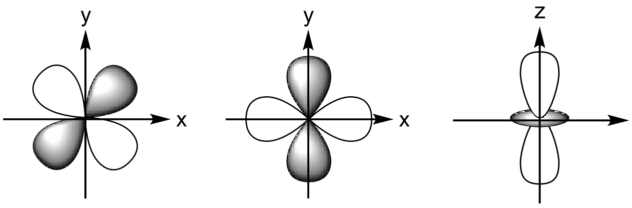
2024 Mid-Year Examination
Pre-University 3

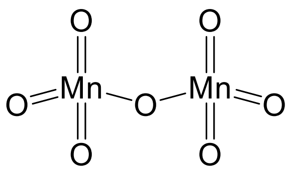
H2 CHEMISTRY **9729/03**

Paper 3 Free Response **5 July 2024**

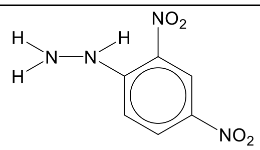
2 hours

Section A

1	**(a)**	**(i)**	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$	
			Marker's comment Many candidates did well for this question.	
		(ii)	 $3d_{xy}$ $3d_{x^2-y^2}$ $3d_{z^2}$	
			Marker's comment Some candidates did not draw the $3d_{xy}$ orbital between the x and y axis.	
		(iii)	forms ions of variable oxidation states / variable oxidation states in compounds forms coloured compounds high density	
			Marker's comment Candidates understand what the question wants. Weaker candidates wrote 'more oxidation number' instead of forms ions of 'variable oxidation state'.	

(b)		MnO has giant ionic structure electrostatic forces of attraction between oppositely-charged ions Mn_2O_7 has simple molecular structure <u>instantaneous dipole-induced dipole</u> forces of attraction between molecules the stronger forces in MnO require more energy to overcome points: (1) identify structure and bonding in MnO (2) identify structure and bonding in Mn_2O_7 (3) identify MnO has stronger forces, compare energy **[2]** all 3 points **[1]** either (1) or (2) **[0]** just (3)	
		<u>Marker's comment</u> This question proved to be challenging to candidates. Many who attempted were unable to identify the correct structure and bonding in MnO and Mn_2O_7. Some candidates explained why Mn_2O_7 has a simple molecular structure, but did not continue to compare with the structure and bonding in MnO.	
(c)	**(i)**	$Mn_2O_7 + H_2O \longrightarrow 2HMnO_4$	
		<u>Marker's comment</u> Many candidates did well for this question.	
	(ii)	hydrolysis	
		<u>Marker's comment</u> Some candidates did not attempt this question. Those who did, some wrote 'hydration' instead of hydrolysis.	
	(iii)		
		<u>Marker's comment</u> Majority of the candidates were unable to do this question.	
(d)		from Ti to Cu, relatively similar atomic radii nuclear charge increases shielding increases but due to electrons added to 3d 4s electrons experience similar effective nuclear charge **[2]** 5 / 5 **[1]** 3 / 5	
		<u>Marker's comment</u> Many candidates confused this explanation with the trend of atomic radii across a period for the main group elements.	

2 (a) (i)

2,4-dinitrophenylhydrazine / 

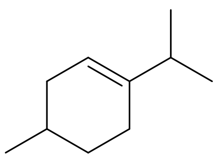
if orange precipitate forms, sample is **O**
if no precipitate forms, sample is **P**

Marker's comment
Some candidates gave tri-iodomethane test as the distinguishing test.
For candidates who gave the correct distinguishing test, some gave 'no visible reaction for P', 'P remains the same' and 'solution remains colourless for P'.

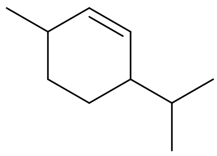
(ii)

information	reaction	inference
L was heated with concentrated H_2SO_4	dehydration / elimination of water (1)	**L** was an alcohol (3) **M** and **N** were alkenes (4)
M and **N** were heated with $KMnO_4$ / H^+	oxidative cleavage / vigorous oxidation (2)	for **O**, the carboxyl carbon and ketone carbon were once joined with C=C in **M** for **P**, the two carboxyl carbon atoms were once joined with C=C in **N**

