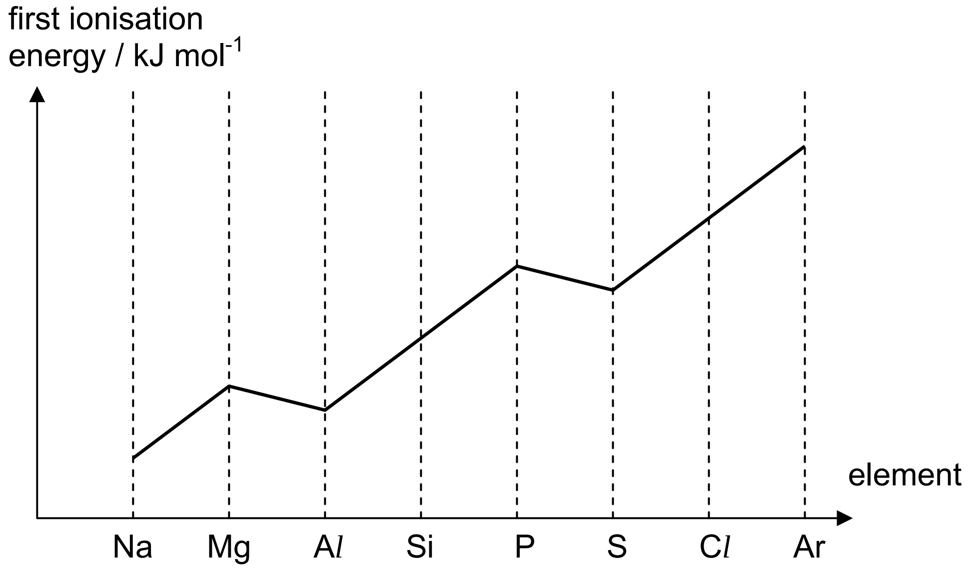
Section A

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

1 This question is about aluminium, an element in the third period of the Periodic Table.

(a) (i) On the grid below, sketch the trend of the first ionisation energies of elements of Period 3 from sodium to argon.



[1]

(ii) Write an equation for the first ionisation energy of aluminium.

$Al(g) \rightarrow Al^{+}(g) + e^{-}$

(iii) Explain why the first ionisation energy of aluminium is lower than magnesium.

first electron of Al is removed from a <u>higher sub-energy level</u> as compared to that of Mg

[3]

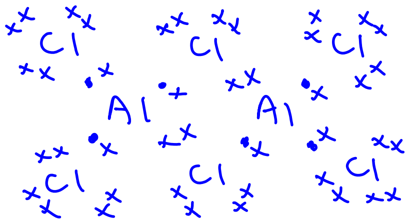
(b) A beam of particles of $^{27}Al^{+}$ and $^{9}Be^{+}$ is passed through an electric field. If the angle of deflection of the $^{27}Al^{+}$ particle is 3°, state the angle of deflection for the $^{9}Be^{+}$ particle.

9°

[1]

$AlCl_3$ is a covalent compound that exists as a white solid at room temperature and pressure. When $AlCl_3$ is heated to a sufficiently high temperature, it sublimes to gives the Al_2Cl_6 dimer.

(c) Draw a dot-and-cross diagram for the Al_2Cl_6 dimer. Name the type of bond responsible for the formation of the dimer.



Type of bond: **dative bond**

[2]

(d) 2.0 mol of gaseous $AlCl_3$ is heated at 800 K in a 750 cm^3 vessel. When dynamic equilibrium is achieved, 0.971 mol of gaseous Al_2Cl_6 is formed in the vessel.

(i) Define the term *dynamic equilibrium*.

rate of forward reaction equals rate of reverse reaction

(ii) Write a balanced equation for the equilibrium.

$2AlCl_3 \rightleftharpoons Al_2Cl_6$

(iii) Calculate the value and state the units of the equilibrium constant, K_c, for this reaction at 800 K.

equation	**$2AlCl_3$** $\rightleftharpoons$	**Al_2Cl_6**
initial amount / mol	**2**	**0**
change in amount / mol	**-2(0.971)**	**+0.971**
equilibrium amount / mol	**0.058**	**0.971**
equilibrium [ ] / mol dm^{-3}	**0.058 / 0.75 = 0.07733**	**0.971 / 0.75 = 1.2947**

[1 (amount) +1 (concentration)]

$$K_c = \frac{[Al_2Cl_6]}{[AlCl_3]^2} = \frac{(1.2947)}{(0.07733)^2} = 216 \text{ mol}^{-1}\text{ dm}^3 \quad [1]$$

[5]

(e) $AlCl_3$ dissolves in water to give an acidic solution, as shown by the following equation.

