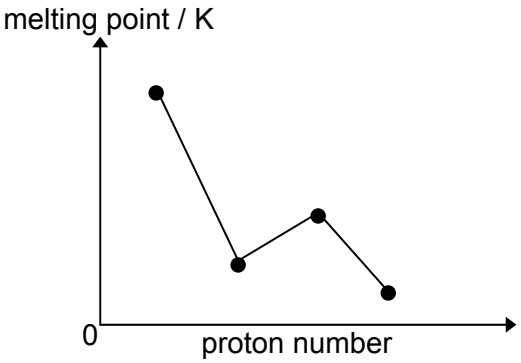
Section B

Answer **two** of the following three questions.

5 (a) The diagram represents the melting points of four consecutive elements in the third period of the Periodic Table.



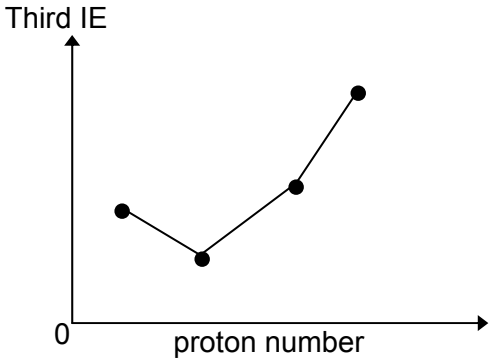
(i) Identify the elements giving reasons for your choice. **[3]**

Si, P, S and Cl

Si has a giant molecular structure with covalent bonds linking the Si atoms that require a lot energy to break on melting.

P and S have simple molecular structures with id-id forces between molecules. As size of polarizable electron cloud is higher for S, its mpt is higher. Cl exists as diatomic molecules with weak id-id forces between the molecules.

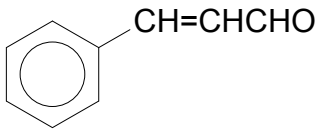
(ii) Sketch a graph to show the third ionization energies of these 4 elements and give reasons for any trends shown in the graph. **[3]**



General trend of increase in 3rd IE moving from Si to Cl as effective nuclear charge increases.

3rd IE of Si is higher as the 3rd electron is removed from the 3s subshell which is more stable (lower in energy) than P where the 3rd electron is removed from the 3p sub shell which is further away from the nucleus.

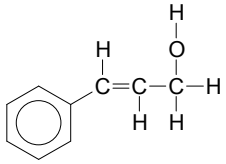
(b) The main component of cinnamon oil is cinnamaldehyde.



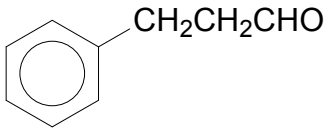
(i) State suitable reagents and conditions required to reduce only the carbonyl functional group of cinnamaldehyde. **[2]**

Draw the full structural formula of the organic product.

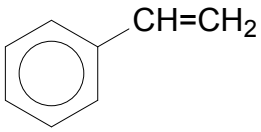
Reagents & Conditions: (i) $LiAlH_4$ in dry ether, (ii) dilute acid



(ii) Suggest simple test-tube reactions (one in each case) that could be used to distinguish cinnamaldehyde from compounds **A** and **B** below. **[4]**



A



B

[Equations are not required.]

To distinguish cinnamaldehyde from A:
Reagents and conditions: Br_2 (aq)
Observation: Cinnamaldehyde will decolourise orange Br_2 but A would not.

To distinguish cinnamaldehyde from B:
Reagents and conditions: 2,4-dinitrophenylhydrazine
Observation: Cinnamaldehyde will form orange ppt but B would not.

(c) Chloroflurocarbons (CFCs) are used in refrigerants, aerosol propellants and fire extinguishers. **[1]**
The table below shows the boiling points of some CFCs and their derivatives.

Compound	Boiling point / ^oC
$CBrF_3$	149
CHF_2Cl	41
CF_2Cl_2	–30

Name one physical property of CFCs that makes them suitable for their uses.

Any one : Inert; non-toxic; non-flammable; low boiling point

(d) Greenhouse gases are those that can absorb and emit infrared radiation but not radiation in or near the visible spectrum. Water, carbon dioxide and ozone are some of the more abundant greenhouse gases.