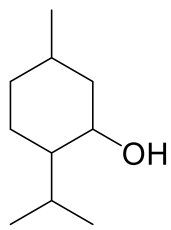
hence



M



N



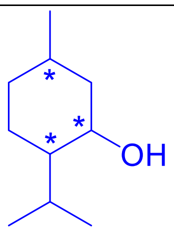
L

[1] for every 2 reactions / inferences

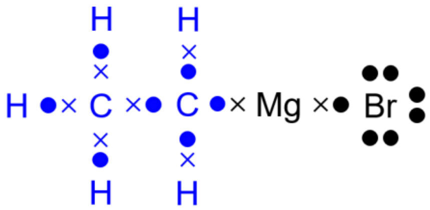
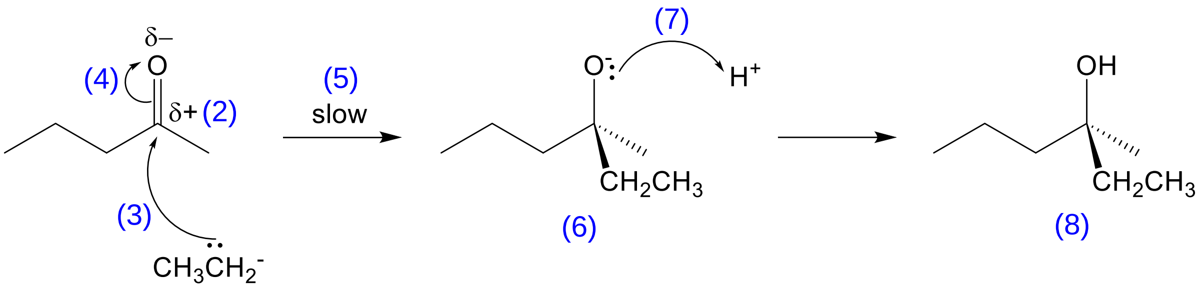
Marker's comment
This question proved to be challenging to candidates. Some candidates wrote 'M and N undergo oxidation' instead of 'vigorous oxidation'.

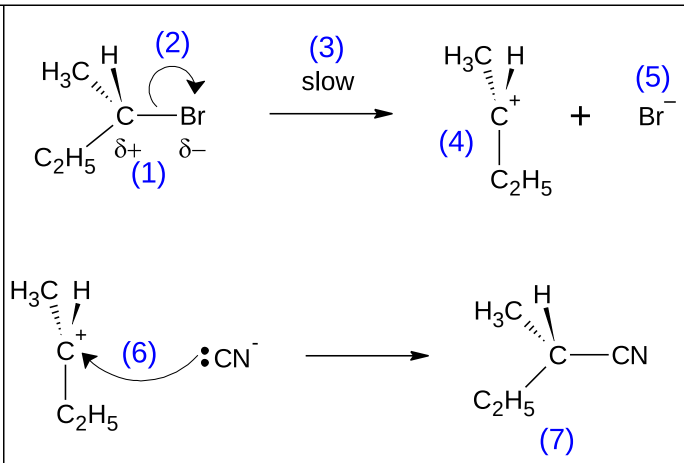
(iii) **M**
alkene functional group is bonded to more substituents /
alkene functional group is bonded to 3 substituents in **M** versus 2 in **N**
Saytzeff's rule

(iv)



number of enantiomers = 2^3 = 8

	(b)	(i)		
		(ii)	generate nucleophile: $CH_3CH_2MgBr \longrightarrow CH_3CH_2^- + MgBr^+$ (1) Mg^{2+} and Br^- okay nucleophilic attack: protonation:  **[3]** 8 / 8 **[2]** 5 / 8 **[1]** 2 / 8	
		(iii)	fewer substituents on carbonyl carbon unhindered nucleophile approach to carbonyl carbon less electron-donating effect to carbonyl carbon carbonyl carbon is more electron-deficient attracts nucleophile more strongly **[2]** 4 / 4 **[1]** 2 / 4	

