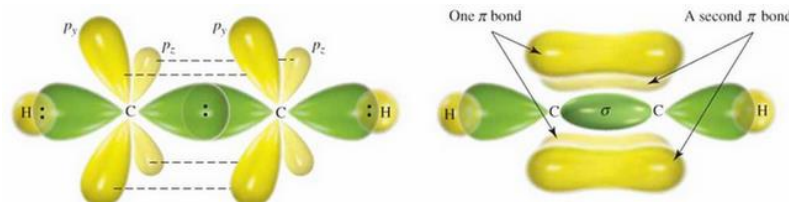


# 2014 Preliminary Examination H1 Chemistry Paper 2

## Section A

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

- 1 (a) Describe the bonding in ethyne,  $\text{CH}\equiv\text{CH}$ , in terms of orbital overlap. You may draw a diagram to illustrate your answer.



The  $\sigma$  bond formed between C and H is by the head-on overlap of the atomic orbital of C atom and the s orbital of H atom

The  $\sigma$  bond formed between C and C is by the head-on overlap of the atomic orbitals of C atoms.

The two  $\pi$  bonds formed between C and C is by the side-way overlap of the p orbitals of carbon. One  $\pi$  bond is formed above and below the two C atoms and one  $\pi$  bond is formed in front and behind the two carbon atoms.

[3]

- (b) Bond energies for some multiple bonds are listed below.

Bond	Bond energy / $\text{kJ mol}^{-1}$
$\text{C}=\text{C}$	610
$\text{C}\equiv\text{C}$	840
$\text{N}\equiv\text{N}$	994

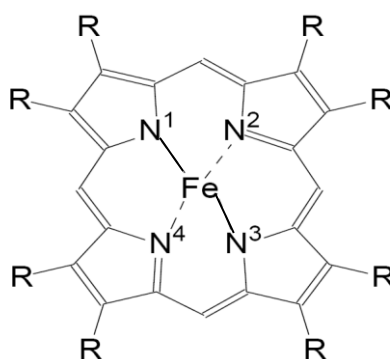
Explain why  $\text{C}\equiv\text{C}$  is a stronger bond than  $\text{C}=\text{C}$  but a weaker bond than  $\text{N}\equiv\text{N}$ .

Comparing  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$ , the two carbon atoms in  $\text{C}\equiv\text{C}$  are more strongly attracted because of a greater number of shared electron pairs than the  $\text{C}=\text{C}$  bond OR the additional pi bond.

Comparing  $\text{C}\equiv\text{C}$  and  $\text{N}\equiv\text{N}$ , the atomic orbitals of C are larger which result in a less effective orbital overlap and a weaker bond.

[2]

- (c) Haemoglobin is an important protein present in the red blood cell, which is responsible for transport of oxygen in the body. It contains a haem group and a metal centre as shown below. The four N atoms and the Fe atom are planar.



- (i) State the nature of the bonding around the iron atom.

Type of bond between Fe atom and  $\text{N}^1$ : covalent bond

Type of bond between Fe atom and  $\text{N}^2$ : dative bond / co-ordinate bond

- (ii) One molecule of haemoglobin (Hb) binds up to four oxygen molecules to form oxyhaemoglobin ( $\text{Hb}(\text{O}_2)_4$ ), as shown in the following equation.



By applying *Le Chatelier's Principle*, explain how oxygen molecules are transported from the lungs to the body tissues.

**In the lungs, the concentration of  $\text{O}_2$  is high, thus, equilibrium position for equilibrium (1) shifts to the right to form oxyhaemoglobin.**

**Oxygen is transported to the body as oxyhaemoglobin.**

**In the tissues, the concentration of  $\text{O}_2$  is low, thus, equilibrium position for equilibrium (1) shifts to the left oxyhaemoglobin starts to dissociate to release oxygen.**

- (iii) The percentage saturation of haemoglobin is defined as the percentage of haemoglobin present in the blood that has been converted to oxyhaemoglobin.

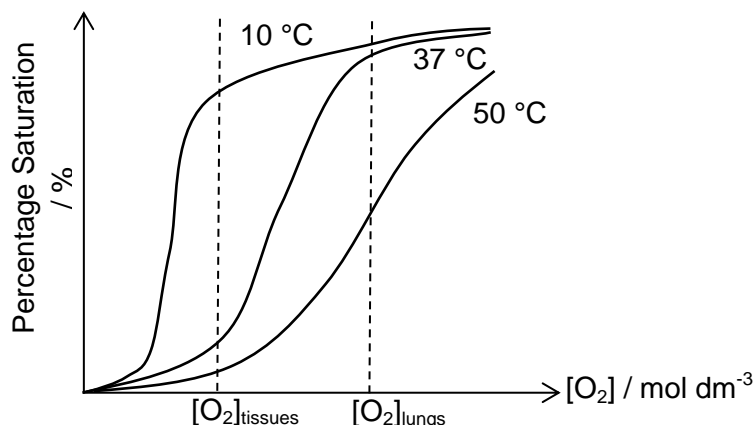
With reference to equilibrium (1), state and explain how the percentage saturation of haemoglobin changes when temperature increases.

**The forward reaction of equilibrium (1) is exothermic, due to formation of dative/coordinate bond between the oxygen and Fe atom in the haemoglobin.**

**When temperature increases, endothermic reaction is favoured thus the backward reaction is favoured to remove excess heat.**

**Oxyhaemoglobin dissociates and the percentage saturation decreases.**

- (iv) The relationship between the percentage saturation of haemoglobin and concentration of oxygen in blood at different temperatures is shown below.



