PRELIMINARY EXAMINATIONS

HIGHER 2

TEMASEK JUNIOR COLLEGE

CANDIDATE NAME									
CIVICS GROUP			/						
CENTER NUMBER	S					INDEX NUMBER			

CHEMISTRY **9729/02**

Paper 2 Structured Questions **28 August 2019**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name 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	**/7**
2	**/10**
3	**/10**
4	**/14**
5	**/20**
6	**/14**
Total	**/ 75**

This document consists of **20** printed pages

1 **(a)** The table below shows the first, second and third ionisation energies of some elements in the Periodic Table.

Element	**First Ionisation energy ($kJ\ mol^{-1}$)**	**Second Ionisation energy ($kJ\ mol^{-1}$)**	**Third Ionisation energy ($kJ\ mol^{-1}$)**
Ca	590	1150	4940
Mn	716	1510	3250
Fe	762	1560	2960
Co	757	1640	3230
Ni	736	1750	3390

(i) Explain why the first and second ionisation energies of the transition metals are relatively invariant.

[2]

(ii) Write the electronic configurations of Ca and Fe atoms at ground state. Explain the differences in the values of the third ionisation energies between iron and calcium.

[2]

(b) Calcium cyanamide, $CaCN_2$, is used as a fertiliser in agriculture. Through hydrolysis in the presence of carbon dioxide, calcium cyanamide produces cyanamide, NH_2CN. Cyanamide can be extracted by organic solvents.

(i) Draw the dot–and–cross diagram for the cyanamide molecule, NH_2CN.

[1]

(ii) With reference to structure and bonding, deduce whether $CaCN_2$ has a higher or lower melting point as compared to NH_2CN.

[2]

[Total: 7]

2 A saturated solution of magnesium methanoate, $Mg(HCO_2)_2$, has a solubility of approximately 143 g dm^{-3} at room temperature. The exact solubility can be determined by titrating magnesium methanoate solution against a standard potassium manganate(VII) solution.

During the titration, the methanoate ion, HCO_2^-, is oxidised to carbon dioxide while the manganate(VII) ion, MnO_4^-, is reduced to Mn^{2+}.

(a) **(i)** Write the overall equation for the reaction between HCO_2^- and MnO_4^- under acidic conditions.

[1]

(ii) Calculate the approximate concentration of HCO_2^- ions present in the saturated solution. [1]

(iii) The titre value from titrating 25.0 cm^3 of saturated magnesium methanoate solution against 0.0500 mol dm^{-3} potassium manganate(VII) solution is found to be too high.

Describe the steps to prepare a suitable solution of magnesium methanoate from the saturated solution. Your plan should include details of quantities measured and apparatus used.

[3]

(b) An industrial chemist introduced 2 atm of carbon dioxide and 2 atm of hydrogen gas into a 1 dm^3 container at 300 K. The temperature is then raised to 900 K, at which the K_p is 0.641.

$$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad \Delta H < 0$$

(i) Calculate the partial pressure of H_2 present at equilibrium at 900 K.

[3]

(ii) Explain if the K_p value at 300 K is higher or lower than 0.641.

[2]

[Total: 10]

3 (a) Sulfur tetrachloride decomposes to sulfur dichloride and a gas that bleaches litmus.

(i) Using the VSEPR theory, deduce and draw the shape of SCl_2. Give a value for the bond angle. [3]

Shape : ____________________

Bond angle : ________________

(ii) State whether the bond angle of SCl_2 is expected to be larger or smaller than SF_2. Explain your answer.

[1]

(b) **(i)** There are two possible molecular arrangements for SCl_4 with different relative stabilities.

Draw these two molecular arrangements in the boxes below, showing clearly the shape around the central atom.

[2]

(I) (II)

(ii) Apply the principles of the VSEPR theory to discuss the relative stabilities of molecular arrangements (I) and (II).

