Catholic Junior College
JC2 Preliminary Examination
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY 9729/02

Paper 2 Structured Questions

Friday 17 August 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

WORKED SOLUTIONS

This document consists of **19** printed pages.

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

1 In atmospheric chemistry, NO_x is a generic term for the nitrogen oxides that are most prevalent for air pollution, namely nitric oxide (NO) and nitrogen dioxide (NO_2). These gases contribute to the formation of smog and acid rain, as well as tropospheric ozone. In the atmosphere, dinitrogen pentoxide (N_2O_5) is an important reservoir of the NO_x species that are responsible for ozone depletion.

(a) In the laboratory, the kinetics involving the decomposition of N_2O_5 into NO_2 and O_2 can be investigated by dissolving it in an organic solvent such as tetrachloromethane, CCl_4. The decomposition of N_2O_5 was found to be a first-order reaction.

$$2N_2O_5 \rightarrow 4NO_2(g) + O_2(g)$$

Table 1.1 below shows the variation of $[N_2O_5]$ with time.

Time / s	$[N_2O_5]$ / mol dm^{-3}	ln $[N_2O_5]$
0	0.910	**-0.0943**
300	0.750	**-0.288**
600	0.640	**-0.446**
1200	0.440	**-0.821**
3000	0.160	**-1.83**

Table 1.1

(i) State the rate equation for the decomposition of N_2O_5.

Rate = k[N_2O_5] ..... [1]

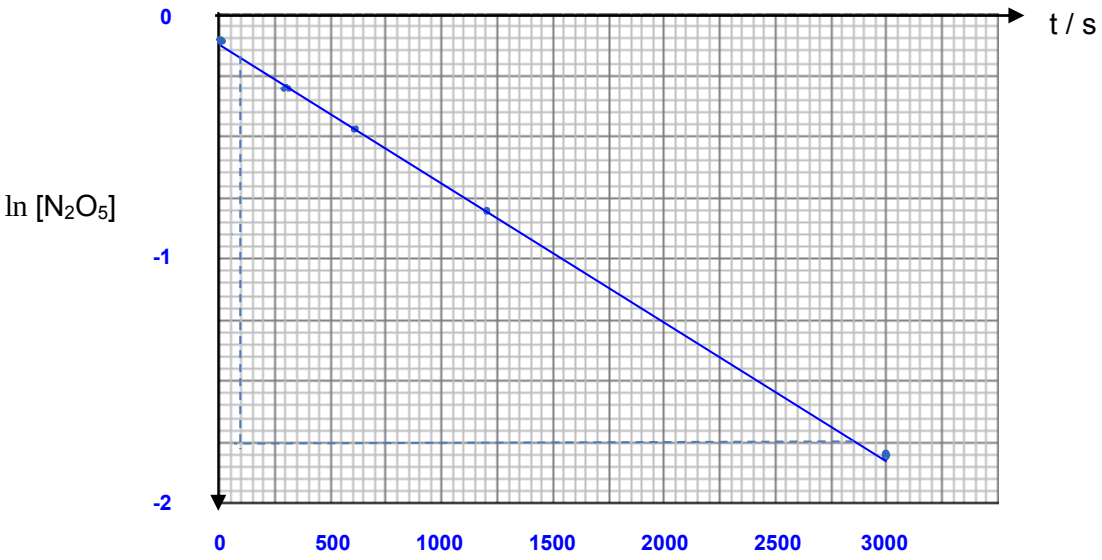
(ii) The rate equation for the decomposition of N_2O_5 can also be expressed as:

$$\ln [N_2O_5]_t = -kt + \ln [N_2O_5]_o$$

where $[N_2O_5]_o$ is the initial concentration of N_2O_5 and $[N_2O_5]_t$ is the concentration of N_2O_5 at time, *t*.

Using relevant data in Table 1.1, calculate the values for ln $[N_2O_5]$ and complete Table 1.1. [1]

(iii) Using the following axes and relevant data in Table 1.1, plot a graph of ln $[N_2O_5]$ against time (in second), showing how the concentration of N_2O_5 changes with time.



[2]

(iv) Using your graph, determine a value for the rate constant, k, for the decomposition of N_2O_5. State the units of k clearly. [2]

Using the points (100, -0.155) and (2850, -1.75)

k = – gradient

$$= -\left[\frac{-0.155-(-1.75)}{100-2850}\right]$$

$$= 5.80 \times 10^{-4}\ s^{-1}$$

(v) Hence determine a value for the half-life of the decomposition of N_2O_5. State the units clearly. [1]

$$t_{1/2} = \frac{\ln 2}{k}$$

$$= \frac{\ln 2}{5.80 \times 10^{-4}}$$

$$= 1195\ s$$

(vi) Outline another experiment to determine the rate constant, k, for the decomposition of N_2O_5 in tetrachloromethane.

You are provided with the same solution of N_2O_5 used in the experiment described in **(a)**.

No details regarding use of specific glassware are required.

1. Measure the volume of gases (NO_2 and O_2) produced OR the colour intensity of the brown NO_2 gas (using a colorimeter) at regular time intervals from the start of reaction

2. Plot a graph of "volume of gases produced against time" OR "colour intensity against time" and determine the half-life from the graph.

