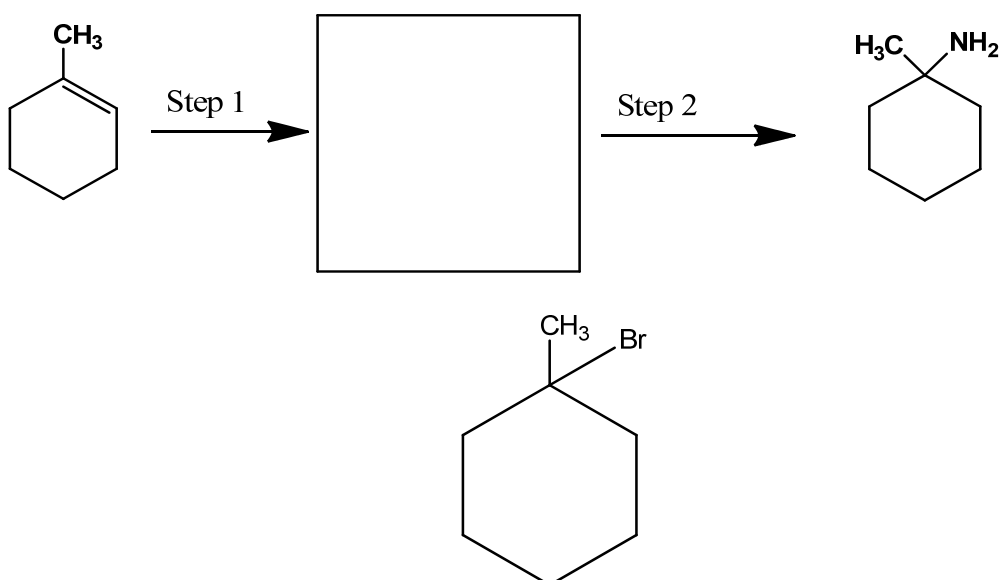


Reagents and conditions

Step 1 ...KMnO₄(aq)/ H₂SO₄(aq) , cold.**Step 2K₂Cr₂O₇(aq) /H₂SO₄(aq) ; heat**

[3]

(ii)

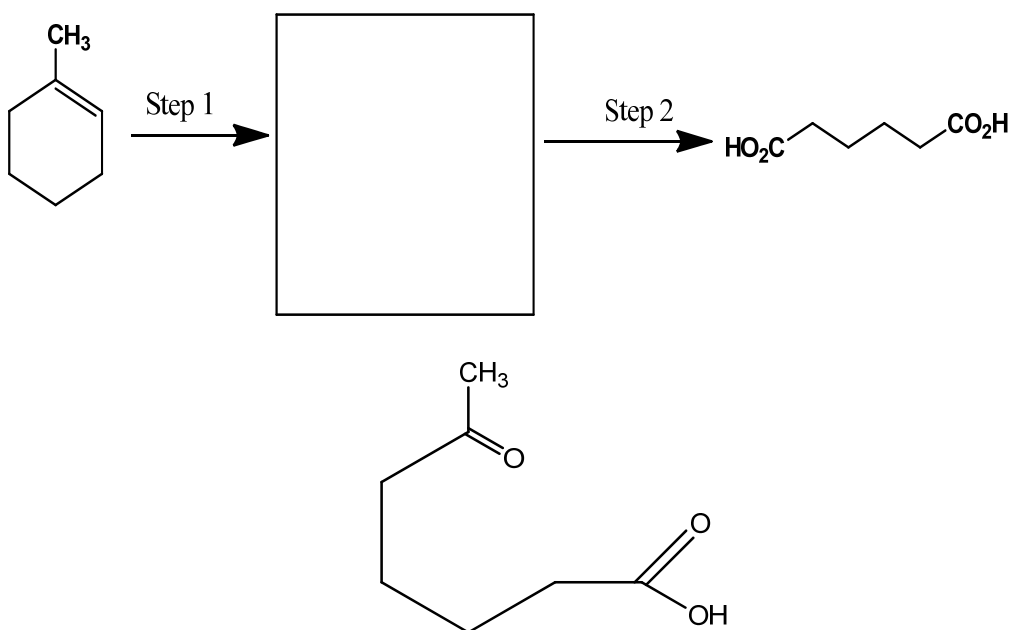


Reagents and conditions

Step 1 HBr(g) room temp...**Step 2 NH₃ in ethanol and heat under pressure**

[3]