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$

(i) Define the term *Bronsted base*. Hence, identify the two *Bronsted* bases and state one conjugate acid-base pair in the equation above.

Definition of *Bronsted base*: **proton acceptor**.

The two *Bronsted* bases are **H_2O** and **$[Al(H_2O)_5(OH)]^{2+}$**

One conjugate acid-base pair: **$[Al(H_2O)_6]^{3+}$ and $[Al(H_2O)_5(OH)]^{2+}$**.
OR H_3O^+ and H_2O

(ii) Write an expression for the acid dissociation constant, K_a, of $[Al(H_2O)_6]^{3+}$.

$$K_a = \frac{[Al(H_2O)_5(OH)^{2+}][H_3O^+]}{[Al(H_2O)_6{}^{3+}]}$$

(iii) When 0.1 mol of $AlCl_3$ is dissolved in 1 dm^3 of solution, the resulting solution is found to have a pH of 3. Using your equation in **(ii)**, calculate the K_a of $[Al(H_2O)_6]^{3+}$.

$[H^+] = [Al(H_2O)_5(OH)]^{2+} = 10^{-3} = 1.0 \times 10^{-3}$ mol dm^{-3}

$$K_a = \frac{(1.0x10^{-3})^2}{0.1} = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$$

OR $$K_a = \frac{(1.0x10^{-3})^2}{(0.1-1.0x10^{-3})} = 1.01 \times 10^{-5} \text{ mol dm}^{-3}$$

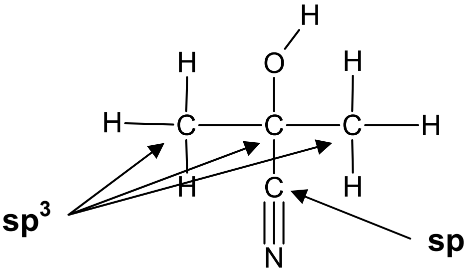
[6]

[Total: 17]

2 Cyanohydrins can be made by reacting ketones with an acidified solution of sodium cyanide. When propanone is reacted as described, compound **T** is formed.

$$(CH_3)_2CO + H^+ + CN^- \rightarrow \mathbf{T}$$

(a) Draw the displayed formula of compound **T**. On your diagram, state the type of hybridisation of all the carbon atoms in **T**.



[2]

An experiment is performed in which 2.00 mol dm^{-3} of propanone is reacted with an excess of an acid and sodium cyanide. The following results are obtained.

time / s	[$(CH_3)_2CO$] / mol dm^{-3}
0	2.00
15	1.30
30	0.84
45	0.55
60	0.35
75	0.23

(b) (i) On the grid provided below, plot a graph of these values on suitable axes.

(ii) Using your graph, deduce the order of reaction with respect to propanone.

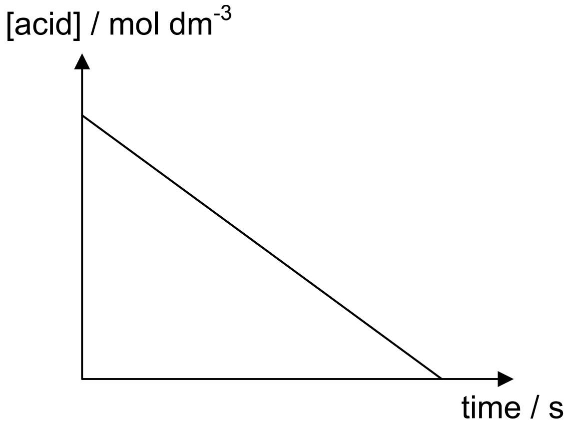
workings of two $t_{\frac{1}{2}}$ on graph
$t_{\frac{1}{2}}$ is constant at 24.5 s
order of reaction w.r.t. propanone is 1

(iii) Why are the concentration of the acid and the concentration of sodium cyanide used in excess?