[1]

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(c) SCl_4 combines with BCl_3 to give **X** with the composition by mass: S, 11.0% ; B, 3.7%.

(i) Derive the empirical formula of **X**.

[1]

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(ii) Draw a likely structure of **X**, showing clearly the shape around the central atom(s). State the type of bond formed when SCl_4 and BCl_3 combine to form **X**.

[2]

Type of bond : ____________________

[Total: 10]

4 **(a)** Hydrogen halides are acids resulting from the chemical reaction of hydrogen with one of the halogens.

(i) Briefly explain the trend in the boiling point for hydrogen chloride, hydrogen bromide and hydrogen iodide.

[2]

(ii) By quoting appropriate data from the *Data Booklet*, explain the trend in the thermal stability of the hydrogen halides.

[2]

(b) The chlorides of aluminium and silicon react differently with water to produce acidic solutions.

(i) A sample of aluminum chloride is dissolved in water.

State and explain the pH and the colour observed when universal indicator is added to the resulting solution. Write equations where appropriate.

[3]

(ii) Explain why $SiCl_4$ can be hydrolysed by water.

[1]

(c) In electrophilic substitution reactions, $AlCl_3$ can function as a Lewis acid catalyst to generate the electrophile.
Deduce whether Al_2Cl_6 can also function in the same manner.

[1]

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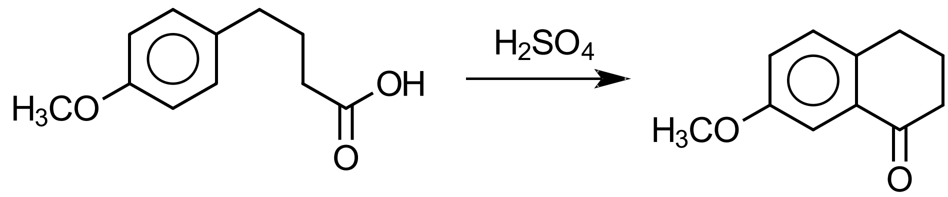
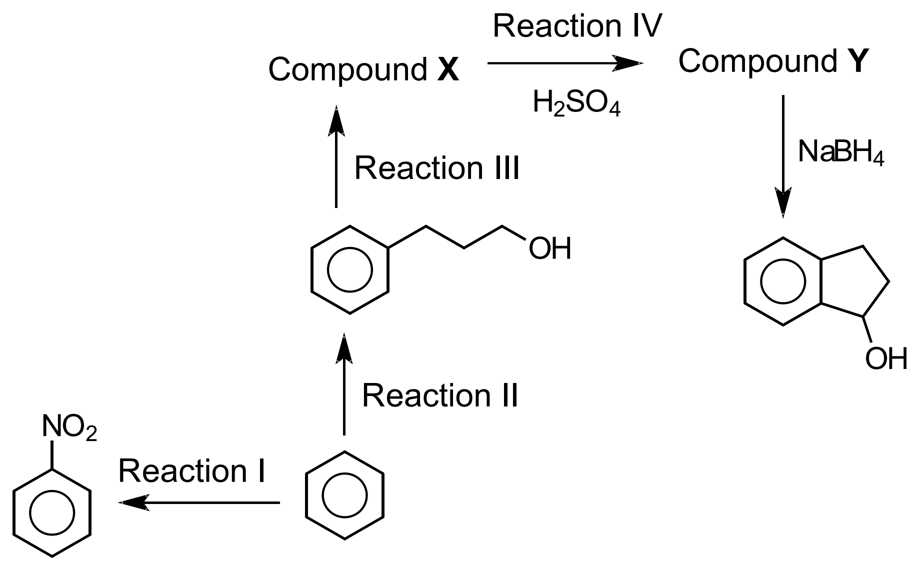
(d) French scientist Charles Friedel and American scientist James Crafts, first discovered Friedel-Crafts Acylation in 1877.

Intramolecular Friedel-Crafts reaction could also work for some carboxylic acids, as seen from the example below.