3	(a)			**[3]** 7 / 7 **[2]** 5 / 7 **[1]** 2 / 7
			Marker's comments: Many are confused between SN1 and SN2, some gave mechanisms with fragments of both mechanisms. Most of those who gave SN1 mechanism, wrote the mechanism in one continuous manner, often missing out the Br^- in the first step as a result.	
	(b)	(i)	make CN^- concentration remain constant with time only decrease of bromoalkane concentration will affect rate	
			Marker's comments Many gave incomplete answers, which include not mentioning that $[CN^-]$ becomes almost constant. Some also gave vague answers such as 'so that the reaction can be pseudo'.	
		(ii)	1 molecule of bromoalkane is present in the rate-determining step of both S_N1 and S_N2 mechanisms	
			Marker's comments Many candidates do not understand the question and went on to state that since the half life is constant, it is first order. Most answers were irrelevant.	
		(iii)	from the graph, $t_{1/2}$ = 21 min with two interpolations shown [1] rate = k [1-bromo-1-methylpropane] $[CN^-]^{0.5}$ = k' [1-bromo-1-methylpropane] where $k' = k\,[CN^-]^{0.5}$ $t_{1/2} = \frac{\ln 2}{k'}$ hence $t_{1/2} = \frac{\ln 2}{k[CN^-]^{0.5}}$ sub in values $21\ min = \frac{\ln 2}{k(2.00)^{0.5}}$ [1] correct substitutions hence rate constant k = 0.0233 $mol^{-0.5}\ dm^{1.5}\ min^{-1}$	
			Marker's comments Many just made use of the data given in the table and the order of reaction given to solve for k. They were not given full credit.	

(iv)

$[CN^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1.5	0.00285 or 0.00286
2.0	0.00330
3.0	0.00404
5.0	0.00521 or 0.00522

Marker's comments
A large number of students did not attempt the question.
Some who attempted did not take into account information given in (iii) assumed that both reactants are first order.

(v) S_N2 because unhindered nucleophile approach
only secondary bromoalkane / only 2 hydrocarbon groups are present

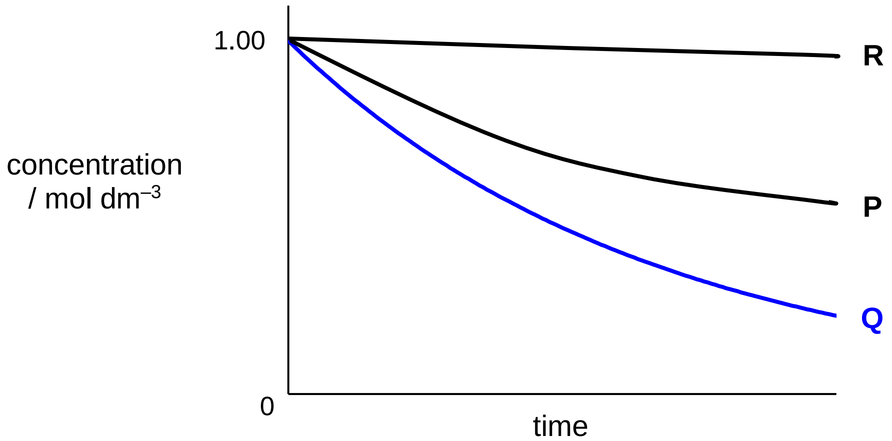
S_N1 because stable carbocation intermediate
electron-donating hydrocarbon groups disperse positive charge on carbon atom

Marker's comments
Majority did not attempt this question.

(vi) S_N2 mechanism forms 1 part (–)-enantiomer (complete stereoinversion)
S_N1 mechanism forms 0.5 part (+)-enantiomer and 0.5 part (–)-enantiomer
hence (+) : (–) enantiomers = 1 : 3 or 75% of enantiomers are (–)
working needs to be shown

Marker's comments
Majority did not attempt this question.
Those who did, did not show working and the answers were incorrect.

(c)



R does not hydrolyse
correct graph drawn [1] completely flat okay

π overlap between p orbitals of iodine atom and benzene ring /
C-I bond has partial double bond character / electron delocalise to C-I bond +
C-I bond is strong and will not break [1]

P hydrolyses slower than **Q**
correct graph drawn [1]

C-C*l* bond is stronger than C-Br bond +
due to smaller C*l* atomic radius / better orbital overlap / shorter bond length [1]