(iii)



Reagents and conditions

Step 1 ... $\text{KMnO}_4(\text{conc}) / \text{H}_2\text{SO}_4(\text{aq})$ and heat.....

Step 2 $\text{I}_2(\text{aq}) / \text{NaOH}(\text{aq})$ and warm ; followed by $\text{H}_2\text{SO}_4(\text{aq})$

[3]

Total [12]

End of Section A

SECTION B

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

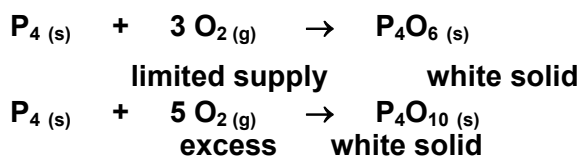
- 4 (a) Describe what you see when magnesium, phosphorus and sulfur are separately burned in air or oxygen.
Write equations for the reactions that occur.

[3]

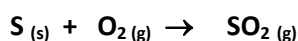
Magnesium burns in air with a bright white light. $2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$ (white solid)

white phosphorus, P_4 , catches fire spontaneously in air, burning with a bright white flame

or red phosphorus (polymeric P) burns on heating with a soft orange flame



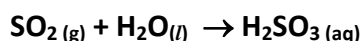
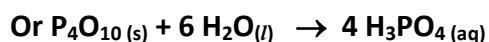
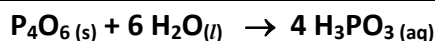
Sulfur burns in air with a blue flame.



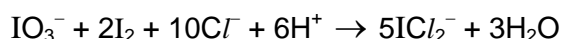
Δ colourless gas with a pungent smell

- (b) The oxides of phosphorus and sulfur resulting from the reactions in (a) both react with water. Write equations, including state symbols for both these reactions.

[2]



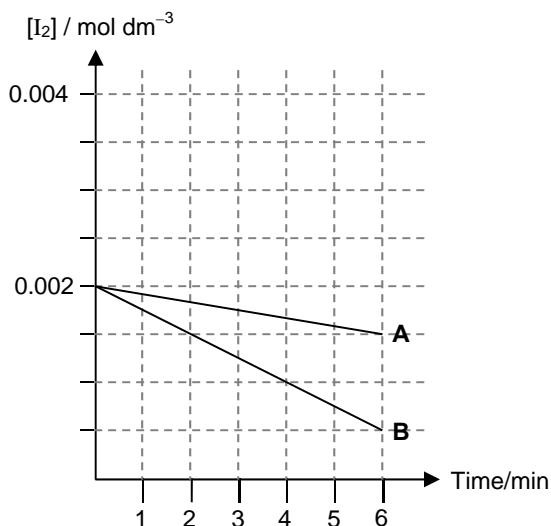
- (c) Potassium iodate(V), KIO_3 , in hydrochloric acid solution oxidises iodine to ICl_2^- .



The rate of this reaction can be measured by following the decrease in colour intensity of brown iodine with the use of a colorimeter.