The synthesis of compound **Y** involves the intramolecular Friedel-Crafts reaction in Reaction **IV**.



Suggest reagents and conditions for Reaction **I** to Reaction **III** and give the structural formula for compounds **X** and **Y**.

[5]

Reaction **I**: ____________________

Reaction **II**: ____________________

Reaction **III**: ____________________

Compound **X**

Compound **Y**

[Total: 14]

[Turn over

5 This question is about the use of catalytic reagents in green chemistry.

Green chemistry is the study and design of chemical processes and products to reduce the use and generation of hazardous chemicals. One principle of green chemistry proposes the use of catalytic reagents over stoichiometric reagents to reduce the amount of by-products and to increase efficiency.

In 1997, Roger Sheldon proposed E factor and Atom Utilisation as indicators of the amount of waste generated in a chemical reaction.

The E factor is defined as the mass of by-products produced per kg of product in chemical industry. The table below shows the typical product mass and E factor for the different industries.

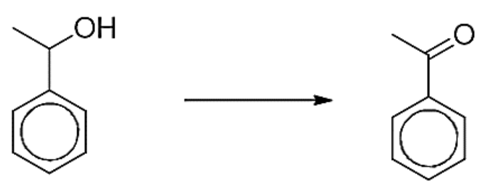
Industry	Typical product mass / 10^3 kg	Typical E factor
Bulk chemicals	10,000	2
Pharmaceuticals	100	50

The Atom Utilisation is defined as

$$\frac{\text{molar mass of the desired product}}{\sum \text{molar mass of all materials produced}} \times 100\%$$

In general, a reaction with a low E factor and a high Atom Utilisation value indicates that less waste is generated.

(a) 1-phenylethanol can be oxidised to phenylethanone via a stoichiometric reaction or via a catalytic reaction.



1-phenylethanol $M_r = 122.0$ → phenylethanone $M_r = 120.0$

Details of each reaction are given in the table below.

Type of reaction	Reagents used	By-product(s)	Atom Utilisation
Stoichiometric reaction	CrO_3 and H_2SO_4	$Cr_2(SO_4)_3$ and H_2O	44%
Catalytic reaction	O_2 and Ruthenium	H_2O	x

(i) Calculate the Atom Utilisation, x, for the oxidation of 1-phenylethanol via catalytic reaction. Hence explain which type of reaction is more efficient for producing phenylethanone.

[2]

The environmental friendliness of a process can be represented by the overall environmental quotient, EQ, of the by-products which is given by

$$\sum_{\text{by-products}} \mathrm{E} \times \mathrm{Q}$$

where E is the E factor and Q is the unfriendliness quotient.

The higher the EQ value, the more toxic the by-product is to the environment. Q values for several substances are given below.

Substance	Q value
$Cr_2(SO_4)_3$	1000
CrO_3	1000
Ru	100
H_2SO_4	100
H_2O	1
O_2	1

(ii) 1-phenylethanol is oxidised to phenylethanone in both bulk chemical and pharmaceutical industry using the stoichiometric reaction.

Determine which industry is more environment-friendly in producing phenylethanone, showing clearly all workings.