(i) Draw the dot−and−cross diagram of the CO_2 and H_2O molecules. State their bond angles and molecular shapes. **[4]**

Dot cross diagrams
180^o for CO_2 and 104.5^o for H_2O
Linear and bent

(ii) The 'hole' in the ozone layer over the Antarctic has been attributed to the reaction between CFCs and ozone in the stratosphere *via* the following:

$CF_2Cl_2 \rightarrow CF_2Cl\bullet + Cl\bullet$ ---------- Step (1); slow

$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$ ---------- Step (2); fast

$ClO\bullet + O_3 \rightarrow Cl\bullet + O_2$ ---------- Step (3); fast

where $CF_2Cl\bullet$, $Cl\bullet$, $ClO\bullet$ are radicals which contain an unpaired electron.

Briefly explain why fluorine radicals, $F\bullet$, are not formed in step (1).

More energy is required to break the stronger C–F bond than C–*Cl* bond.

(iii) State one effect of ozone depletion and a measure that has been taken to reduce ozone depletion. **[3]**

Increase in uv radiation leads to lowering of body immunity system/global warming effect of the planet/ eye cataract (any one)

Restriction on the use of CFCs / use alternative products (HFCs) / decrease the production of compounds containing chlorine and bromine. (any one)

[Total: 20 marks]

6 Acetals are compounds formed when aldehydes or ketones are reacted with an alcohol and an acid catalyst. For example, propanal and ethanol were reacted in an inert solvent dioxin with an acid catalyst to produce acetal **Z** as shown in **reaction 1** below.

Reaction 1

$$CH_3CH_2CHO\ (l) + 2CH_3CH_2OH(l) \overset{H^+}{\rightleftharpoons} \underset{\text{acetal Z}}{CH_3CH_2CH(OCH_2CH_3)_2\ (l)} + H_2O(l)$$

(a) When the initial rate of the above **reaction 1** was measured at various starting concentrations of the three reactants, the following results were obtained.

Experiment Number	$[CH_3CH_2CHO]$/ mol dm^{-3}	$[CH_3CH_2OH]$/ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	Rate/ mol dm^{-3} s^{-1}
1	0. 20	0. 10	0.050	0.100
2	0. 25	0. 10	0.050	0.125
3	0. 25	0. 16	0.050	0.200
4	0. 20	0. 16	0.100	0.320

(i) Use the data in the table to determine the order with respect to each reactant. **[7]**

Compare expt 1 and expt 2
$[CH_3CH_2CHO]$ increases by 1.25 times, rate increases by 1.25 times
Ist order w.r.t. CH_3CH_2CHO

Compare expt 2 and expt 3
$[CH_3CH_2OH]$ increases by 1.6 times, rate increases by 1.6 times
Ist order w.r.t. CH_3CH_2OH

Let rate = $k[CH_3CH_2CHO]\ [CH_3CH_2OH][H^+]^n$
Compare expt 1 and expt 4

$$\frac{0.32}{0.10} = \frac{(0.16)(0.10)^n}{(0.10)(0.05)^n}$$

$$3.2 = (1.6)(2)^n$$
$$2 = 2^n$$
n = 1 Ist order w.r.t. H^+

(ii) Use your results from **(a)(i)** to write the rate equation for the reaction.

rate = $k[CH_3CH_2CHO]\ [CH_3CH_2OH][H^+]$

(iii) Calculate the rate constant and state its units.

$k = 0.1/(0.2)(0.1)(0.05) = 1.00 \times 10^2\ mol^{-2}\ dm^6\ s^{-1}$

(iv) Calculate the rate of the reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm^{-3}.

Rate = $(1 \times 10^2)(0.2)(0.2)(0.2) = 0.800$ mol dm^{-3} s^{-1}

(b) The concentration of the acetal **Z** was measured when experiment 1 in **(a)** was allowed to reach equilibrium. The result is included in the following table.