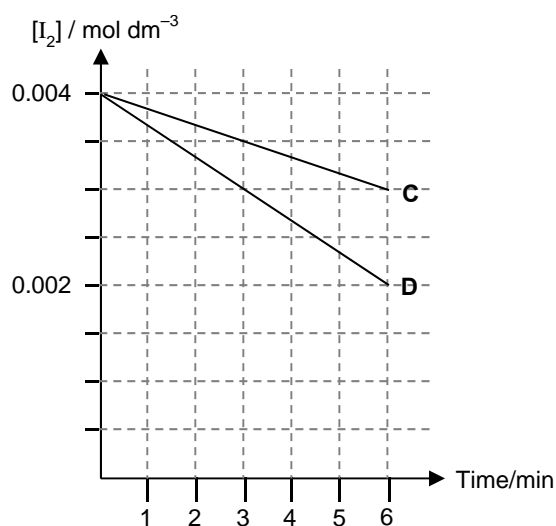
Two sets of experiments were performed in which the initial concentrations of KIO_3 and H^+ were varied. The results are shown below in graphical form.

Set 1



A: [KIO₃] = 0.4 mol dm⁻³
 B: [KIO₃] = 1.2 mol dm⁻³

Set 2



C: [H⁺] = 0.4 mol dm⁻³
 D: [H⁺] = 0.8 mol dm⁻³

- (i) Use the graphs to determine the order of reaction with respect to the concentrations of KIO₃, iodine and H⁺. Show your reasoning clearly.

Since all the graphs obtained are straight line with a negative gradient,

$$\text{reaction rate} = -\frac{\Delta[\text{I}_2]}{\Delta t} = -\text{gradient of graph} \\ = \text{constant}$$

Hence, the reaction is **zero order** wrt I₂.

Consider graph A and graph B.

$$\text{For A, rate} = -\frac{0.0015 - 0.002}{6 - 0} = 8.33 \times 10^{-5} \text{ mol dm}^{-3} \text{ min}^{-1}$$

$$\text{For B, rate} = -\frac{0.0005 - 0.002}{6 - 0} = 2.50 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$$

When [KIO₃] was tripled (1.2/0.4 = 3 times),
 the reaction rate tripled (2.50 × 10⁻⁴ / 8.33 × 10⁻⁵ = 3 times).
 Hence, the reaction is **first order** wrt KIO₃.

Consider graph C and graph D.

$$\text{For C, rate} = -\frac{0.003 - 0.004}{6 - 0} = 1.67 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$$

$$\text{For D, rate} = -\frac{0.002 - 0.004}{6 - 0} = 3.33 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$$

When [H⁺] was doubled (0.8/0.4 = 2 times),
 the reaction rate doubled (3.33 × 10⁻⁴ / 1.67 × 10⁻⁴ = 2 times).
 Hence, the reaction is **first order** wrt H⁺.

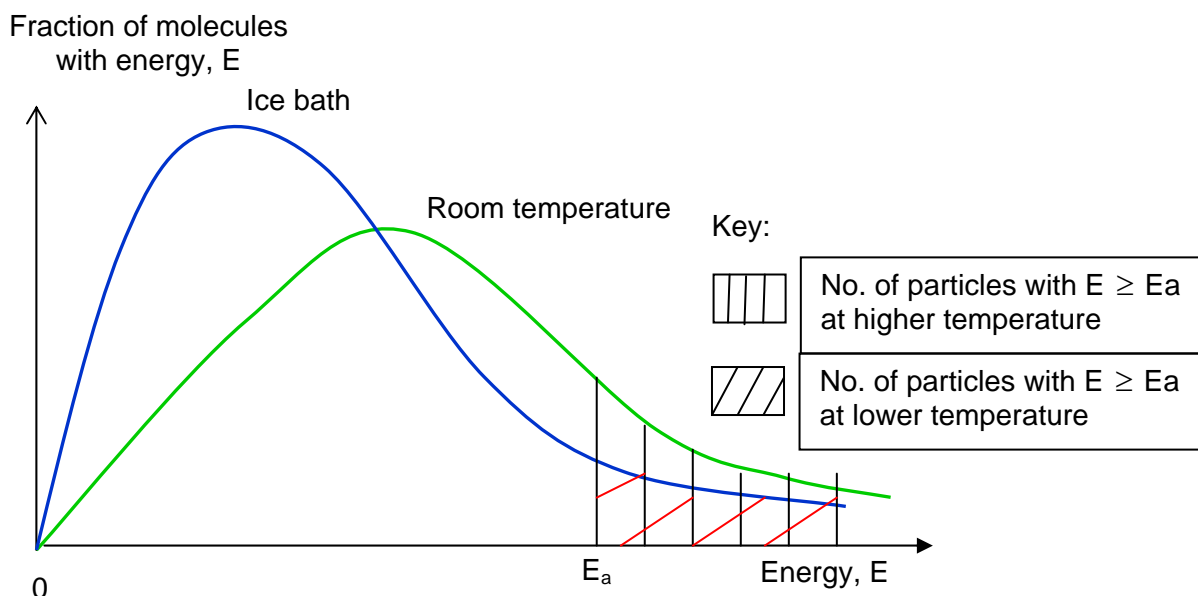
- (ii) Given that the reaction is zero order with respect to Cl^- , write the overall rate equation for the reaction, stating the units of the rate constant.