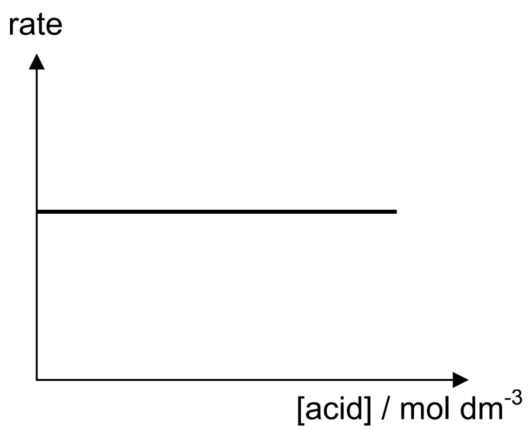
to ensure their concentration remain relatively constant during the reaction and not affect the change in rate of reaction

[5]

(c) When the experiment is repeated using 1.00 mol dm^{-3} of the acid and an excess of propanone and sodium cyanide, the following **Graph 1** of concentration of the acid against time is obtained.



Graph 1



Graph 2

On **Graph 2** above, sketch a graph for the rate of reaction of the acid against the concentration of the acid. Hence, state the order of reaction with respect to the acid.

Order of reaction with respect to the acid: **zero order**

[2]

(d) The order of reaction with respect to sodium cyanide is one. Together with your answers in **(b)(ii)** and **(c)**, write the rate law for this reaction.

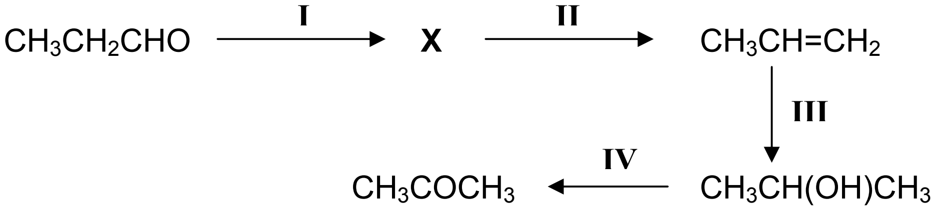
rate = k [$(CH_3)_2CO$] [CN^-]

[1]

(e) (i) Propanal is a functional group isomer of propanone. Suggest a simple chemical test to distinguish between propanal and propanone. State any observations seen.

Test	Propanal	Propanone
I_2(aq), NaOH(aq), heat	**no yellow ppt seen**	**yellow ppt of CHI_3 seen**
$K_2Cr_2O_7$(aq) / $KMnO_4$(aq), H_2SO_4(aq), heat	**purple MnO_4^- decolourised / orange $Cr_2O_7^{2-}$ turned green**	**no observable change**
Tollens' reagent, warm / heat	**silver mirror seen**	
Fehling's solution, warm / heat	**brick red ppt of Cu_2O seen**	

(ii) Propanal can be converted to propanone in the laboratory as follows.



Identify compound **X**. State the reagent and conditions for Step **I** and **III**.

Compound **X**: **$CH_3CH_2CH_2OH$**

Step **I**: **$LiAlH_4$ in dry ether OR H_2(g), Ni, 200 °C**

Step **III**: **(i) concentrated H_2SO_4 (ii) H_2O(l), heat**
OR concentrated H_3PO_4, H_2O(g), 300 °C, 60 atm

(iii) Draw the structural formula of the compound formed when propanal reacts with 2,4-dinitrophenylhydrazine.

$CH_3CH_2CH=N\text{-}NH_2C_6H_3(NO_2)_2$

[6]

[Total: 16]

3 Olive oil is a popular flavouring used in Mediterranean cuisine. The main constituent of olive oil is oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$.

(a) Name the functional groups that are present in oleic acid.

alkene and carboxylic acid

[1]

(b) State the reagent and condition to synthesise oleic acid **from** $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$.

$K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat

[1]

(c) State the reagents and conditions needed to convert oleic acid **into** each of the following.

compounds	reagents and conditions
$CH_3(CH_2)_7CH(OH)CHBr(CH_2)_7CO_2H$	**$Br_2(aq)$**
$CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_7CO_2H$	**$KMnO_4(aq)$, $H_2SO_4(aq)$, cold (if NaOH(aq), no full credit]**
$CH_3(CH_2)_7CHCl(CH_2)_8CO_2H$	**$HCl(g)$**

[3]

(d) Another constituent of olive oil is linoleic acid. Linoleic acid has the same functional groups as oleic acid. When linoleic acid is oxidised, the following compounds are obtained in **equimolar** quantities.

$CH_3(CH_2)_4CO_2H$, $HO_2CCH_2CO_2H$, $HO_2C(CH_2)_7CO_2H$

Write the **two** possible structural formula of linoleic acid.