Suggest the optimum temperature at which haemoglobin operates. Explain your answer.

**37 °C**

**Optimum condition occurs at high percentage saturation at the lungs and**

**low percentage saturation at the tissues.**

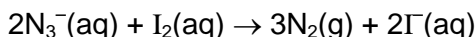
**OR large percentage difference between the percentage saturation at the lungs and at the tissues.)**

[8]

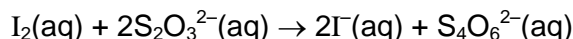
[Total: 13]

- 2 (a) Sodium azide,  $\text{NaN}_3$ , is the gas-forming component in many car airbag systems. On heating, it decomposes to give nitrogen gas which expands the air bag.

The concentration of sodium azide may be determined by titration against iodine under suitable conditions as shown by the following equation.



A 0.800 g sample of sodium azide was dissolved in water and made up to  $100\text{ cm}^3$ . To a  $25.0\text{ cm}^3$  portion of this solution,  $25.0\text{ cm}^3$  of acidified  $0.100\text{ mol dm}^{-3}\text{ I}_2(\text{aq})$  was added. The excess of iodine reacted completely with  $22.00\text{ cm}^3$  of  $0.100\text{ mol dm}^{-3}$  sodium thiosulfate. The equation for the reaction of iodine with thiosulfate ions is as follows.



- (i) Calculate the amount of iodine that reacted with  $25.0\text{ cm}^3$  of sodium azide solution.

**Amount of  $\text{Na}_2\text{S}_2\text{O}_3$  used**

$$= 0.100 \times \frac{22.00}{1000}$$

$$= 2.20 \times 10^{-3}\text{ mol}$$

**Amount of excess  $\text{I}_2$**

$$= 2.20 \times 10^{-3} \div 2$$

$$= 1.10 \times 10^{-3}\text{ mol}$$

**Original amount of  $\text{I}_2$  added**

$$= 0.100 \times \frac{25.0}{1000}$$

$$= 2.50 \times 10^{-3}\text{ mol}$$

**Amount of  $\text{I}_2$  reacted with  $25.0\text{ cm}^3$  of  $\text{NaN}_3$**

$$= 2.50 \times 10^{-3} - 1.10 \times 10^{-3}$$

$$= 1.40 \times 10^{-3}\text{ mol}$$

- (ii) Calculate the percentage purity by mass of the sodium azide.

**Amount of  $\text{NaN}_3$  in  $100\text{ cm}^3$  solution**

$$= 1.40 \times 10^{-3} \times 2 \times \frac{100}{25.0} \text{ (ecf)}$$

$$= 0.0112\text{ mol}$$

**Mass of  $\text{NaN}_3$**

$$= 0.0112 \times 65.0$$

$$= 0.728\text{ g}$$

**Percentage purity of  $\text{NaN}_3$**

$$= \frac{0.728}{0.8} \times 100\%$$

$$= 91.0\%$$

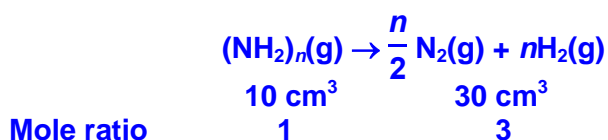
[4]

- (b) (i) A hydride of nitrogen, **Q**, contains 12.5% of hydrogen by mass. Find its empirical formula.

Element	N	H
% by mass	87.5	12.5
Mole ratio	$87.5 \div 14.0$ $= 6.25$	$12.5 \div 1.0$ $= 12.5$
Simplest mole ratio	1	2
Empirical formula of <b>Q</b> is $\text{NH}_2$ .		

- (ii) When **Q** is heated very strongly, it decomposes into its elements.  $10 \text{ cm}^3$  of **Q** produces  $30 \text{ cm}^3$  of products (all volumes are measured under the same conditions).

What is the molecular formula of **Q** and the oxidation state of nitrogen in **Q**.

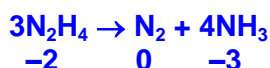


$$\begin{array}{l}
 \frac{n}{2} + n = 3 \text{ (ecf)} \\
 n = 2
 \end{array}$$

Molecular formula of **Q** is  $\text{N}_2\text{H}_4$ .

Oxidation state of N in **Q** =  $-2$

- (iii) **Q** is an unstable compound which will disproportionate to give two nitrogen-containing products when heated gently. The oxidation numbers of nitrogen in the two products are 0 and  $-3$  respectively. Write a balanced equation for the reaction and use oxidation numbers to explain what is meant by *disproportionation* in this reaction.



**Disproportionation has occurred as **Q** is oxidised and reduced at the same time where oxidation number of nitrogen in **Q** increases from  $-2$  to 0 and decreases from  $-2$  to  $-3$ .**

[5]

- (c) On Planet Uranus, it is postulated that the number of subshells associated with each principal quantum number and the respective energy levels of the subshells are similar to that on Earth. Each orbital contains a maximum of two electrons. However, the number of orbitals that make up a subshell may or may not be identical to that on Earth.

Figure 1 represents the sketch of the successive ionisation energies of **all** the electrons of an element **T** on Planet Uranus.