3. Use the equation $t_{1/2} = \frac{In2}{k}$ to determine the value of k.

[2]

(b) The NO_2 produced in the decomposition reaction in **(a)** can exist in equilibrium with dinitrogen tetroxide (N_2O_4):

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

An experiment was conducted at 25 °C by varying initial concentrations of N_2O_4 and NO_2 contained in a closed reaction vessel. The initial and equilibrium concentrations of the two gases are shown in Table 1.2.

Experiment No	Initial concentration / mol dm^{-3}		Equilibrium concentration / mol dm^{-3}	
	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$[NO_2]$
1	0.000	0.200	0.0898	0.0204
2	0.600	0.040	0.594	0.0523
3	0.500	0.030	0.491	0.0475
4	0.446	0.050	0.448	0.0457
5	0.670	0.000	0.643	0.0547

Table 1.2

(i) State *Le Chatelier's Principle*.

***Le Chatelier's Principle* states that if a *change* (e.g. change in concentration, pressure and temperature) is made to a system *in equilibrium*, the system reacts in such a way as to tend to oppose the change, and a *new equilibrium* is formed.** [1]

(ii) State what will be observed when the pressure in the reaction vessel is decreased.

The brown colour of the gas (NO_2) darkens.

.....[1]

(iii) Identify the experiment that gives the initial concentration of N_2O_4 : NO_2 in the ratio 15:1.

Experiment 2

.....[1]

(iv) Based on the experiment identified in **(b)(iii)**, calculate a value for the equilibrium constant, K_c. [1]

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$
$$= \frac{(0.0523)^2}{(0.594)}$$
$$= 4.60 \times 10^{-3} \text{ mol dm}^{-3}$$

(v) For reversible reactions involving gases, the concentrations of the gaseous reactants and products can also be expressed in terms of their partial pressures, and the value of the corresponding K_p can then be determined. K_p and K_c is related by the following expression:

$$K_p = K_c(0.0821T)^{\Delta n}$$

where Δn = moles of gaseous products – moles of gaseous reactants based on given stoichiometric equation and T is temperature in Kelvin.

Using your answer in **(b)(iv)** and the above expression, calculate a value for the K_p for the reversible reaction between N_2O_4 and NO_2.

$$K_p = K_c(0.0821T)^{\Delta n}$$
$$= (4.60 \times 10^{-3})(0.0821)(298)^{(2-1)}$$
$$= 0.113$$

[2]

[Total: 15]

2 **(a)** Marine organisms such as crabs use peptide signaling molecules such as glycyl-L-histidyl-L-lysine (GHK) to detect predators. In order for this peptide signaling molecule to function in water, it must exist in the form of a zwitterion.

However, due to the increase in carbon dioxide levels in the ocean, the pH of the ocean decreases as shown in Fig. 2. This affects the structure and function of the peptide signaling molecule and thus affecting the survival of these marine organisms.

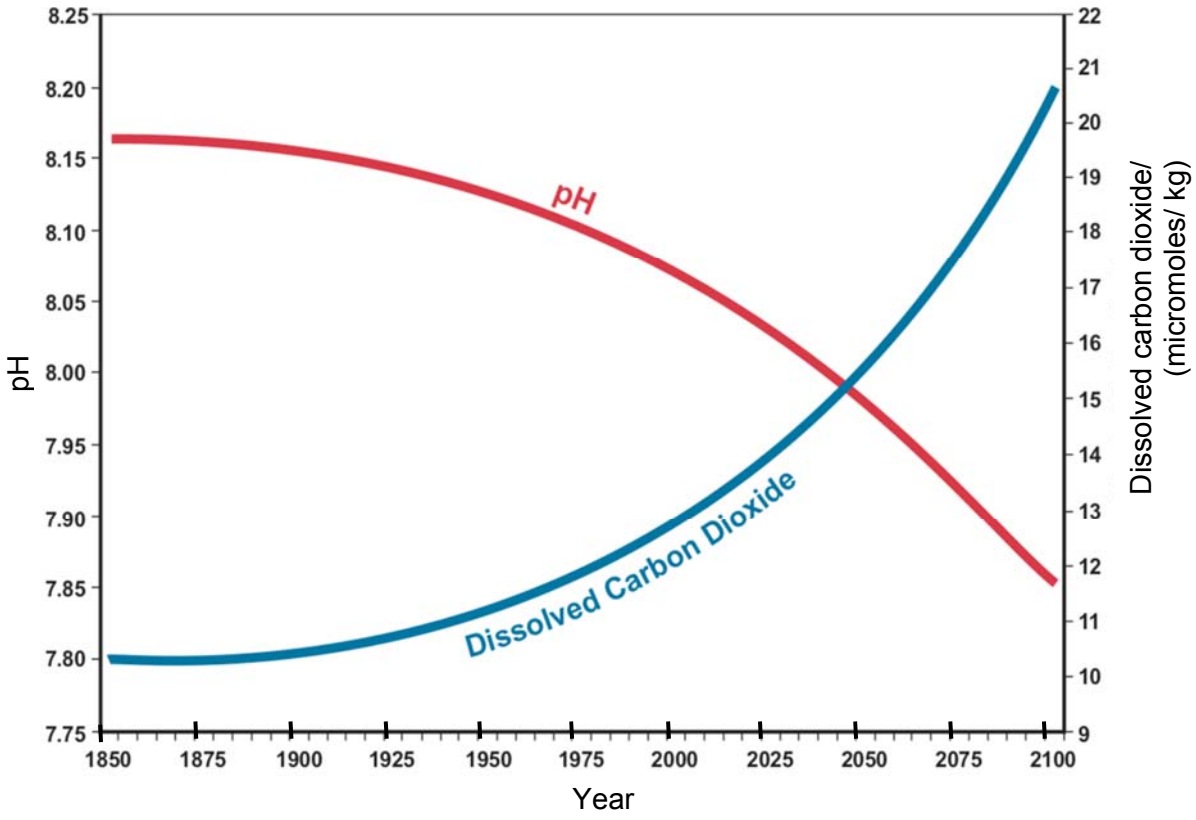


Fig. 2

(i) State what is meant by a *zwitterion*.