	$[CH_3CH_2CHO]$ / mol dm^{-3}	$[CH_3CH_2OH]$ / mol dm^{-3}	$[H^+]$ /mol dm^{-3}	[acetal **Z**] /mol dm^{-3}	$[H_2O]$ /mol dm^{-3}
At start	0.20	0.10	0.05	0.00	0.00
At equilibrium				0.025	

(i) Given that the equilibrium concentration of acetal **Z** is 0.025 mol dm^{-3}, calculate the equilibrium concentrations of the reactants, catalyst and product. **[8]**

At equilibrium,

$[H^+]$ = 0.05 mol dm^{-3}

$[H_2O]$ = 0.025 mol dm^{-3}

$[CH_3CH_2CHO]$= 0.20-0.025 =0.175 mol dm^{-3}

$[CH_3CH_2OH]$ = 0.10-2(0.025) = 0.050 mol dm^{-3}

(ii) Write the expression for the equilibrium constant for this reaction, K_c, stating its units.

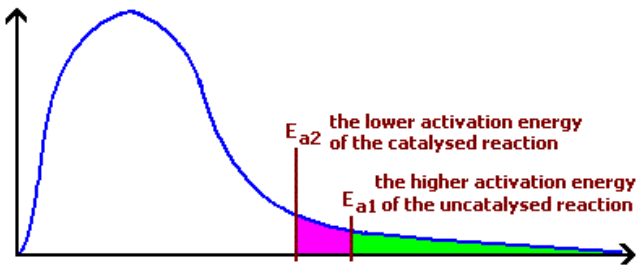
$$K_c = \frac{[\text{acetal } \mathbf{A}][H_2O]}{[CH_3CH_2CHO][CH_3CH_2OH]^2}$$ **[1]** **Units: mol^{-1} dm^3** **[1]**

(iii) Use the equilibrium concentration values to calculate the value of K_c.

$K_c = 0.025^2/(0.175)(0.05^2) = 1.43$ mol^{-1} dm^3

(iv) Explain, with the aid of the Maxwell Boltzmann distribution curve, how the acid catalyst can speed up the reaction between propanal and ethanol as shown in **reaction 1.**

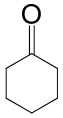
A catalyst increases reaction rate by providing an **alternative reaction pathway** that has **lower** activation energy without itself undergoing any permanent chemical change i.e. it is **regenerated**



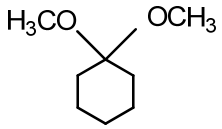
As the activation energy is lowered i.e. $E_{a2} < E_{a1}$,

The proportion of particles with kinetic energy ≥ activation energy **increases**. Consequently, the frequency of effective collisions **increases** thus reaction rate **increases.**

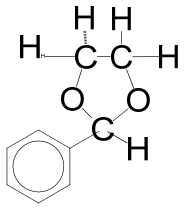
(c) (i) Give the structural formula of the acetal formed when cyclohexanone, **[5]**



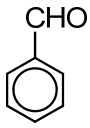
, is reacted with methanol, CH_3OH, in the presence of an acid catalyst.



(ii) Predict the aldehyde and alcohol used to prepare ethylene acetal as shown below.

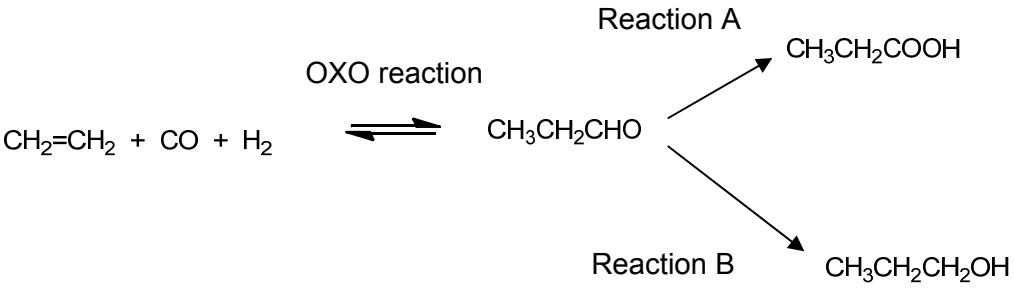


ethylene acetal



$+ HOCH_2CH_2OH$ **[1] +[1]**

(iii) Propanal used in **reaction 1** can be prepared by the "OXO" reaction. This reaction is an important homogeneously catalyzed industrial process for the production of aldehydes from alkenes. This chemical reaction entails the addition of a CHO group and a hydrogen atom to a carbon-carbon double bond. Propanal can also be used to prepare other useful products as shown below.