$$\text{rate} = k[\text{KIO}_3][\text{H}^+]$$

- (iii) Explain how the rate of reaction would change if chlorine is used instead of iodine.

No change as it is zero order wrt iodine.

- (iv)



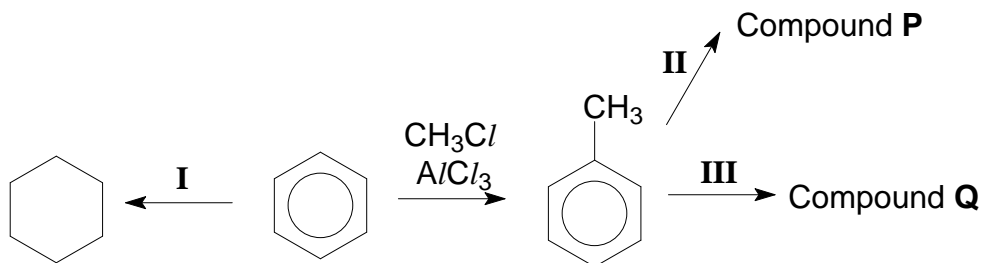
Diagram

When temperature of the reaction decreases,

- **average kinetic energy** of the reactant particles **decreases**
- **less reactant particles with energy $\geq E_a$ less effective collisions**

Since rate of reaction is proportional to the frequency of effective collisions, **rate** of reaction **decreases**

- (d) Benzene and methylbenzene are important starting material for the synthesis of other organic compounds. The following reaction scheme shows some reactions.



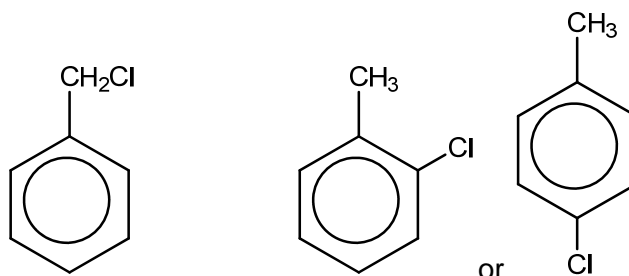
- (i) State the type of reaction that took place for the conversion of benzene to methylbenzene
(electrophilic) Substitution
- (ii) State the type of reaction that took place in reaction I.
Addition

- (iii) Compounds **P** and **Q** are formed from methylbenzene using **two different sets** of reagents. Both are isomers with molecular formula **C₇H₇Cl**

Draw the structures of compound **P** and **Q** and propose the reagents and conditions required for reaction **II** and **III** respectively.

[6]

Total [20]



Reaction II **Cl₂(g) / uv** **Reaction III** : **Cl₂(g) / AlCl₃ ; warm**

- 5 (a) Magnesium, silicon and phosphorus are all elements in Period 3 of the periodic table. Describe the variations in atomic radius, melting point, electrical conductivity and bonding for these three elements.