Zwitterion is a species where it is dipolar ion and have no nett charge. [1]

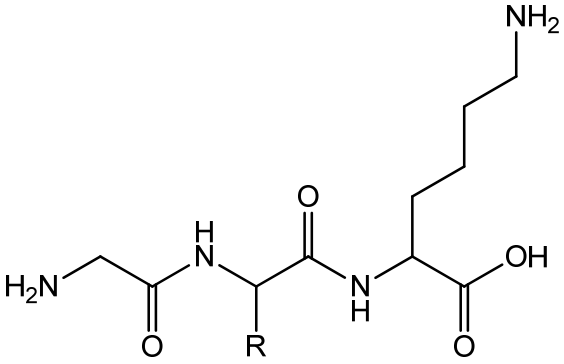
(ii) Explain briefly why GHK, as a *zwitterion*, is highly soluble in water.

GHK as a zwitterion is able to form ion-dipole attraction with water molecules. [1]

(iii) Write an equation showing how the pH of the ocean decreases due to rising concentration of CO_2.

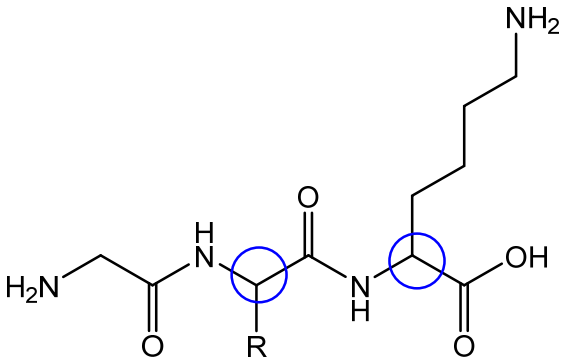
$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$ [1]

The structure of GHK is shown below where R, which is the histidine side chain, need not be considered for this question.

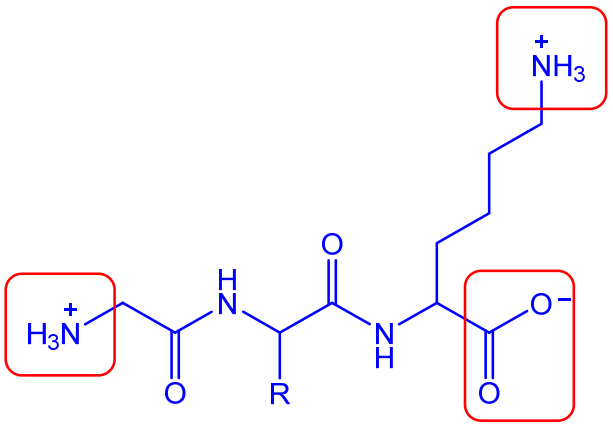


GHK

(iv) Circle any chiral carbon atom on the above structure, GHK. [1]



(v) There can be three pK_a values associated with GHK: 2.80, 7.98, 11.44. Make use of these pK_a values to suggest the major species present in solutions of GHK at pH 7.

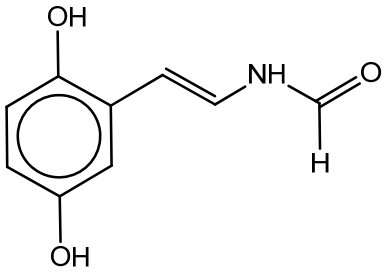


[2]

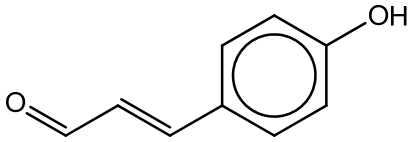
(vi) Use the graph in Fig. 2 to determine from which year onwards more than 50% of GHK in marine organisms no longer can function as a signaling molecule. Explain why this is so.

2050. For GHK no longer function as a signaling molecule, it cannot exist as a zwitterion which both the $-NH_2$ groups are protonated. Since the pKa value of $-NH_2$ is 7.98, the pH value lower than that will result in $-NH_2$ to be protonated. [2]

(b) Bioactive molecules containing dehydrotyrosine derivatives such as erbstatin and 4-hydroxy cinnamaldehyde found in marine organisms are responsible for antibacterial properties.



erbstatin

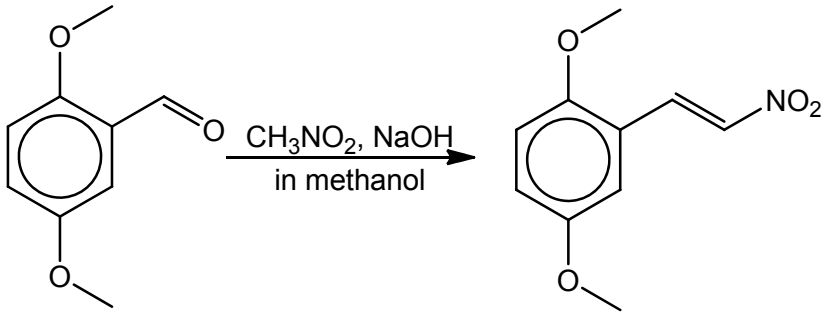


4-hydroxy cinnamaldehyde

(i) State and explain whether erbstatin or 4-hydroxy cinnamaldehyde has a higher boiling point.