State the reagents and conditions needed for

- Reaction A
- Reaction B

Reaction A-$K_2Cr_2O_7/H_2SO_4$/heat under reflux or $KMnO_4/H_2SO_4$/heat under reflux
Reaction B-H_2(g), Ni/heat or $NaBH_4$ or $LiAlH_4$/dry ether/reflux

[Total: 20 marks]

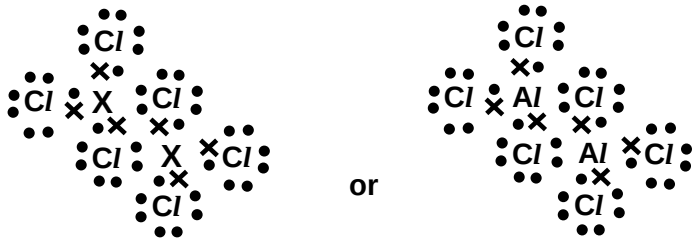
7 Elements **X**, **Y** and **Z** are consecutive elements in period 3 of the Periodic Table.

It is known that the element **X** and **Y** both form chlorides which hydrolyse in water to form acidic solutions and oxides which have high melting point.

(a) At room temperature, the chloride of **X** exists as a yellow-white solid and has the empirical formula of **X**C*l*$_3$ and a relative molecular mass of 267. **[2]**

Suggest the molecular formula of the solid and draw a dot-and-cross diagram to illustrate its bonding.

X_2Cl_6 or Al_2Cl_6



(b) The chloride of **X** can react with water in two separate ways.

1) When a few drops of water are added to the chloride of **X**, a violent reaction is observed. Steamy white fumes are produced and a white solid, which is insoluble in water, is formed.

2) When the chloride of **X** is added to excess amount of water, a weakly acidic solution is formed instead.

Write balanced equations, including state symbols, for the above two reactions and briefly explain the result in the second reaction. **[3]**

Al_2Cl_6 (s) + $6H_2O$ (*l*) ⟶ $2Al(OH)_3$ (s) + 6HC*l* (g) or
X_2Cl_6 (s) + $6H_2O$ (*l*) ⟶ $2X(OH)_3$ (s) + 6HC*l* (g) [1]

$[Al(H_2O)_6]^{3+}$(aq) + H_2O(*l*) ⇌ $[Al(H_2O)_5(OH)]^{2+}$(aq) + H_3O^+(aq) or
$[X(H_2O)_6]^{3+}$(aq) + H_2O(*l*) ⇌ $[X(H_2O)_5(OH)]^{2+}$(aq) + H_3O^+(aq) [1]

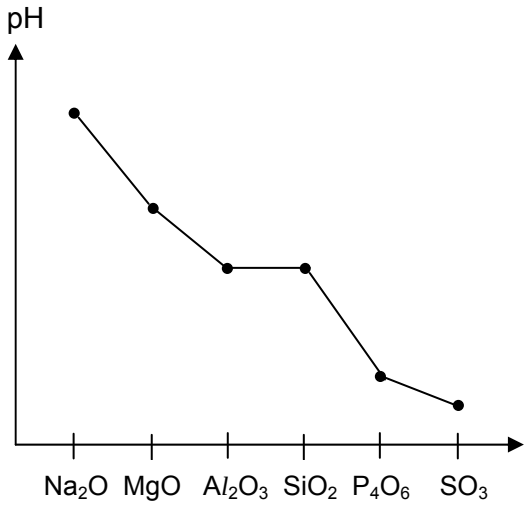
Due to the <u>high polarising power of the small, highly charged X^{3+}/Al^{3+}</u> in solution, <u>substantial hydrolysis</u> of X_2Cl_6 / Al_2Cl_6 occurs, which then releases H^+, forming a weakly acidic solution.