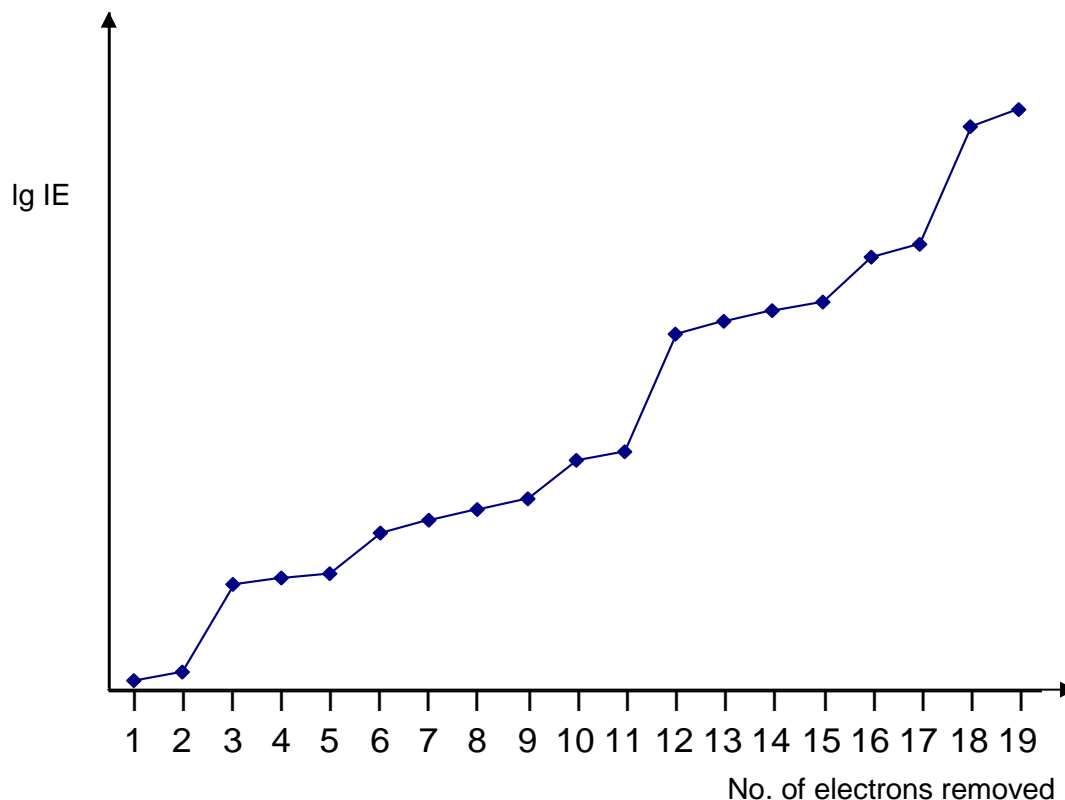
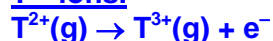


Figure 1

- (i) With the aid of a relevant equation, explain what is meant by the *third ionisation energy* of element T.

**Third ionisation energy (3<sup>rd</sup> IE) is the energy required to remove 1 mol of electrons from 1 mol of gaseous T<sup>2+</sup> ions to form 1 mol of gaseous T<sup>3+</sup> ions.**



$\Delta H = \text{third ionisation energy}$

- (ii) By interpreting Figure 1, suggest with reasoning, which period of the Periodic Table element T belongs to.

**Since there are a total of three large increments between successive ionisation energies, this implies that the 3<sup>rd</sup>, 12<sup>th</sup> and 18<sup>th</sup> electrons are removed from different principal quantum shells. Hence, T belongs to the fourth period of the Periodic Table.**

- (iii) Using Figure 1, deduce the number of 2p orbitals present in element T.

**The 18<sup>th</sup> and 19<sup>th</sup> IE belong to 1s subshell.**

**OR The 16<sup>th</sup> and 17<sup>th</sup> IE belong to 2s subshell.**

**Thus, 12<sup>th</sup> to 15<sup>th</sup> IE, i.e. four electrons are removed from a 2p subshell.**

**Since each orbital can accommodate a maximum of 2 electrons, there are two 2p orbitals.**

- (iv) State the full electronic configuration of element T.



[5.5, max 5]  
[5]

[Total: 14]

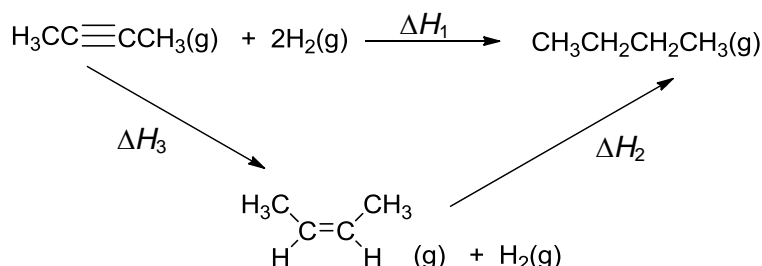
- 3 This question is on the reactions of the hydrocarbons and their halogen derivatives.

(a) What do you understand by the term *bond energy*?

**Bond energy is the energy required to break one mole of covalent bonds between two atoms in the gaseous state.**

[1]

(b) The hydrogenation of the hydrocarbons, butyne and *cis*-but-2-ene, are shown in the energy cycle below.