Erbstatin has a higher boiling point since it can form more extensive intermolecular hydrogen bonds therefore requires more energy to overcome the intermolecular hydrogen bonds in Erbstatin compared to 4-hydroxy cinnamaldehyde. [3]

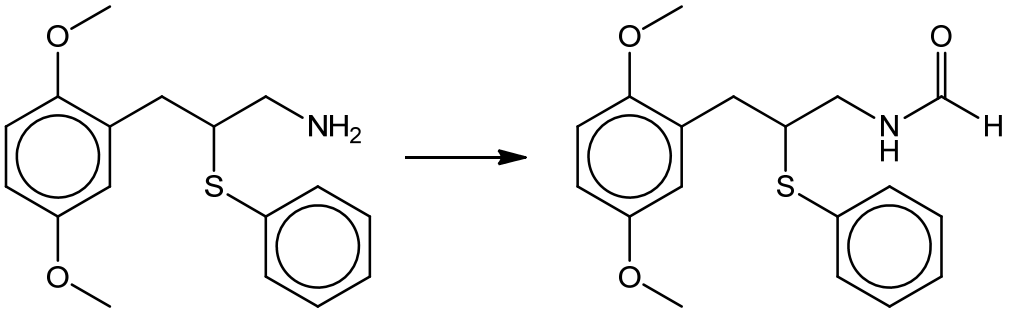
The synthesis of erbstatin involved the following step.



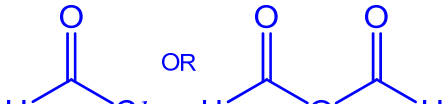
(ii) Given that NaOH is used as a base to form $^-CH_2NO_2$ as a nucleophile, suggest the type of reaction in the above step.

Condensation OR Addition-elimination [1]

Another step in the synthesis of erbstatin is shown below.

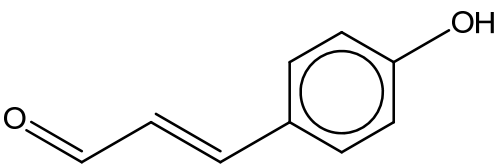


(iii) Suggest suitable reagents for the above step.

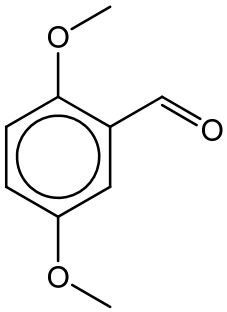


[1]

(iv) Describe a simple chemical test to distinguish between 4-hydroxy cinnamaldehyde and 2,5-dimethoxybenzaldehyde as shown below.



4-hydroxy cinnamaldehyde



2,5-dimethoxybenzaldehyde

Add neutral $FeCl_3$ to separate test tubes containing each sample.

Purple coluration is observed with erbstatin. No purple colouration observed with 2,5-dimethyoxybenzaldhyde.

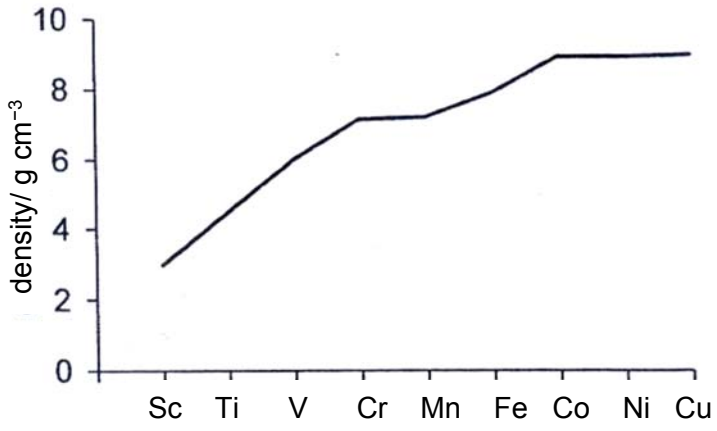
[2]

[Total: 15]

3 **(a)** d-block elements are remarkably similar to each other in physical properties. In general, they are hard, dense and good conductors of heat and electricity. Transition elements belong to d-block elements in the Periodic Table.

Although all d-block elements are metals, they do show significant physical differences when compared to s-block elements i.e., Group 1 and 2 metals.