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$

and $CH_3(CH_2)_4CH{=}CH(CH_2)_7CH{=}CHCH_2CO_2H$

[2]

[Total: 7]

Section B

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

4 Silver is a precious metal with the highest electrical and thermal conductivity of any metal.

(a) The two naturally occurring isotopes of silver are ^{107}Ag and ^{109}Ag. The *relative atomic mass* of silver, to two decimal places, is 107.87.

(i) Define the term *relative atomic mass*.

relative atomic mass is ratio of the average mass of one atom of an element to 1/12 of the mass of one ^{12}C atom / isotope.

(ii) Calculate the percentage abundance of ^{107}Ag.

$$\frac{107x + 109(100 - x)}{100} = 107.87$$

x = 56.5%

[3]

(b) The electronic configurations of elements in the periodic table show a recurring trend from one period to another. Thus, silver has similar electronic configuration as copper, but with one more principal quantum shell.

(i) Using your knowledge of this recurring trend, as well as the electronic configuration of Cu$^+$, write the electronic configuration of Ag$^+$.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$ OR [Ar] $3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$

(ii) State the number of protons, neutrons and electrons in one ^{107}Ag$^+$ ion.

Number of protons = 47
Number of electrons = 46
Number of neutrons = 60

[3]

(c) Three samples of bromocyclohexane, chlorocyclohexane and chlorobenzene are provided. All three are colourless liquids at room temperature and pressure. The three samples are randomly labeled as **P**, **Q** and **R**.

To distinguish between the three, ethanolic silver nitrate is shaken separately with the three unknown samples. The observations are presented as follow.

sample	colour of precipitate	length of time taken for precipitate to be seen
P	no precipitate seen	
Q	cream	2 minutes
R	white	7 minutes

State which of the samples **P**, **Q** and **R** are bromocyclohexane, chlorocyclohexane and chlorobenzene. Explain the observations. [5]

P is chlorobenzene, Q is bromocyclohexane and R is chlorocyclohexane. The cream ppt is AgBr and the white ppt is AgC*l*.

For P, lone electron pair on C*l* is delocalised into benzene ring. The C – C*l* bond has partial double bond character.

R reacts slower than Q because the C – C*l* bond is stronger than the C – Br bond. There is a greater extent of orbitals overlap between C and C*l* in R than C and Br in Q.

(d) Silver is widely used as a catalyst in some industrial reactions. Gaseous epoxyethane, $C_2H_4O(g)$, is produced by the oxidation of ethene with oxygen at 250 ^oC with a silver-based catalyst.

$$7C_2H_4(g) + 6O_2(g) \rightleftharpoons 6C_2H_4O(g) + 2CO_2(g) + 2H_2O(g)$$

(i) Using a Maxwell-Boltzmann distribution curve, explain how the silver-based catalyst increases the rate of the reaction.

(Maxwell-Boltzmann curve)
Catalyst provides an alternative reaction pathway with lower activation energy. Frequency of effective collision increases

(ii) The standard enthalpy changes of formation of the compounds in the production of epoxyethane, $C_2H_4O(g)$, are given as follow.

compound	ΔH_f^θ / kJ mol^{-1}
$C_2H_4(g)$	+ 52.5
$C_2H_4O(g)$	- 52.6
$CO_2(g)$	- 393.5
$H_2O(g)$	- 241.8

Write an equation to define for the standard enthalpy change of formation of gaseous epoxyethane. Using the ΔH_f^θ given, calculate the enthalpy change of the reaction shown.

$$2C(s) + 2H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_4O(g)$$

$$\begin{aligned}\Delta H &= \textstyle\sum m\Delta H_f^\theta(\text{products}) - \sum n\Delta H_f^\theta(\text{reactants})\\ &= [6\Delta H_f^\theta(C_2H_4O) + 2\Delta H_f^\theta(CO_2) + 2\Delta H_f^\theta(H_2O)] - [7\Delta H_f^\theta(C_2H_4) + 6\Delta H_f^\theta(O_2)]\\ &= [6(-52.6) + 2(-393.5) + 2(-241.8)] - [7(+52.5) + 6(0)]\\ &= -1950 \text{ kJ mol}^{-1}\end{aligned}$$

(iii) Explain how an increase in pressure will affect the reaction.

A higher pressure increases the rate of the reaction.
When pressure increases, position of equilibrium shifts to the right. There will be a higher yield at equilibrium.