[5]

Atomic radius decreases across the period:

Melting point increased from Mg to Si and decreased for P

649 °C ; 1410 °C; 44 °C

Mg is good conductor ; Si is semi-conductor ; P is non conductor

Bonding is giant metallic for Mg ; giant covalent for Si and discrete covalent for P₄ with dispersion forces between P₄ molecules.

- (b) In an experiment to determine the enthalpy change of combustion of ethanol, •H_c, a quantity of the fuel was burned underneath a copper can containing 200 g of water. It was found that the temperature of the water rose by 30.0 °C after 1.50 g ethanol had been burned.

- (i) Calculate the apparent •H_c of ethanol from these figures. Ignore the heat capacity of the copper can, and use the figure 4.18 Jg⁻¹K⁻¹ for the specific heat capacity of water.

$$\begin{aligned}\text{Energy absorbed by water} &= mc\Delta T \\ &= (200)(4.18)(30) \\ &= 25080 \text{ J}\end{aligned}$$

$$n_{\text{ethanol}} = 1.50 / (2 \times 12.0 + 5.0 + 16.0 + 1.0) = 0.0326 \text{ mol}$$

$$\therefore \Delta H_c = -(25080/0.0326) = -769 \text{ kJ mol}^{-1} \text{ (3.s.f)}$$

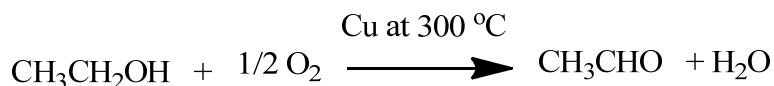
- (ii) The true value of •H_c of ethanol is -1367 kJ mol⁻¹. What is the percentage efficiency of this combustion experiment **and** suggest a reason for the inefficiency.

[5]

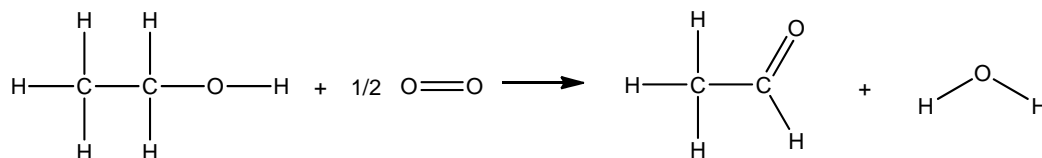
% efficiency is -769/-1367 x 100 = 56.3%

Some heat produced during combustion is lost to the surrounding and absorbed by the copper can

- (c) An industrial method for manufacturing ethanol involves passing ethanol vapour and air over a heated copper catalyst.



- (i) Using bond energy data from the *Data Booklet*, calculate the enthalpy change for this reaction.