(i) Use the bond energy values from the *Data Booklet* to calculate  $\Delta H_1$ .

$$\begin{aligned}
 \Delta H_1 &= 6\text{BE}(\text{C-H}) + 2\text{BE}(\text{C-C}) + \text{BE}(\text{C}\equiv\text{C}) + 2\text{BE}(\text{H-H}) - 10\text{BE}(\text{C-H}) - 3\text{BE}(\text{C-C}) \\
 &= 6(410) + 2(350) + 840 + 2(436) - 10(410) - 3(350) \\
 &= 840 + 2(436) - 4(410) - 350 \\
 &= -278 \text{ kJ mol}^{-1}
 \end{aligned}$$

(ii) Calculate  $\Delta H_2$ , given that the enthalpy change of formation of gaseous *cis*-but-2-ene and gaseous butane are  $-8 \text{ kJ mol}^{-1}$  and  $-127 \text{ kJ mol}^{-1}$  respectively.

$$\begin{aligned}
 \Delta H_2 &= -127 - (-8) \\
 &= -119 \text{ kJ mol}^{-1}
 \end{aligned}$$

(iii) By using your answers to (b)(i) and (b)(ii), calculate  $\Delta H_3$ .

$$\begin{aligned}
 \Delta H_3 &= \Delta H_1 - \Delta H_2 \\
 &= -278 - (-119) \\
 &= -159 \text{ kJ mol}^{-1} \text{ (ecf)}
 \end{aligned}$$

[4]

(c) Gas used in camping stoves is available in canisters, which contain mainly butane.

(i) When 3.40 g of butane was used to heat 500 g of water, it was found that the temperature of water increased by  $44^\circ\text{C}$ . Assuming that the specific heat capacity of water is  $4.2 \text{ J K}^{-1} \text{ cm}^{-3}$ , calculate the enthalpy change of combustion of butane.

$$\begin{aligned}
 \text{Heat evolved} &= 500 \times 4.2 \times 44 \\
 &= 92400 \text{ J} \\
 &= 92.4 \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 \text{No. of moles of butane} &= \frac{3.4}{4(12.0) + 10(1.0)} \\
 &= 0.0586 \text{ mol}
 \end{aligned}$$

$$\begin{aligned}
 \Delta H_c \text{ of butane} &= -\frac{92.4}{0.0586} \\
 &= -1580 \text{ kJ mol}^{-1}
 \end{aligned}$$

- (ii) The standard enthalpy change of combustion of butane is  $-2877 \text{ kJ mol}^{-1}$ . Suggest a reason for the difference between this value and that obtained in (c)(i).

Calculated value is much less exothermic due to heat loss to the surroundings. Not all the heat from the combustion of butane is used to heat up the water.

The standard enthalpy changes of combustion,  $\Delta H_c^\ominus$ , for some common fuels are given below.

fuel	formula	$M_r$	$\Delta H_c^\ominus / \text{kJ mol}^{-1}$	$\frac{\Delta H_c^\ominus}{M_r} / \text{kJ g}^{-1}$
methane	$\text{CH}_4$	16	-890	-55.6
ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	46	-1367	-29.7
butane	$\text{C}_4\text{H}_{10}$	58	-2877	-49.6
octane	$\text{C}_8\text{H}_{18}$	114	-5470	-48.0

- (iii) Explain why  $\Delta H_c^\ominus$  values become more exothermic with  $M_r$ .

$\Delta H_c^\ominus$  values becomes more exothermic as size of fuel molecule increases / number of moles of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  formed increases.

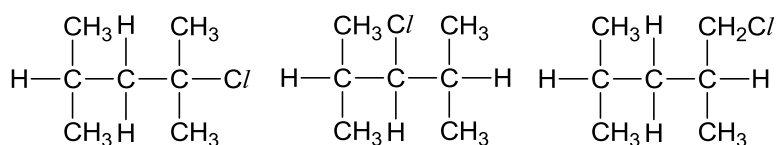
- (iv) Explain why ethanol has a much less exothermic  $\frac{\Delta H_c^\ominus}{M_r}$  compared to alkanes.

Lower energy output per unit mass for ethanol as ethanol is partially oxidised compared with the alkanes.

[5]

- (d) Upon irradiation of ultra-violet light, 2,4-dimethylpentane undergoes monochloro-substitution.

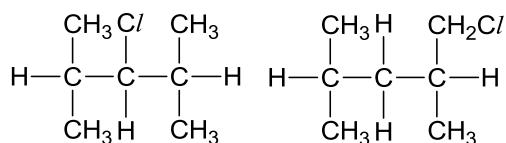
- (i) Draw the structural formula of all the possible monochlorinated products.



- (ii) Predict the mole ratio of the monochlorinated products in (d)(i).

2:2:12 = 1:1:6

- (iii) With reference to structures drawn in (d)(i), indicate those that form only one organic product when reacted with hot ethanolic KOH.



[3]

[Total: 13]

## Section B

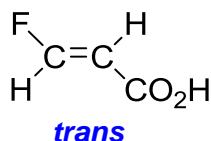
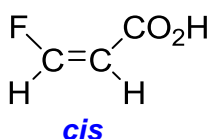
Answer **two** questions from this section on separate answer paper.

- 4 (a) 3-fluoroprop-2-enoic acid,  $\text{CHF}=\text{CHCO}_2\text{H}$ , is used as building blocks of polymers, which shows exceptional mechanical and optical properties. This compound can exhibit *geometric isomerism*.

- (i) What do you understand by the term *geometric isomerism*?

**It occurs due to restricted rotation about C=C bond, and will be shown when there are two different groups attached to each C in the C=C bond.**

- (ii) Draw the possible geometric isomers of the above compound.



- (iii) The geometric isomers differ in some physical properties, including boiling point. By considering the bonding and structure of the above isomers, suggest and explain which isomer will have a higher boiling point.

**Trans isomer will have higher boiling point.**

**Both *cis* and *trans* isomers have simple molecular structures.**

**In *cis* isomer, the  $\text{CO}_2\text{H}$  group and F atom are in close proximity.**

**Hence it has more extensive intramolecular hydrogen bonding, and less extensive intermolecular hydrogen bonding compared to *trans* isomer (or an equivalent diagram).**

**More energy is required to overcome the intermolecular forces in *trans* isomer.**

- (iv) Suggest how the acidity of 3-fluoroprop-2-enoic acid might compare to that of  $\text{CHF}=\text{CHCH}_2\text{OH}$ ?