[9]
[Total: 20]

5 Na_2O, Al_2O_3 and P_4O_{10} are oxides of Period 3 elements.

(a) Compare and explain the difference in melting point of sodium metal and aluminium metal. [2]

Aluminium has a higher melting point than sodium.
More delocalised electrons, stronger metallic bond.

(b) Both Al_2O_3 and P_4O_{10} exist as white solids under room temperature and pressure. The two oxides can be differentiated by dissolving them separately in water containing universal indicator. State your observations when the two are dissolved separately. Write balanced equations for any reaction which takes place. [3]

Al_2O_3 does not dissolve in water. Universal indicator remains green.
P_4O_{10} dissolves to give a red / orange solution.
$P_4O_{10}(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(aq)$

(c) Enthalpy change of reaction 1, ΔH_1, can be determined using enthalpy change of reaction 2, ΔH_2, and enthalpy change of reaction 3, ΔH_3, in the energy cycle below.

$$\begin{tikzcd}
Na_2O(s) + H_2O(l) + 2HCl(aq) \arrow[rr, "\Delta H_1"'] \arrow[dr, "\Delta H_2"'] & & 2NaOH(aq) + 2HCl(aq) \arrow[dl, "\Delta H_3"] \\
& 2NaCl(aq) + 2H_2O(l) &
\end{tikzcd}$$

(i) ΔH_2 can be calculated from the reaction between $Na_2O(s)$ and $HCl(aq)$. When 6.2 g of $Na_2O(s)$ is dissolved in 250 cm^3 of 1.0 mol dm^{-3} $HCl(aq)$, the temperature of the solution rose by 17 °C. Calculate ΔH_2.

$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$
$n(Na_2O) = 6.2 / 62.0 = 0.100$ mol (limiting)
$n(HCl) = 0.250 \times 1.0 = 0.250$ mol (excess)
Hence, $n(H_2O$ produced$) = 0.100$ mol

$\Delta H_2 = -(0.25 \times 4.18 \times 17) / 0.100 = -178$ kJ mol^{-1}

(ii) The enthalpy change of neutralisation between $NaOH(aq)$ and $HCl(aq)$ is known to be - 57.3 kJ mol^{-1}. Define the term enthalpy change of neutralisation. Hence, calculate ΔH_3.

Enthalpy change of neutralisation is the heat energy evolved when acid and base react to form one mole of water under standard condition of 298 K and 1 atm.

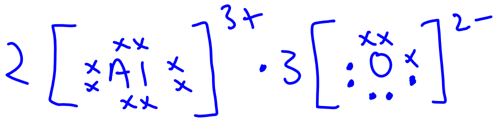
OR $H^+(aq) + OH^-(aq) \rightarrow H_2O$

$\Delta H_3 = 2(-57.3) = -114.6$ kJ mol^{-1}

(iii) Using your answer in **(i)** and **(iii)**, calculate ΔH_1.

$\Delta H_1 = \Delta H_2 - \Delta H_3 = -178 - (-115) = -63$ kJ mol^{-1} [6]

(d) (i) Draw the dot-and-cross diagram of Al_2O_3.



(ii) With reference to your dot-and-cross diagram in **(i)**, or otherwise, state and explain one main physical properties of Al_2O_3.

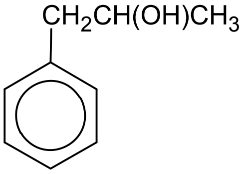
able to conduct electricity in the molten and aqueous state
presence of free ions to act as charge carriers

OR high melting point
strong electrostatic attractive force between oppositely charged ions

(Reject: ionic compound dissolves in water because Al_2O_3 does not)

[3]

(e) Draw the organic product formed when Compound **Y** is reacted separately with each of the reagents and conditions stated below. For each, name the type of reaction that has taken place.



Compound **Y**

(i) Al_2O_3, heat

$C_6H_5CH{=}CHCH_3$ OR $C_6H_5CH_2CH{=}CH_2$, dehydration

(ii) Cl_2 in $AlCl_3$

***o*- or *p*-$ClC_6H_4CH_2CH(OH)CH_3$, substitution**

(iii) Na metal

$C_6H_5CH_2CH(O^-)CH_3$, reduction

[6]

[Total: 20]

6 Both thionyl chloride, $SOCl_2$, and phosphorus trichloride, PCl_3, are colourless liquids at room temperature and pressure. Both are used extensively in organic reactions.