			Marker's comments Mark scheme was loosened a little. Explanations given by candidates were mostly incomplete. Some quoted bond energy from data booklet even though question did not mention the use of DB. Many knew that R doesn't undergo hydrolysis but still drew a curve downwards for R, albeit with a more gradual gradient. Students must show understanding that R doesn't undergo hydrolysis to gain credit. This question shows that some students still do not understand that the trend of ease of hydrolysis is due to the bond strength. Some compared the electronegativity instead.		
(d)	**(i)**		$K_{sp} = [Ag^+]^2\,[CO_3^{2-}]$ let the solubility of $Ag_2CO_3 = x$ mol dm^{-3} $8.46 \times 10^{-12} = (2x)^2\,(x)$ $= 4x^3$ hence $x = 1.28 \times 10^{-4}$ mol dm^{-3}		
			Marker's comments Common mistakes include failing to take into the stoichiometry of the equilibrium, hence using x, instead of 2x, for $[Ag^+]$. Some also did not give the units.		
	(ii)		dissolution of silver carbonate: $Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$ – equilibrium 1 in the presence of CO_3^{2-}, less Ag_2CO_3 can dissolve / forward reaction is suppressed before the ionic product exceeds K_{sp} [1] in the presence of NH_3, $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$ complex ion is formed [1] Ag^+ concentration decreases / Ag^+ is used up equilibrium 1 position shifts right to offset this more Ag_2CO_3 can dissolve [1] in the presence of H^+, H^+ reacts with CO_3^{2-} / CO_3^{2-} concentration decreases equilibrium 1 position shifts right to offset this more Ag_2CO_3 can dissolve [1]		
			Marker's comments Very poorly done, especially for NH_3 and HNO_3. Candidates were not able to recognise that the NH_3 reacts with the Ag^+ and that the H^+ reacts with CO_3^{2-}.		

4	(a)	(i)		$n_T = n_1 + n_2$ $p_T V_T = p_1 V_1 + p_2 V_2$ [1] $p_T(1.2) = (240000)(0.2) + (102000)(1.0)$ hence p_T = 125000 Pa [1]	
				Marker's comment Common mistake happens when students do not read the question thoroughly, and included the percentages in their calculations. The percentage composition of Nitrox is not necessary.	
		(ii)		*p* is inversely proportional to *V* $p_1 V_1 = p_2 V_2$ $(1)(1.5) = (230)(V_2)$ volume of compressed nitrox, V_2 = 6.52×10^{-3} m^3	
				Marker's comment Some students did not recall the correct relationship between *p* and *V*.	
	(b)	(i)		CO_2 concentration increases equilibrium 1 position shifts right to offset H_2CO_3 concentration increases equilibrium 2 position shifts right to offset hence H^+ concentration increases **[2]** 5 / 5 **[1]** 3 / 5	
		(ii)		identify: H_2CO_3 / HCO_3^- explain (any one): H_2CO_3 lost one H^+ (to form HCO_3^-) HCO_3^- is short of one H^+ HCO_3^- is the conjugate base (of H_2CO_3)	

(c) (i)

anode half-cell (reverse direction)	E^θ / V	remarks
Cl_2 / Cl^-	+1.36 (1)	
O_2 / H_2O	+1.23	less positive

in dilute NaC*l*,
H_2O is preferentially oxidised to form O_2 (2)

in concentrated NaC*l*,
Cl^- is preferentially oxidised to form Cl_2 (3)
because equilibrium Cl_2 / Cl^- position shifts left to offset high Cl^- concentration (4)
E becomes less positive than +1.23 V (5)

[2] 5 / 5
[1] 3 / 5

(ii)
anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$
cathode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

(iii)
bleach forming reaction:
[O] $Cl_2 + 4OH^- \longrightarrow 2ClO^- + 2H_2O + 2e^-$
[R] $Cl_2 + 2e^- \longrightarrow 2Cl^-$
overall: $Cl_2 + 2OH^- \longrightarrow ClO^- + H_2O + Cl^-$