(c) Deduce and explain if the melting point of the chloride of **X** is higher or lower than that of the chloride of **Y**. **[2]**

The melting point of the chloride of X is <u>higher</u> than that of the chloride of Y as the chloride of X exists as X_2Cl_6 which has <u>a larger and more polarizable electron cloud</u> than that of the chloride of Y. Thus <u>more energy is needed to overcome the weaker induced dipole-induced dipole / van der waals' forces.</u>

(d) The oxides of Period 3 elements can dissolve in or react with water to form solutions of different pH.

(i) Considering only the higher oxides of sodium to sulfur, sketch a graph to show the variation in pH of the solutions produced. Label your axes clearly. **[5]**



(ii) Briefly explain the general shape of your graph, relating to the nature of the oxides.

Na_2O is a <u>basic/ionic oxide</u> which is readily soluble in water and reacts to form a <u>strongly alkaline solution</u> of NaOH.

MgO(s) is also a <u>basic/ionic oxide</u>, it is <u>slightly soluble</u> in water due to its high lattice energy and reacts with water to give a <u>weakly alkaline</u> solution of $Mg(OH)_2$.

Al_2O_3 <u>does not dissolve</u> in water because of its high lattice energy and likewise for SiO_2, it does not dissolve in water because of the strong covalent bonds between Si and O atoms in the giant covalent structure. Since the oxides do not dissolve in water, the <u>pH of the solution remains at 7</u>.

P_4O_{10} and SO_3 are <u>acidic/covalent oxides</u> which react readily with water to form <u>strongly acidic</u> solutions.

(e) Samples of the oxide of **X** and the oxide of **Y** are accidentally mixed up. Describe a simple chemical test to distinguish these two samples and state the observation. Write a balanced equation for the reaction that occurs. **[3]**

Add <u>dilute hydrochloric / sulfuric acid</u> to both samples.

The oxide that reacts with acid and <u>dissolves</u> will be the oxide of X. The <u>oxide of Y will remain undissolved</u>.

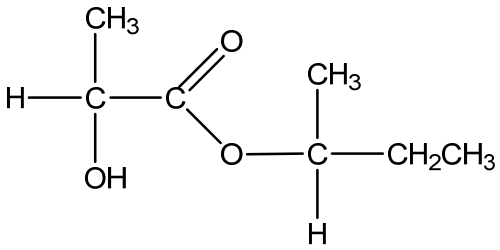
$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$ or
$X_2O_3(s) + 6H^+(aq) \rightarrow 2X^{3+}(aq) + 3H_2O(l)$

(f) The higher chloride of **Z** and the oxide of **X** are common chemical reagents that are widely used in organic reactions. The following reactions show how they are used in the chemical conversion of organic compounds. **[5]**

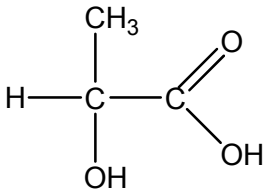
A neutral compound **A**, $C_7H_{14}O_3$, is heated in dilute sulfuric acid to form compounds **B**, $C_3H_6O_3$ and **C**, $C_4H_{10}O$ respectively. Compound **B** can react with 2 moles of the higher chloride of **Z** to give compound **D**. Compound **B** can also react with the oxide of **X** at 350^{o}C to form compound **E**. It is known that both compounds **B** and **C** give positive results with alkaline aqueous iodine.

Identify compounds **A** to **E**. Explanation is not required.

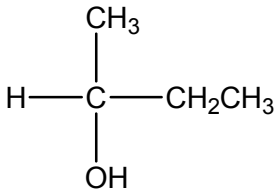
Compound A:



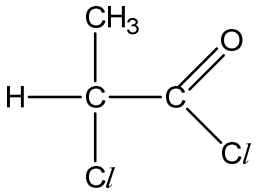
Compound B:



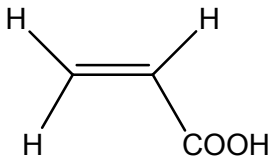
Compound C:



Compound D:



Compound E:



[Total: 20 marks]