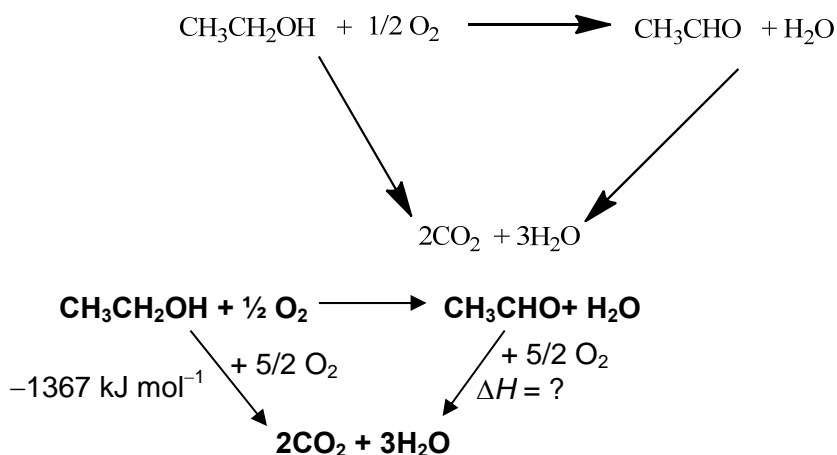


Considering what bonds are different in reactants and products

Bonds broken	B.E. / kJ mol ⁻¹	Bonds formed	B.E. / kJ mol ⁻¹
1 C-H	410	1 C=O	740
1 C-O	360	1 O-H	460
1 O-H		1 O-H	
$\frac{1}{2} \text{O}=\text{O}$	$\frac{1}{2}(496)$		$\Sigma \text{B.E.} = 1200$
	$\Sigma \text{B.E.} = 1018$		

$$\Delta H_r = 1018 - 1200 = -182 \text{ kJ mol}^{-1}$$

- (ii) Using your result from c(i) and the value for ΔH_c of ethanol given in b(ii) deduce the enthalpy change of combustion of ethanal with the aid of the Hess law cycle below.



$$\Delta H_c (\text{ethanal}) = -(-182) + (-1367) = -1185 \text{ kJ mol}^{-1}$$

- (iii) Would you expect the enthalpy change of combustion for ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, to be more or less exothermic than that for ethanal? Explain your answer.

[4]

It is less exothermic, as the combustion of ethanoic acid requires the breaking of the (strong) C-O and O-H bonds, that do not occur in ethanal.

OR As ethanal is more oxidised than ethanol, and its ΔH_c is less exothermic (from (ii)), therefore the even more oxidised ethanoic acid will have an even less exothermic ΔH_c .

- (d) A student is given two containers without labels and told they contain pure sample of two of the following four compounds.

propanoic acid, propanone, propanal, propanol

- (i) Describe **one** test that could show that the samples are propanal and propanol and not the other compounds.

**$\text{K}_2\text{Cr}_2\text{O}_7(\text{aq}) / \text{H}_2\text{SO}_4(\text{aq})$; heat
Orange $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ decolorised to green**

- (ii) Describe **two** other tests that could distinguish between propanal and propanone.

In each case state the required reagent and conditions used and what observations you would make.

[6]

$\text{I}_2(\text{aq}) / \text{NaOH}(\text{aq})$ and warm : yellow ppt of CHI_3 with propanone

Fehling's solution / warm : with propanal a red precipitate of copper(I) oxide

Tollens' reagent (ammoniacal silver nitrate) : with propanal silver mirror is seen.

Total [20]

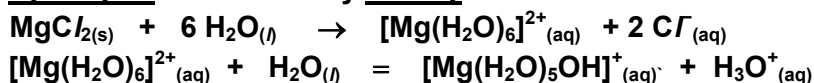
- 6 (a) Both magnesium and silicon react with chlorine to give their chlorides, which differ in their reaction with water.

Write equations for the reactions with water.

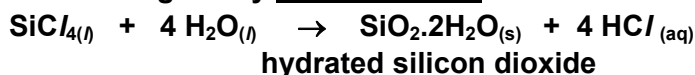
Describe these differences, and explain them in terms of the different structures and types of chemical bonding with the chlorides.

[4]

$\text{MgCl}_{2(\text{s})}$, a giant ionic salt, dissolves in water to form hydrated magnesium ions with a slightly acidic pH. The higher charge density of Mg^{2+} undergoes slight hydrolysis to form a very weakly acidic solution of around pH 6.5.

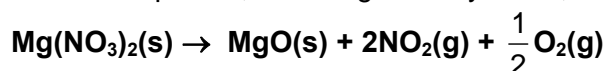


$\text{SiCl}_{4(\text{l})}$, a simple covalent molecule, undergo complete hydrolysis ; reacts with water forming a very acidic solution.



- (b) On heating, magnesium nitrate decomposes to give magnesium oxide, nitrogen dioxide gas and oxygen gas.

- (i) Write an equation, including state symbols, for the above reaction.