**$\text{CHF}=\text{CHCO}_2\text{H}$  will be more acidic than  $\text{CHF}=\text{CHCH}_2\text{OH}$ .**

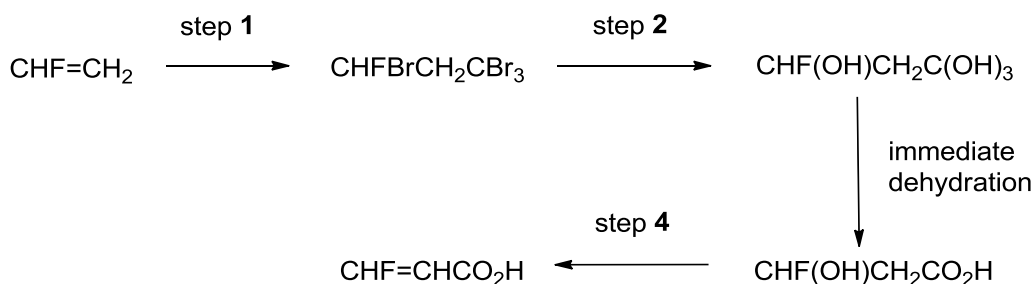
**$\text{CHF}=\text{CHCO}_2^-$  formed after deprotonation is resonance stabilised.**

**OR The negative charge on  $\text{CHF}=\text{CHCO}_2^-$  is dispersed by resonance.**

**Hence, the equilibrium position for dissociation of  $\text{CHF}=\text{CHCO}_2\text{H}$  lies greater to the right.**

[5]

- (b) There are not many synthetic routes for 3-fluoroprop-2-enoic acid. One route is shown below:





- (i) Suggest the reagents required for steps 1, 2 and 4.

Step 1:  $\text{CBr}_4$

Step 2:  $\text{NaOH(aq)}$ , heat

Step 4: excess concentrated  $\text{H}_2\text{SO}_4$ ,  $170^\circ\text{C}$

- (ii) Explain why the  $\text{CHF=CHCO}_2\text{H}$  dissolves better in aqueous  $\text{NaOH}$  than water.

$\text{CHF=CHCO}_2\text{H}$  reacts with  $\text{NaOH}$  to form  $\text{CHF=CHCO}_2^-$

The ion-dipole interaction formed between the  $\text{CHF=CHCO}_2^-$  and water releases more energy than the hydrogen bonding formed between  $\text{CHF=CHCO}_2\text{H}$  and water to overcome the hydrogen bonding between water molecules.

- (iii) 0.422 g of an organic compound,  $\text{C}_3\text{H}_x\text{I}_y$  ( $M_r = 422$ ) is subject to alkaline hydrolysis. After cooling the products, excess dilute  $\text{HNO}_3(\text{aq})$  is added and then  $\text{AgNO}_3(\text{aq})$  is added. The mass of the precipitate,  $\text{AgI}$  formed is 0.705 g. Determine the values of  $x$  and  $y$ .

$$\text{Amount of organic compound} = \frac{0.422}{422} = 1.00 \times 10^{-3} \text{ mol}$$

$$\text{Amount of AgI} = \frac{0.705}{235} = 3.00 \times 10^{-3} \text{ mol}$$

$$\text{Mole ratio of organic compound : AgI (and hence I)} = 1 : 3, \text{ thus } y = 3$$

$$x = [2(3) + 2] - 3 = 5$$

[6]

- (c) The acid–base properties of the oxides of Period 3 elements show a distinctive trend across the period.

Illustrate the above statement with reference to the oxides,  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_4\text{O}_{10}$ . Write relevant equations for the reactions involved and discuss how the bonding in  $\text{Al}_2\text{O}_3$  accounts for its acidic or basic character.

$\text{Na}_2\text{O}$  is a basic oxide and reacts with aqueous acids, e.g.  $\text{HCl(aq)}$ .



$\text{P}_4\text{O}_{10}$  is an acidic oxide and reacts with  $\text{NaOH(aq)}$ .



$\text{Al}_2\text{O}_3$  is an amphoteric oxide, which reacts with both acids and bases.



$\text{Al}_2\text{O}_3$  is predominantly ionic with some covalent character.

The ionic character of the bond imparts the basic character.

And the covalent character imparts the acidic character.

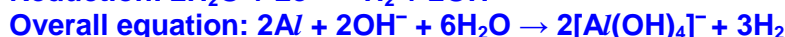
The covalent character arises due to  $\text{Al}^{3+}$  having a high charge density, causing it to polarise the  $\text{O}^{2-}$  anion to some extent.

[5]

- (d) Alloys of aluminium and magnesium are often used in the aircraft manufacture because of their high strength and low density.

A 1.50 g sample of one such alloy was reacted with an excess of aqueous sodium hydroxide and the volume of hydrogen given off was measured. 1.50 dm<sup>3</sup> of gas was produced at room temperature and pressure.

- (i) The aluminium containing product of this reaction is the same as that from the reaction between aluminium oxide and sodium hydroxide. Based on this information, construct relevant half equations and hence write the equation for the reaction between aluminium and sodium hydroxide.