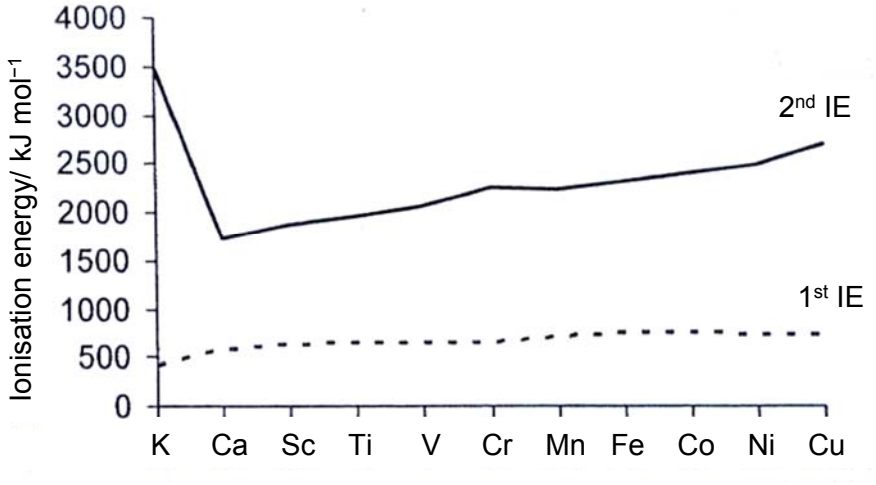
The graph below shows the densities of the elements Sc to Cu.



(i) Suggest why the densities of the elements increase from Sc to Cu.

From Sc to Cu, relative atomic mass increases and atomic radius decreases slightly(or remain invariant). The elements have a more close-packed structure and thus have a higher mass per unit volume, which is density. [2]

(ii) The graph below shows the first (dashed line) and second (solid line) ionisation energies (IE) for the element K to Cu inclusive.



Explain why the first ionisation energy remains relatively constant from Sc to Cu.

From Sc to Cu, the number of protons increases, hence the nuclear charge increases. Electrons are added to the inner 3d subshell which provides increased effective shielding between nucleus and valence 4s electron. Therefore, increase in nuclear charge almost cancel out the increase in shielding effect (effective nuclear charge increases slightly). Energy required to remove the outer 4s electrons from Sc to Cu is almost constant.

[2]

(iii) Explain briefly why is the second ionisation energy of potassium so much higher than that of the other elements.

The second electron in K to be removed is from an inner 3p orbital which is more strongly attracted by the nucleus as it experiences less shielding.

[1]

(b) Scandium, copper and zinc are d-block elements. However, copper is a transition element while scandium and zinc are not.

(i) Define the term *transition element*.

A transition element is a d-block element which forms one or more stable ions with partially filled d subshells.

[1]

(ii) State the full electronic configuration of Sc^{3+}.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

[1]

(iii) Explain why scandium is not classified as a transition element.

Sc is not a transition element as it only forms stable Sc^{3+} ion which has empty d subshell.

[1]

(c) **X** and **Y** are period 3 elements.

Element **X** forms a white oxide that is slightly soluble in cold water. Its chloride dissolves in water to form a weakly acidic solution.

Element **Y** forms two oxides. 0.03 moles of one of the two oxides produces 7.00 g of white precipitate when mixed with excess barium chloride solution. The white precipitate is insoluble in dilute strong acid. A solution is obtained when equimolar of the oxide of element **Y** is added to the oxide of element **X** with water.

Identify the elements **X**, **Y**, and the oxide of **Y**.

Explain the observations with the aid of relevant equations.

Element X: Magnesium Element Y: Sulfur

Formula of the oxide of element Y: SO_3

$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$ when MgO reacts with water, sparingly soluble $Mg(OH)_2$ is formed

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

$MgCl_2$ hydrolyses slightly to form a weakly acidic solution of pH 6.5

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

Upon addition of excess barium chloride solution, $BaSO_4(s)$ is formed.

7.00 g of white ppt corresponds to the mass of 0.03 mol of $BaSO_4$.

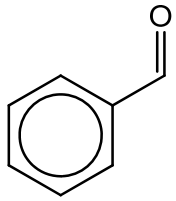
$SO_3(g) + H_2O(l) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2HCl(aq)$

OR $SO_4^{2-} + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

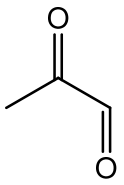
$SO_3(g) + MgO(aq) \rightarrow MgSO_4(aq)$ [7]

[Total: 15]

4 **(a)** Carbonyl compounds occur naturally, giving many signature flavours. For example, benzaldehyde in almonds and 2-oxopropanal in burnt sugar.



benzaldehyde



2-oxopropanal

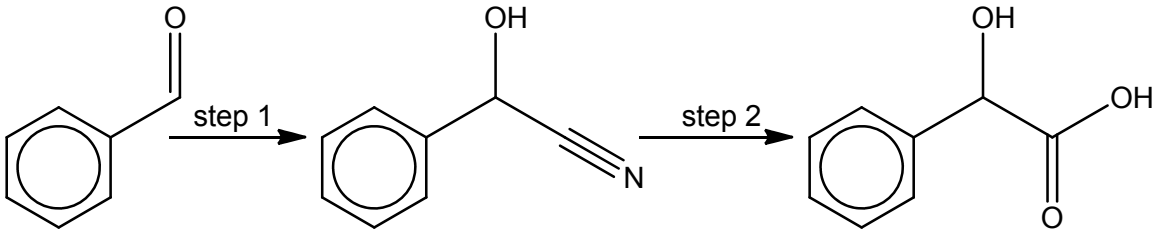
(i) Suggest a simple chemical test that could distinguish between the two compounds above. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: I_2 (aq), NaOH (aq), heat **or** Fehling's reagent/solution, heat

	Observations:	Products:
benzaldehyde	**No Yellow ppt** seen. OR **No Red ppt** seen.	No products
2-oxopropanal	**Yellow ppt** seen. OR **Red ppt** seen.	CHI_3(s) *for iodoform* Cu_2O(s) *for Fehling's Reagent used*

[3]

(ii) Benzaldehyde undergoes a possible reaction sequence as shown below to form mandelic acid, which is used as an antibacterial agent.



benzaldehyde mandelic acid

State the reagents and conditions for steps 1 and 2.