- (ii) The lattice energies of sodium bromide is -733 kJ mol^{-1} and that for magnesium oxide is $-3890 \text{ kJ mol}^{-1}$. Explain why the two ionic compounds have different magnitude of lattice energies.

[2]

$$|L.E.| = \frac{q_+ q_-}{r_+ + r_-}$$

Both Mg^{2+} and O^{2-} have higher charges and smaller radii than Na^+ and Br^- respectively.

Hence, the lattice energy of MgO is of a higher magnitude than that of NaBr.

- (c) The water–gas shift reaction is often used to produce hydrogen. This involves the highly exothermic reaction of carbon monoxide with steam to produce carbon dioxide and hydrogen.



The equilibrium constant, K_c is found to be 0.64 at 1000 K.

- (i) Write an expression for K_c for this reaction.

$$K_c = \frac{[CO_2(g)] \cdot [H_2(g)]}{[CO(g)] \cdot [H_2O(g)]}$$

- (ii) A mixture containing 0.80 mol of CO, 0.80 mol of H_2O , 0.40 mol of CO_2 and 0.40 mol of H_2 was placed in a 2 dm³ flask and allowed to come to equilibrium at 1000 K.

Calculate the amount, in moles, of each substance present in the equilibrium mixture at 1000 K.

[4]

Let the change in concentration of CO(g) be x.

	CO(g)	H ₂ O(g)		CO ₂ (g)	H ₂ (g)
Initial conc./ mol	0.80	0.80		0.40	0.40
Change in conc./ mol	-x	-x		+x	+x
Eqm. / mol	0.80-x	0.80-x		0.40+x	0.40+x

[] n/V V= 2 cancelled off

$$0.64 = \frac{(0.40 + x)^2}{(0.8-x)^2}$$

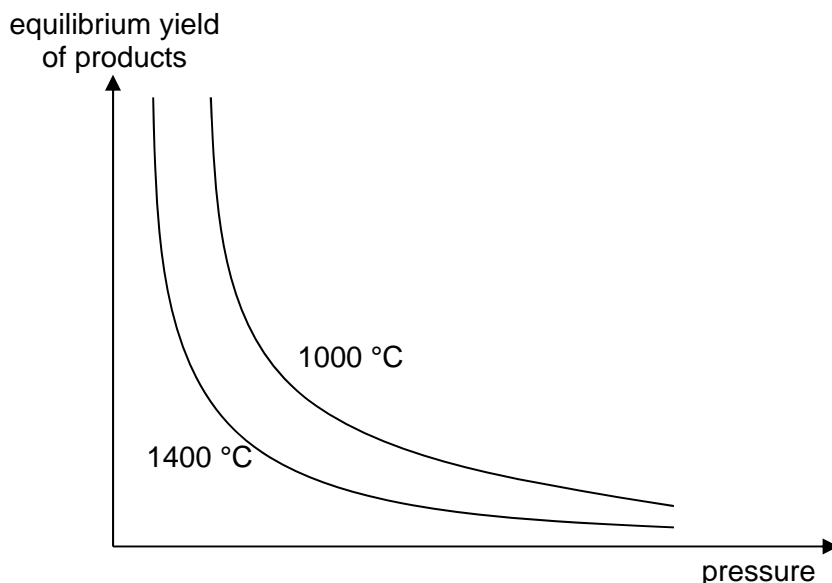
$$0.8 (0.8-x) = (0.4 + x)$$

$$X = 0.133$$

$$n_{CO(g)} = n_{H_2O(g)} = 0.667 \text{ mol}$$

$$n_{CO_2(g)} = n_{H_2(g)} = 0.533 \text{ mol}$$

- (d) The graph below shows the variation in equilibrium yield of the products with temperature and pressure for the water–gas shift reaction.