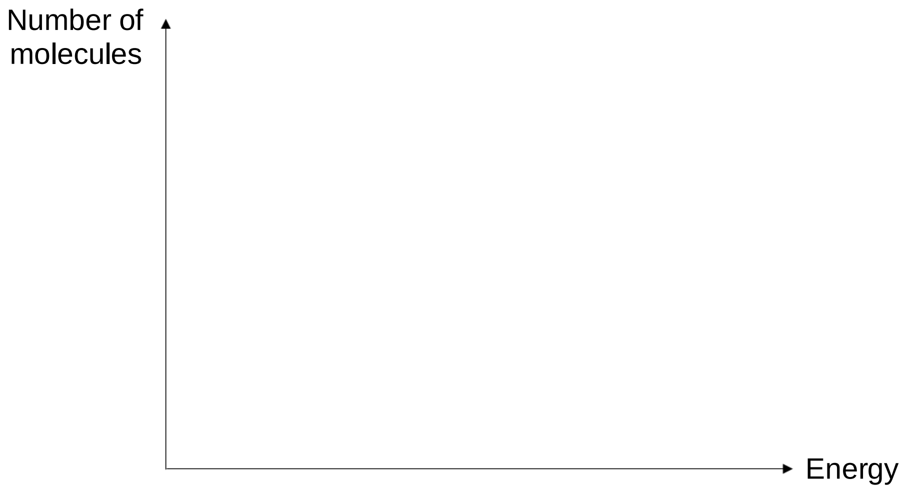
[2]

(b) Catalysts such as ruthenium are known as *heterogeneous* catalysts.

(i) Outline briefly how this type of catalyst speeds up the reaction between oxygen and 1-phenylethanol. [2]

(ii) Sketch a suitable Boltzmann distribution curve below and hence explain the effect of ruthenium on the rate constant of the reaction.

[3]



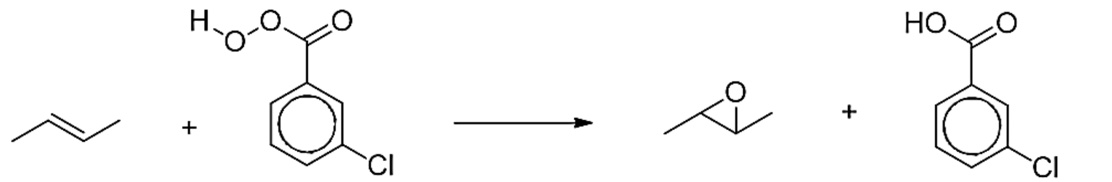
(iii) The reaction rate between oxygen and 1-phenylethanol can be increased by pumping more oxygen gas into a constant-volume reaction vessel.

On the same graph in **(b)(ii)**, sketch a new curve to represent energy distribution of reactants when more oxygen gas is added. Label the graph clearly as **(b)(iii)**.

[1]

(c) Epoxidation is a reaction to synthesise epoxides from alkenes.

Trans-2,3-epoxybutane, an epoxide, is synthesised by reacting trans-but-2-ene with m-CPBA.



trans-but-2-ene   *m*-CPBA   *trans*-2,3-epoxybutane   *meta*-chlorobenzoic acid

To study the kinetics between trans-but-2-ene and m-CPBA, several experiments were conducted using different volumes of m-CPBA and trans-but-2-ene, topped up with suitable volumes of hexane solvent. The set-up is placed on a piece of paper with an "X" mark.

The product, meta-chlorobenzoic acid, has low solubility in hexane and is precipitated out as soon as it is formed and the reaction is monitored by measuring the time taken for the "X" to disappear.

Experiment	Volume of trans-but-2-ene / cm^3	Volume of m-CPBA / cm^3	Volume of hexane / cm^3	Time taken for "X" to disappear / s
1	20	10	15	10.0
2	20	15	10	6.7
3	10	5	30	40.0
4	40	20	30	y

(i) Briefly explain the low solubility of the product meta-chlorobenzoic acid in hexane. [2]

(ii) Determine the order of reaction with respect to trans-but-2-ene and m-CPBA. Showing your workings clearly.

[2]

(iii) Hence, construct a rate equation for the reaction between trans-but-2-ene and m-CPBA.

[1]

(iv) State the value of y in experiment 4.

[1]

(d) A thermal experiment was conducted to determine the enthalpy change of combustion of trans-2,3-epoxybutane.

8.26 g of trans-2,3-epoxybutane was burnt in excess oxygen and the temperature of water in the bomb calorimeter was measured. The following data was collected.

Heat capacity of calorimeter: 154 J K^{-1}

Volume of water: 400 cm^3

Temperature rise: 32 ^{o}C

The experiment was only 20% efficient.