Step 1: HCN (aq), trace amount of NaOH (aq), cold 10-20 °C

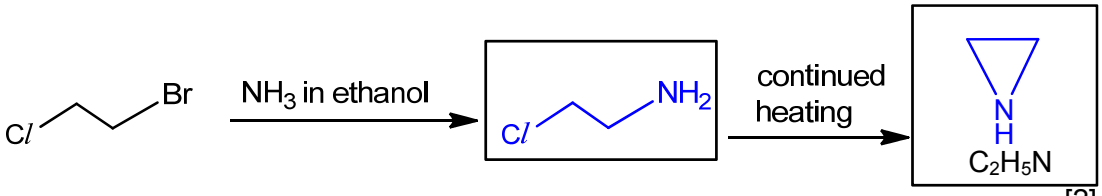
Step 2: Dilute H_2SO_4 (aq), heat under reflux [2]

(b) Another class of naturally occurring organic compounds is halogenoalkanes, e.g. bromomethane found in vegetables, chloromethane found in algae and trichloromethane found in termites.

(i) With bromomethane and chloromethane as examples, describe and explain briefly the relative reactivities of bromo- and chloro-compounds with respect to hydrolysis.

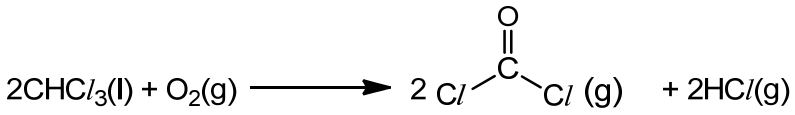
CH_3Br would be **more reactive** towards hydrolysis than CH_3Cl. This is because the **C–Br bond is weaker** than C–Cl bond and would be more easily broken during hydrolysis. [1]

(ii) This difference in reactivity can also be observed in organic reactions. Suggest the structural formulae of the compounds formed in the boxes below. The final product is a cyclic compound.



[2]

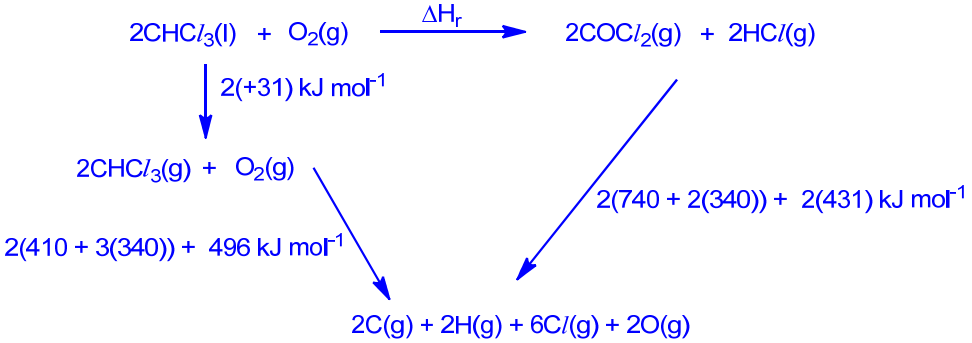
(c) Trichloromethane was previously used as an anesthetic, but chronic exposure can harm the liver where it is metabolised to toxic phosgene, $COCl_2$. This reaction can also take place slowly in the presence of oxygen and light, as represented below.



(i) Construct a fully labelled energy cycle relating the reactants and products of this reaction to their gas phase atoms. Use your cycle to calculate the enthalpy change of the above reaction.

Your cycle should include relevant data from the Data Booklet together with the following data shown below:

The enthalpy change of vaporisation of $CHCl_3(l)$ is +31 kJ mol^{-1}.



[3]

$\Delta H_r = 2(31) + 2[\mathbf{410} + 3(\mathbf{340})] + \mathbf{496} - [2(\mathbf{740}+2(\mathbf{340})) + 2(\mathbf{431})]$

$= -284$ kJ mol^{-1} (3.s.f.)

(ii) Predict, with reasons, the sign of the entropy change of the reaction in **(c)(i)**.

Entropy change of the reaction should be **positive**, as the number of **moles of gas increases** from 1 mole to 4 moles, there are more ways of arranging the particles, hence the system **increases in disorderness.** [2]