(iv)
calculate number of moles of electrons passed first

$Q = It = nF$
$(2.5)(7200) = n_{e^-}(96500)$
n_{e^-} = 0.1865 mol [1]

then find the number of moles of chlorine gas produced

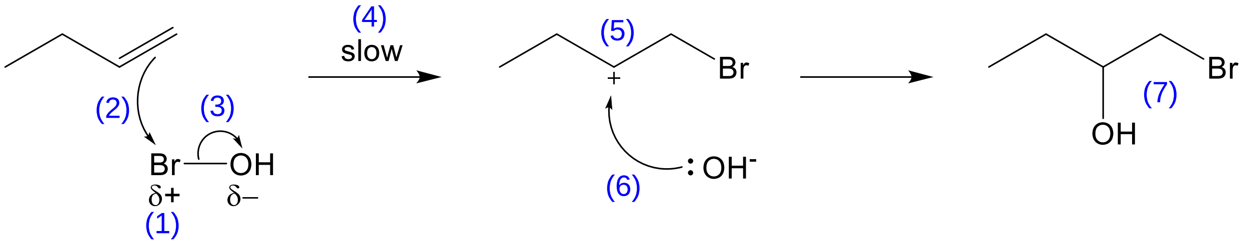
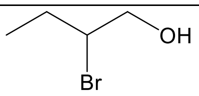
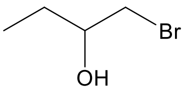
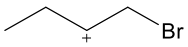
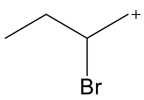
from the anode half-equation, since $\frac{n_{Cl_2}}{n_{e^-}} = \frac{1}{2}$
hence n_{Cl_2} = $\frac{1}{2} \times 0.1865$ mol = 0.09326 mol

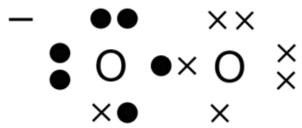
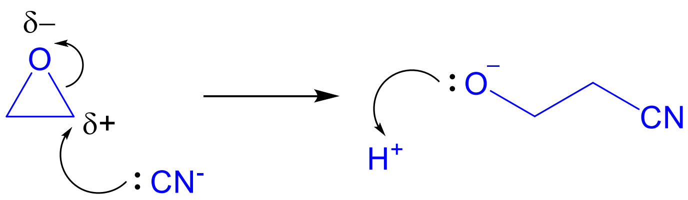
then find the number of moles of bleach produced

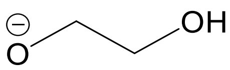
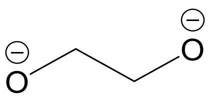
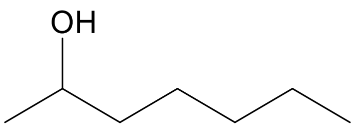
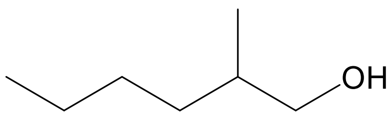
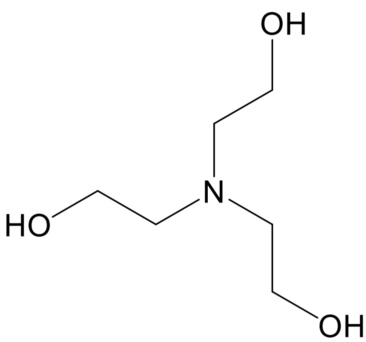
since $\frac{n_{ClO^-}}{n_{Cl_2}} = \frac{1}{1}$
hence $n_{ClO^-} = n_{NaClO}$ = 0.09326 mol
mass of NaC*l*O = 0.09326 mol × 74.5 g mol^{-1} = 6.95 g [1]

M1 find n_{e^-}
M2 find n_{Cl_2}, n_{ClO^-}, and mass of NaC*l*O

Section B

5	(a)	(i)	 **[3]** 7 / 7 **[2]** 5 / 7 **[1]** 2 / 7 <u>Marker's comment</u> - Many students did not read the question properly, using ethene instead of but-1-ene. - Some students did not recognise that "step 2" was a single step, opting incorrectly to break the Br–O bond separately in an additional step.
		(ii)	 **[1]**  is formed from the carbocation  which has two electron-donating substituents (1) one more okay dispersing the positive charge on the carbon atom (2) to a greater extent okay hence is more stable than  **[1]** 2 / 2
	(b)	(i)	C in ethylene oxide: –1 C in carbon dioxide: +4 <u>Marker's comment</u> - Many students could not get the formula of ethylene oxide right
		(ii)	increase rate of oxidation of ethylene oxide / ethene to form carbon dioxide OR ethylene oxide has high ring strain and decomposes
		(iii)	higher concentration of oxygen, increased rate of reaction no side reactions with other gases in air (eg. nitrogen with ethene or oxygen; water vapour with ethene by electrophilic addition) no poisoning of catalyst by other gases in air <u>Marker's comment</u> - Students who did not phrase their answer as a "benefit" were penalised
	(c)	(i)	has different phase / state from reactants provides alternative reaction mechanism of lower activation energy <u>Marker's comment</u> - Students should note that "phase" is preferred over "state" as it could be e.g. two immiscible liquids