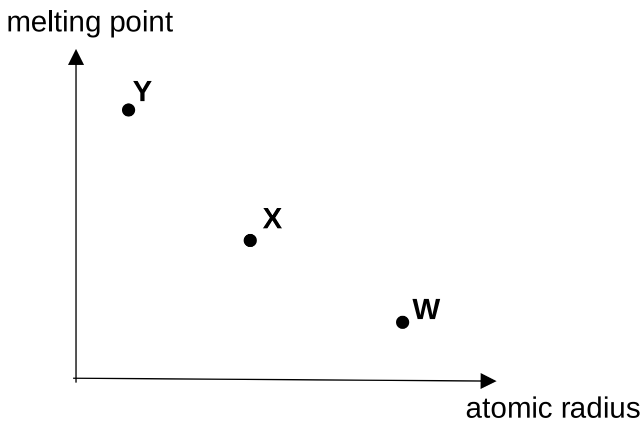
(i) Calculate the enthalpy change of combustion of trans-2,3-epoxybutane.

[3]

(ii) Suggest one modification to the set-up so that the experiment can be made more efficient. [1]

[Total: 20]

6 **(a)** **W**, **X** and **Y** represent consecutive elements in Period 3. The following shows a graph of their melting points plotted against the atomic radius (not drawn to scale).



The oxide of **Y** is insoluble in water but dissolves when the oxide of **W** is subsequently added.

(i) Suggest the identities of **Y** and **W**. [1]

(ii) Explain the above observations and write equations for all the reactions that has occurred. [3]

(b) An experiment was conducted to investigate the thermal decomposition of Group 2 carbonates.

Equal amounts of carbonates of magnesium, strontium and barium were heated for two minutes. The gas produced was bubbled through calcium hydroxide and the time taken for the white ppt to be formed was recorded as follows:

Group 2 Carbonate	$MgCO_3$	$SrCO_3$	$BaCO_3$
Time taken for white ppt to be formed / s	40	240	never

(i) Using relevant data from the *Data Booklet*, explain the results obtained.

[3]

(ii) If the experiment was repeated with calcium carbonate under the same conditions, suggest a value for the time needed for the white ppt to be observed.

[1]

(c) Inorganic reducing agents such as lithium aluminium hydride and sodium borohydrides are commonly used in organic chemistry.

A student attempted to synthesise propanal by reducing propanoic acid. He found that there was no reaction when sodium borohydride was used and the product formed with lithium aluminium hydride was not propanal.

(i) Explain why lithium aluminium hydride can be used to reduce propanoic acid but not sodium borohydride.

[1]

(ii) Draw the displayed formula of the organic product formed instead of propanal.

[1]

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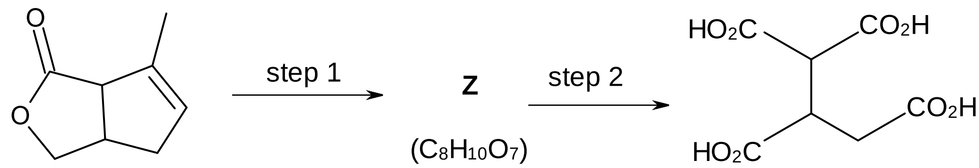
(d) Carboxylic acids can be made from a variety of other compounds. In the following reaction scheme, identify the intermediate compound **Z** and suggest reagents and conditions for the two steps.



[3]

Step 1: ____

Step 2: ____

Compound **Z**

(e) Carboxylic acids are also useful compounds to synthesise esters such as propyl ethanoate which is responsible for the smell of pears and is used as a flavor additive.

In the synthesis of propyl ethanoate, the oxygen atom in a suitable alcohol is labelled with the oxygen isotope, ^{18}O.

Write an equation for this reaction, indicating clearly where the ^{18}O atom(s) are.

[1]

[Total: 14]

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