- (ii) Calculate the percentage by mass of aluminium in the sample of alloy.

$$\text{Amount of H}_2 = \frac{1.50}{24} = 0.0625 \text{ mol}$$

$$\text{Amount of Al} = \frac{2}{3} \times 0.0625 = 0.0417 \text{ mol}$$

$$\text{Mass of Al} = 0.0417 \times 27.0 = 1.13 \text{ g}$$

$$\% \text{ by mass of Al} = \frac{1.13}{1.50} \times 100\% = 75.3\%$$

[4]

[Total: 20]

- 5 (a) When hydrocarbon **P**, C<sub>10</sub>H<sub>12</sub>O is heated with acidified potassium manganate (VII), compound **Q**, C<sub>8</sub>H<sub>8</sub>O is obtained as the **only** organic product. **P** gives effervescence when sodium metal is added. When **P** is treated with gaseous HBr, compound **R**, C<sub>10</sub>H<sub>12</sub>Br<sub>2</sub> is formed. When **Q** is added to 2,4-dinitrophenylhydrazine, an orange precipitate is obtained.

Deduce the structures for each lettered compound, **P**, **Q** and **R** and give an account of the chemistry involved.

**P** undergoes oxidative cleavage with MnO<sub>4</sub><sup>-</sup> to form compounds **Q** and CO<sub>2</sub>.

**P** contains C=C.

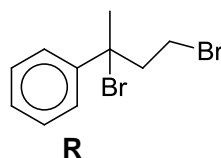
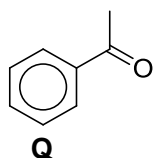
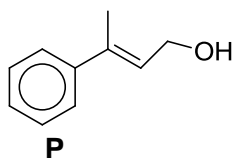
**P** undergoes redox with Na to give H<sub>2</sub> gas.

**P** contains alcohol.

**P** undergoes addition of alkene and substitution of alcohol with HBr to form compound **R**.

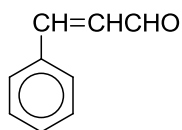
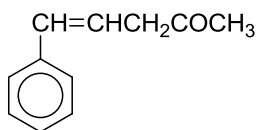
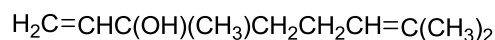
**Q** undergoes condensation with 2,4-DNPH.

**Q** is a ketone.



[6]

- (b) Recent research has suggested that cinnamon could be an effective pesticide against the larvae of mosquitoes, thus helping in the fight against malaria. Each of the following three compounds, which are present in cinnamon, appears to be effective as a pesticide.

**A****B****C**

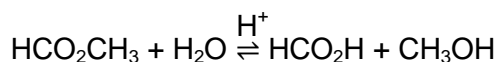
For each of the compounds **A** to **C**, state the reagents and conditions which would distinguish it from the other two and describe the observations that would be seen.

Compound	Test and Observation
<b>A</b>	<p><b>Test:</b> Add <u>Tollens' reagent</u> to the 3 samples separately and <u>warm</u>.</p> <p><b>Observation:</b> <u>Silver mirror</u> formed only for <b>A</b> but no silver mirror formed for <b>B</b> and <b>C</b></p> <p><b>Alt. test:</b> Fehling's solution; warm; brick-red ppt</p>
<b>B</b>	<p><b>Test:</b> Add <u>I<sub>2</sub>(aq)</u> and <u>NaOH(aq)</u> to the 3 samples separately and <u>warm</u>.</p> <p><b>Observation:</b> <u>Yellow ppt of CHI<sub>3</sub></u> observed only for <b>B</b> but no yellow ppt formed for <b>A</b> and <b>C</b>.</p>
<b>C</b>	<p><b>Test:</b> Add <u>PCl<sub>5</sub></u> to the 3 samples separately at <u>room temperature</u>.</p> <p><b>Observation:</b> <u>White fumes</u> formed only for <b>C</b> but no white fumes formed for <b>A</b> and <b>B</b>.</p> <p><b>Alt. tests:</b> SOC<sub>2</sub>; heat; white fumes / Na(s); room temperature; effervescence observed.</p>

[4.5 max 4]

[4]

- (c) The acid-catalysed hydrolysis of methyl methanoate may be represented by the equation:



When the hydrolysis was carried out in the presence of excess aqueous hydrochloric acid in a constant-temperature bath, the following results were obtained.

Time / min	Fraction of methyl methanoate remaining
0	1.00
10	0.62
20	0.38
30	0.24
40	0.14
50	0.08
60	0.05
70	0.03
80	0.02

- (i) Explain what is meant by the term 'order of reaction'.

The order of reaction with respect to a given reactant is defined as the power to which the concentration of that reactant is raised in the rate equation.

OR

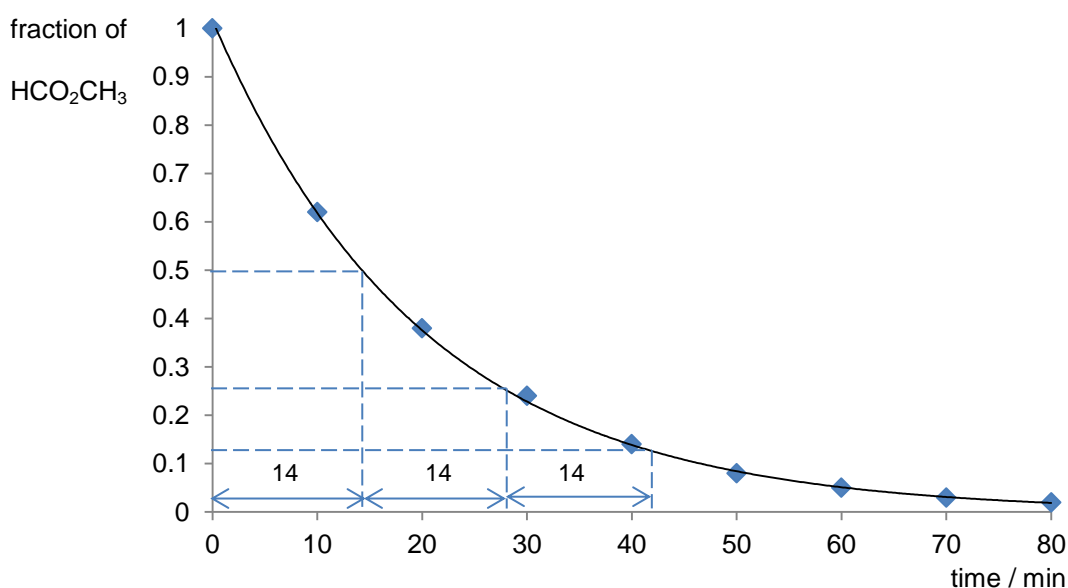
For a given rate equation,  $\text{Rate} = k[A]^m[B]^n$  where A & B are the reactants.