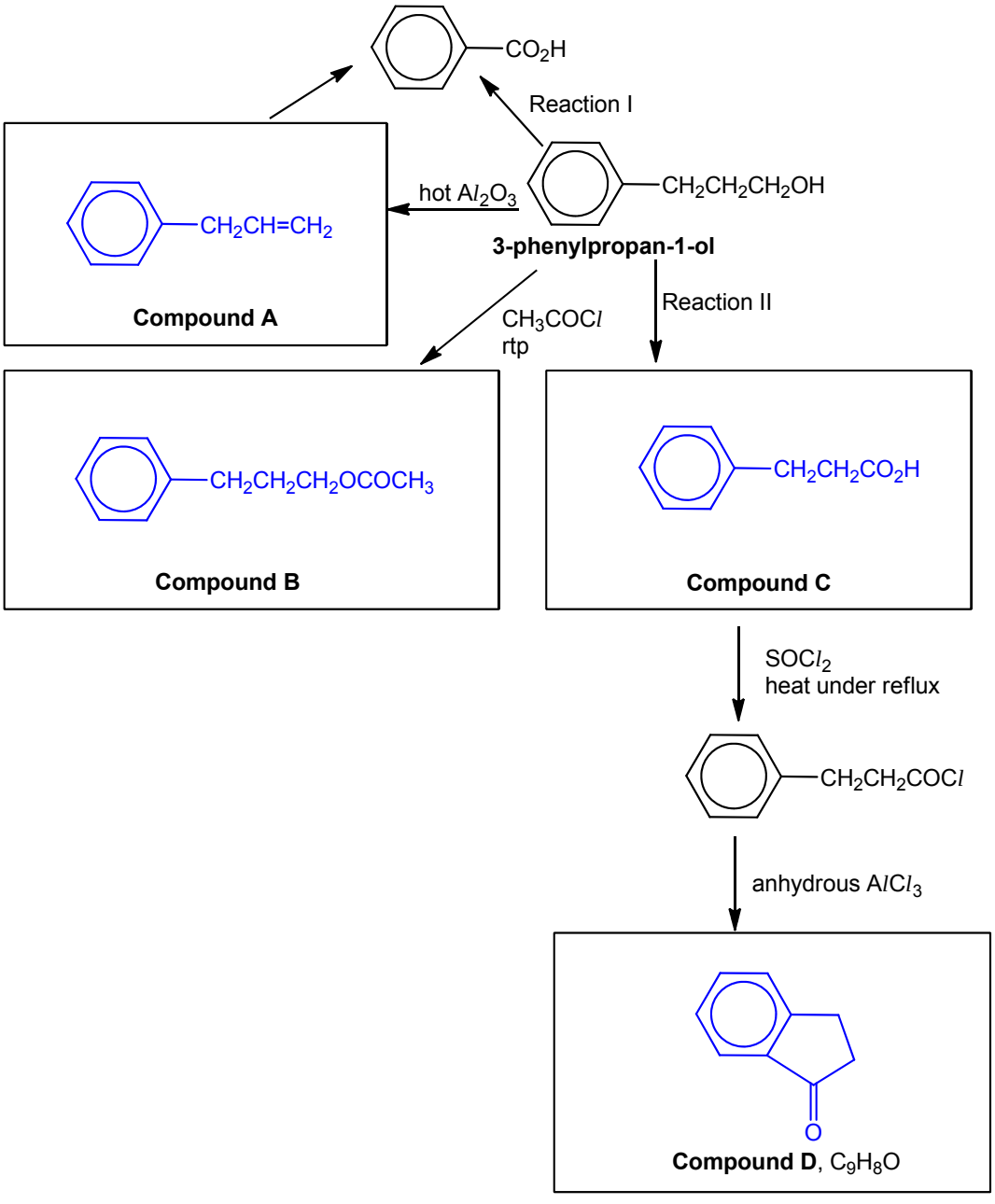
(iii) Hence, state the sign of the standard Gibbs free energy change and comment on the spontaneity of the reaction.

$\Delta G = \Delta H - T\Delta S$, standard Gibbs free energy change should be **negative**, since the enthalpy change is negative, and entropy change is positive. Thus, the reaction is always **spontaneous** at all temperature. [2]

[Total: 15]

5 **(a)** Benzene is an important precursor in the production of many chemicals. 3-phenylpropan-1-ol is an example of an organic compound which contains the benzene ring as a substituent.

(i) The following reaction scheme shows the reactions of 3-phenylpropan-1-ol. Suggest the structural formulae of compounds **A**, **B**, **C** and **D** in the boxes below.



[4]

(ii) Using the reaction scheme for the reactions of 3-phenylpropan-1-ol, state the reagents and conditions for reactions I and II. [2]

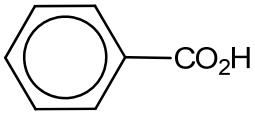
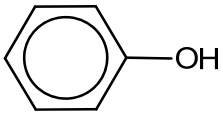
Reaction I **$KMnO_4$, dilute H_2SO_4, heat under reflux**

Reaction II **$K_2Cr_2O_7$, dilute H_2SO_4, heat under reflux**

(b) There is another form of important organic compounds which are derived from benzene. Benzene derivatives are formed when one of the hydrogens on the ring is replaced with a different functional group.

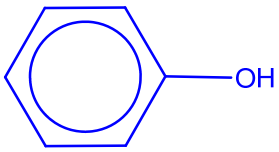
Benzoic acid and phenol are examples of such benzene derivatives which exhibit acidic character when dissolved in water.

The K_a values of benzoic acid, carbonic acid and phenol are given in the table below.

acid	**structural formula**	**K_a / mol dm^{-3}**
benzoic acid		6.3×10^{-5}
carbonic acid	H_2CO_3	4.5×10^{-7}
phenol		1.3×10^{-10}

Both benzoic acid and phenol are reacted with sodium hydroxide to form sodium benzoate and sodium phenoxide respectively.

(i) Draw the organic product formed when CO_2 is bubbled through a solution of aqueous sodium phenoxide. [1]



(ii) However, no reaction occurs when CO_2 is bubbled through a solution of aqueous sodium benzoate. Explain why this is so. [1]

CO_2 dissolves in water to give carbonic acid, H_2CO_3 which is a weaker acid ($K_a = 4.5 \times 10^{-7}$) compared to benzoic acid ($K_a = 6.3 \times 10^{-5}$) and therefore it is not able to donate proton to benzoate ion to form benzoic acid.