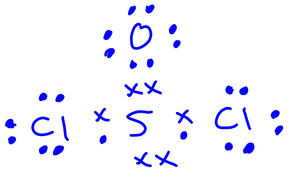
(a) Draw the electronic configuration of phosphorus and sulfur. Hence, briefly explain why sulfur has a lower first ionisation energy compared to phosphorus. [2]

P: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

Inter-electronic repulsion of valence electron in S

(b) Draw the dot-and-cross diagram of $SOCl_2$ and state the shape of the molecule. [2]

trigonal pyramidal



(c) SO_2 can be used to synthesis $SOCl_2$ in industry, as shown by the following equation.

$$SO_2 + Cl_2 + SCl_2 \rightarrow SOCl_2$$

(i) Use oxidation numbers to explain why this reaction is described as a redox reaction.

oxidation of S from +2 in SCl_2 to +4 in $SOCl_2$
reduction of Cl from 0 in Cl_2 to -1 in $SOCl_2$

(ii) SO_2 is produced in small quantity from motorised vehicles in their internal combustion engines. Besides SO_2, NO_2 and CO are also produced. These are environmental pollutants. Write an equation to show how NO_2 and CO can react to produce less harmful products in a catalytic converter.

$2NO_2 + 4CO \rightarrow N_2 + 4CO_2$

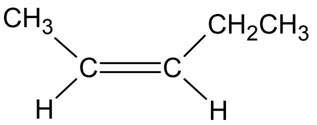
[3]

(d) Write balanced equations when $SiCl_4$ and PCl_3 are dissolved separately in water. State the pH values of the resulting solutions. [3]

$SiCl_4(l) + 2\ H_2O(l) \rightarrow SiO_2(s) + 4\ HCl(aq)$
$PCl_3(l) + 3\ H_2O(l) \rightarrow H_3PO_3(aq) + 3\ HCl(aq)$
pH about 1 to 3

(e) Among all the *non-cyclic* compounds with molecular formula C_5H_{10}, only **E** and **F** are geometric isomers of each other. Both **E** and **F** undergo hydration respectively to give the same compound **G**, $C_5H_{12}O$. When **G** reacts with alkaline aqueous iodine, **H** is formed. Upon acidification, **J** is produced. **G** also reacts with PCl_3 to give **K**. **G** reacts with **J** to form **L**.

(i) Draw the structural formula of **E** and **F** to show the geometric isomerism.



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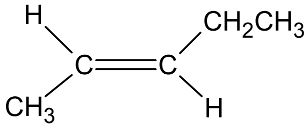

(ii) State the observation and write a balanced equation for the reaction of **G** to **H**.

yellow ppt of CHI_3 observed
$CH_3CH(OH)(CH_2)_2CH_3 + 4I_2 + 6NaOH \rightarrow CHI_3 + CH_3(CH_2)_2CO_2^-Na^+ + 5NaI + 5H_2O$

(iii) Identify **K** and **L**. State the conditions for the reaction of **G** with **J**.

K is $CH_3CHClCH_2CH_2CH_3$
L is $CH_3CH_2CH_2CO_2CH(CH_3)CH_2CH_2CH_3$

concentrated H_2SO_4, heat

[7]

(f) **M** is an unknown metal. A hydrated chloride salt, $MCl_2 \cdot nH_2O$ has a relative formula mass of 244. The salt can be dehydrated using $SOCl_2$, as shown by the following equation.

$$MCl_2 \cdot nH_2O + nSOCl_2 \rightarrow MCl_2 + nSO_2 + 2nHCl$$

When 2.44 g of the salt is reacted with excess $SOCl_2$, the HC*l* produced is completely dissolved in water and the solution made up to 250 cm^3. 25.0 cm^3 sample of the resulting solution require 20.0 cm^3 of 0.200 mol dm^{-3} NaOH(aq) for complete neutralisation.

Calculate the value of *n*. Hence, deduce the identity of **M**. [3]

$n(MCl_2 \cdot nH_2O) = 2.44 / 244 = 0.01$ mol
$n(NaOH) = n(HCl \text{ in } 25.0\ cm^3) = 4.0 \times 10^{-3}$ mol
$n(HCl \text{ in } 250\ cm^3) = 0.04$ mol
$n = 2$

$A_r(M) = 244 - 2(18.0) - 2(35.5) = 137$
M is Ba

[Total: 20]