Order of reaction with respect to A = m

Order of reaction with respect to B = n

Overall order of reaction = m + n

- (ii) Plot an appropriate graph to show that the reaction is first-order with respect to ester and hence determine the rate constant for the reaction.



Proper label of axes with units

Correct plotting of points

Smooth curve on graph

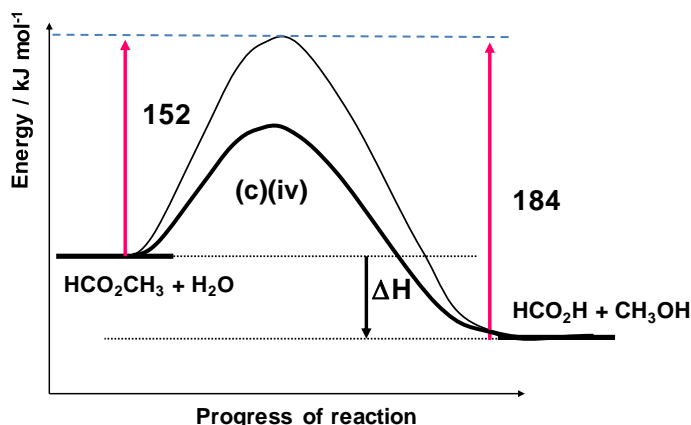
3 consistent half lives

Correct  $t_{1/2} \approx 14 \text{ min}$

Hence  $k = 0.046 \text{ min}^{-1}$

- (iii) Sketch a labelled reaction pathway diagram for the uncatalysed hydrolysis reaction given that the activation energy of the forward reaction is  $+152 \text{ kJ mol}^{-1}$  and that for the reverse reaction is  $+184 \text{ kJ mol}^{-1}$ .

Determine the enthalpy change of the reaction.



Correct labels for reactants and products

Correct axes

Correct labels for two  $E_a$

Correct pathway

$$\Delta H = 152 - 184 = -32 \text{ kJ mol}^{-1}$$

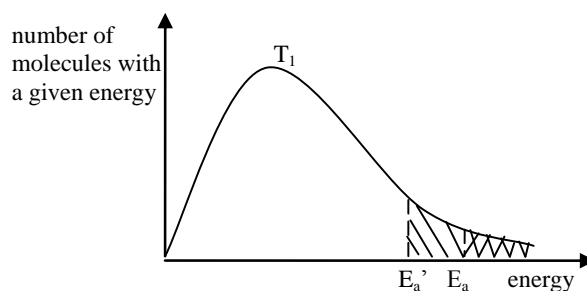
- (iv) On your sketch in (c)(iii), draw the reaction pathway of the acid catalysed reaction. Label this clearly.

Correct pathway showing a lower  $E_a$ .

- (v) With the help of a Maxwell Boltzmann distribution, explain how the use of a catalyst may help to speed up the rate of this reaction.

Correct axes with correct curve drawn.

Correct shaded areas for catalysed and uncatalysed reactions



$E_a'$  = activation energy for catalysed reaction

Catalyst provides an alternative pathway of lower activation energy.

Thus, there are more molecules with energy  $\geq E_a$

Frequency of effective collisions increases resulting in an increase in rate.

[10]

[Total: 20]

- 6 (a) Vitamin C,  $C_6H_8O_6$ , also known as ascorbic acid, is a monobasic acid. When 500 mg tablet of vitamin C is swallowed, it dissolves in the stomach before being absorbed into the bloodstream. The stomach may be assumed to contain  $1.00 \text{ dm}^3$  of  $0.100 \text{ mol dm}^{-3}$  hydrochloric acid. 0.0794% of the vitamin C tablet is ionised in the stomach.

- (i) Determine the acid dissociation constant  $K_a$  of vitamin C.

$$\text{Number of moles of vitamin C} = (500 \times 10^{-3}) \div 176 = 2.84 \times 10^{-3} \text{ mol}$$

$$\text{Concentration of vitamin C} = 2.84 \times 10^{-3} \text{ mol dm}^{-3}$$



$$[A^-] = \frac{0.0794}{100} \times (2.84 \times 10^{-3}) = 2.25 \times 10^{-6} \text{ mol dm}^{-3}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{(2.25 \times 10^{-6} + 0.1)(2.25 \times 10^{-6})}{(2.84 \times 10^{-3} - 2.25 \times 10^{-6})} = \frac{(2.25 \times 10^{-7})}{(2.84 \times 10^{-3})} = 7.92 \times 10^{-5} \text{ mol dm}^{-3}$$

- (ii) Blood has a pH of 7.35 and is saturated with carbon dioxide. Concentration of  $H_2CO_3$  in blood is  $3.20 \times 10^{-3} \text{ mol dm}^{-3}$ . The equilibrium reaction acts as a buffer.