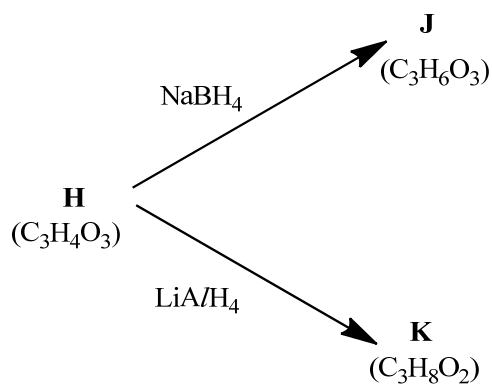
- (i) State *Le Chatelier's Principle*.
***Le Chatelier's Principle* states that if a system at equilibrium is subjected to a change which disturbs the equilibrium, the position of equilibrium will shift in a direction to reduce the change.**
- (ii) Hence, comment on the accuracy of the graph with respect to both temperature and pressure.

[5]

***Le Chatelier's Principle* states that if temperature increases, equilibrium position will shift to favour the endothermic side to absorb the excess heat. Since the forward reaction is exothermic, equilibrium position will shift to the left, resulting in a decrease in equilibrium yield. Hence the graph is correct with respect to temperature**

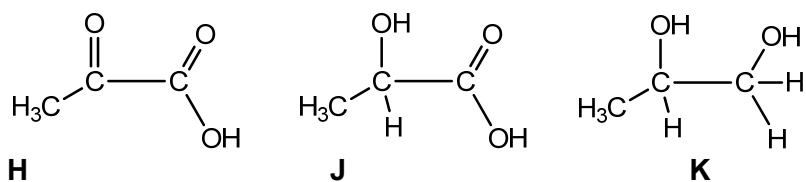
***Le Chatelier's Principle* states that if pressure increases, equilibrium position will shift to side with less gaseous particles to reduce the pressure. However, since the no. of moles of gaseous reactants is equal to the no. of moles of gaseous products, equilibrium yield remain constant with increasing pressure. Hence the graph is incorrect with respect to pressure**

- (e) LiAlH_4 and another complex hydride, sodium borohydride, NaBH_4 , are useful reducing agents in organic chemistry. LiAlH_4 is the more powerful of the two, as the following scheme shows.

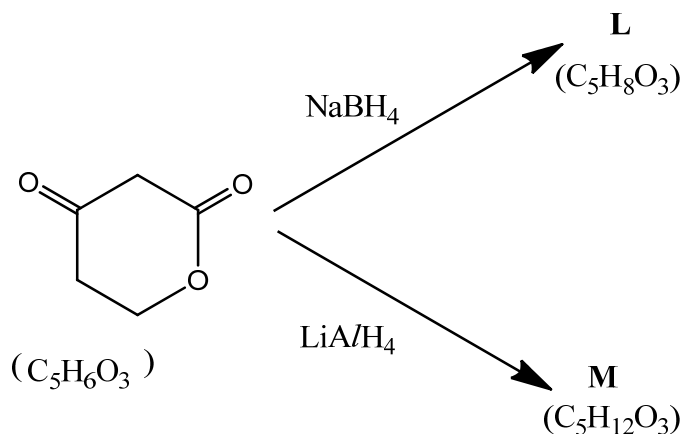


All three compounds **H**, **J** and **K** give a yellow precipitate with alkaline aqueous iodine, and all three react with sodium metal. Compounds **H** and **J** also react with $\text{Na}_2\text{CO}_3(\text{aq})$, but compound **K** does not.

(i) Suggest structures for **H**, **J** and **K**.



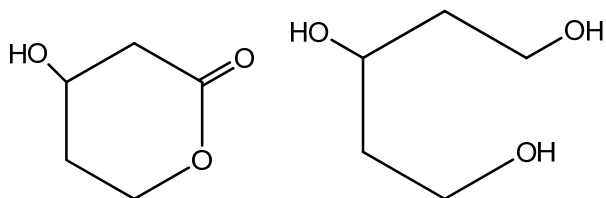
(ii) Predict the structures of the products, **L** and **M**, of the following reactions.



[5]

Total [20]

L and M



The **END**