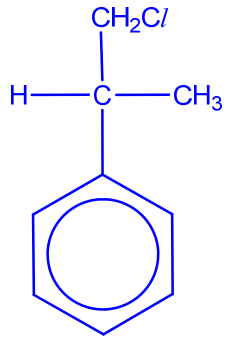
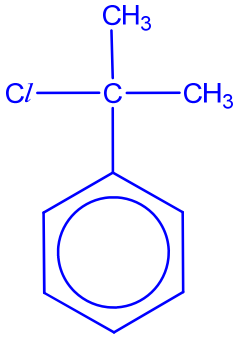
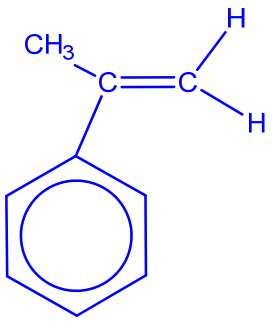
(c) Cumene, C_9H_{12}, is another benzene derivative that can be used to produce phenol and propanone.

When a sample of cumene is reacted with limited chlorine in the presence of UV light, only two monochlorinated products, **X** and **Y** are formed. Only compound **X** has a chiral carbon. Both **X** and **Y** react with reagent **W** under heat to form hydrocarbon **Z**. Hydrocarbon **Z** is able to decolourise aqueous bromine.

(i) State reagent **W**. [1]

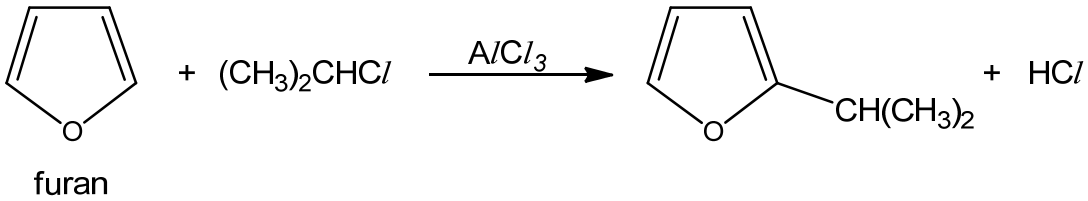
NaOH dissolved in ethanol / alcoholic NaOH/ NaOH (alc)

(ii) In the space below, give the structural formula of compound **X**, **Y** and **Z**. [3]

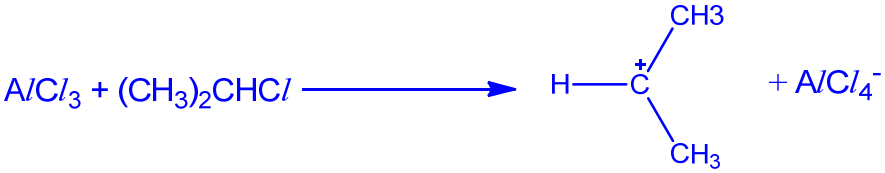
Compound X	Compound Y	Compound Z
		

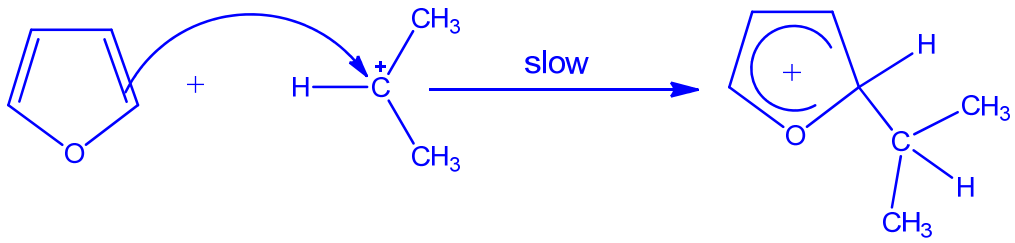
(d) As an aromatic compound, benzene undergoes electrophilic substitution reactions. Like benzene, furan, a heterocyclic five-membered aromatic ring with one O atom and four carbon atoms, is also able to undergo electrophilic substitution reactions under suitable conditions.

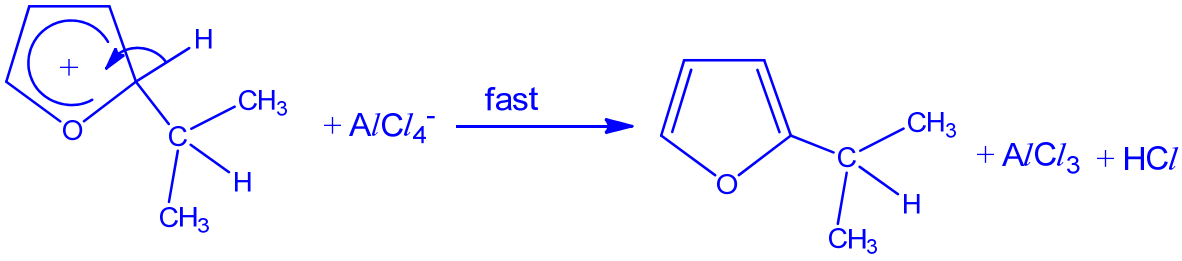
Outline the mechanism of the reaction below, clearly showing all the steps involved.



furan







[3]

[Total: 15]