With the aid of balanced equations, explain clearly how this buffering action minimizes the change in pH on the addition of either acid or alkali.

When acid is added,



There is a large reservoir of  $HCO_3^-$  to remove the addition of small amount of acid and keep the pH almost constant.

When base is added,



There is a large reservoir of  $H_2CO_3$  to remove the addition of small amount of base and keep the pH almost constant.

- (iii) Calculate the concentration of  $HCO_3^-$  in the blood.

$$\text{When } [H^+] = 10^{-7.35} = 4.47 \times 10^{-8} \text{ mol dm}^{-3}$$

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

$$[HCO_3^-] = \frac{[H_2CO_3](4.5 \times 10^{-7})}{[H^+]} = \frac{(3.2 \times 10^{-3})(4.5 \times 10^{-7})}{4.47 \times 10^{-8}} = 3.22 \times 10^{-2} \text{ mol dm}^{-3}$$

- (iv) Explain qualitatively how the extent of ionisation of vitamin C changes as it moves from the stomach to the bloodstream.

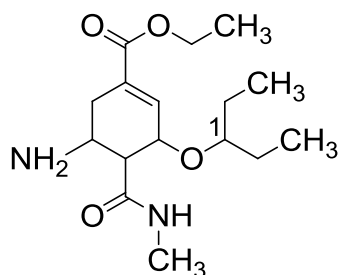
Blood has higher pH than stomach/more alkaline, concentration of  $H^+$  ions is lower.



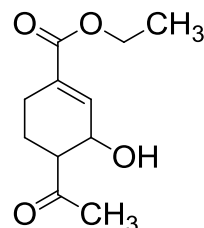
Extent of ionization of vitamin C increases

[9]

- (b) Oseltamivir (Tamiflu) is an antiviral drug that slows the spread of non-resistant strains of the influenza virus between cells in the body. It blocks the action of a viral enzyme called neuraminidase and has since been indicated for the treatment of H5N1 and H1N1 infection. The standard adult dosage is 75 mg twice daily. Compound **C** is a derivative of Oseltamivir that may be investigated for antiviral activities.



**Oseltamivir**  
 $M_r = 312.4$



**Compound C**

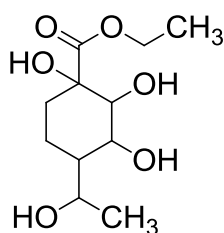
- (i) A male adult patient has been put on a 1 week oseltamivir treatment. Calculate the total number of moles of oseltamivir taken by this patient over the period of treatment.

$$\text{No of moles of oseltamivir} = \frac{(75 \times 10^{-3})}{312.4} \times 2 \times 7 = 3.36 \times 10^{-3} \text{ mol}$$

- (ii) State the shape and bond angle about the carbon atom labelled '1'.

**Shape: Tetrahedral**  
**Bond angle:  $109.5^\circ$**

- (iii) Compound **D** can be synthesised from **C** in two steps. Give the reagents, conditions and intermediates for this two-step synthesis. Name the types of reactions involved.

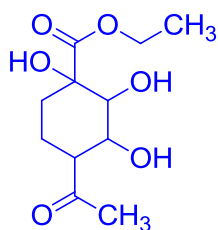


**Compound D**

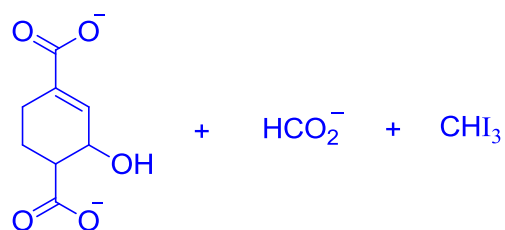
**Step I:**  
**Reagent:  $\text{KMnO}_4$ ,  $\text{OH}^-$**   
**Condition: Cold / r.t.**  
**Type of reaction: oxidation**

**Step II:**  
**Reagent:  $\text{H}_2$**   
**Condition: Pt, r.t.**  
**Type of reaction: reduction**

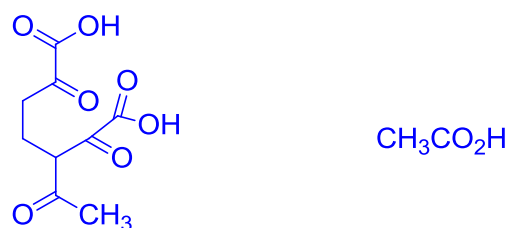
## Intermediate



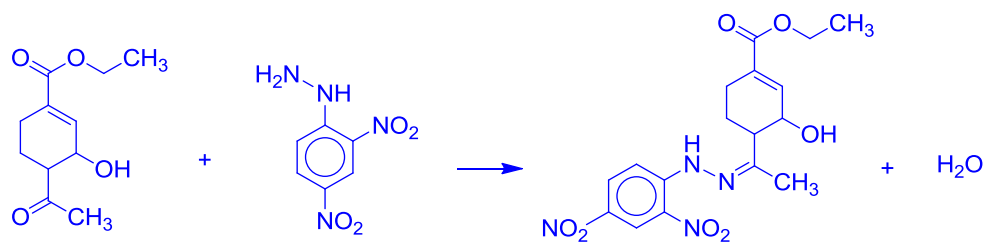
- (iv) Draw the organic products formed when compound **C** is reacted with  
(I) hot aqueous alkaline iodine



- (II) hot aqueous acidic  $\text{KMnO}_4$



- (v) Write the balanced equation for the reaction of compound **C** with 2,4-dinitrophenylhydrazine.



[11]

[Total: 20]