<table>
<tr><td></td><td></td><td>(ii)</td><td>adsorption of reactants on silver surface
increase local concentration / orientates reactants
weaken and form bonds for reaction
desorption
[2] 4 / 4
[1] 2 / 4
Marker's comment
- Some students did not use the proper terminology</td><td></td></tr>
<tr><td></td><td></td><td>(iii)</td><td>
Marker's comment
- Many students drew a double bond, not recognising that it results in one of the O atoms having 9e$^-$</td><td></td></tr>
<tr><td></td><td>(d)</td><td>(i)</td><td>
(1) dipoles
(2) CN$^-$ lone pair with arrow
(3) epoxide bond break arrow
(4) O$^-$ lone pair with arrow

[2] 4 / 4
[1] 2 / 4
Marker's comment
- Generally well done</td><td></td></tr>
<tr><td></td><td></td><td>(ii)</td><td>nucleophilic addition
Marker's comment
- Generally well done</td><td></td></tr>
<tr><td></td><td></td><td>(iii)</td><td>
<table>
<tr><td>T</td><td></td><td></td></tr>
<tr><td>U</td><td>
preferred</td><td>
not preferred</td></tr>
<tr><td>V</td><td></td><td></td></tr>
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				Marker's comment - Not very well done, especially for **V** as students did not pay attention to the mole ratio. - Some students miscounted the number of carbons in their structures.	

<table>
<tr><td>6</td><td>(a)</td><td>(i)</td><td></td><td colspan="2">although nuclear charge and shielding increase
distance between valence electrons and nucleus increases
weaker electrostatic forces of attraction between them
increasing atomic radii down Group 2

[2] 4 / 4
[1] 2 / 4
Marker's comment
- Generally well done, but perfect answers were rare</td><td></td></tr>
<tr><td></td><td></td><td>(ii)</td><td></td><td colspan="2">down Group 2,
M^{2+} ions have lower charge density
M^{2+} ion polarises NO_3^- towards itself less
N–O bond remains strong requiring more energy to break
hence increasing thermal stability

[2] 4 / 4
[1] 2 / 4
Marker's comment
- Some students still confuse charge density with lattice energy.
- Many students were imprecise with their answers – e.g. "charge density decreases", but not mentioning of what; "atomic radii increases" instead of ionic radii</td><td></td></tr>
<tr><td></td><td></td><td>(iii)</td><td></td><td colspan="2">let η_{O_2} be x mol
total mass of $NO_2 + O_2$ gases = $4x(46.0) + x(32.0)$ = 2.55 g
hence $x = \eta_{O_2}$ = 0.0118056 mol [1]</td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td>either

since $\frac{\eta_{XO}}{\eta_{O_2}} = \frac{2}{1}$
η_{XO} = 2 × 0.0118056 mol
= 0.023611 mol

mass of XO = 5.00 – 2.55 = 2.45 g

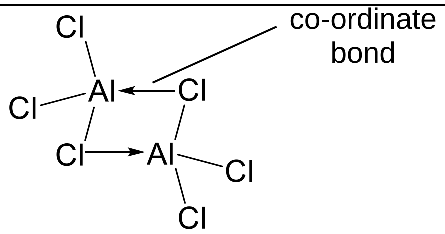
hence molar mass of XO = $\frac{2.45\ g}{0.023611\ mol}$
= 103.8 g mol^{–1} [1]

hence A_r of X = 103.8 – 16.0 = 87.8
X is Sr [1]</td><td colspan="2">or

since $\frac{\eta_{X(NO_3)_2}}{\eta_{O_2}} = \frac{2}{1}$
$\eta_{X(NO_3)_2}$ = 2 × 0.0118056 mol
= 0.023611 mol

hence molar mass of X$(NO_3)_2$ = $\frac{5.00\ g}{0.023611\ mol}$
= 211.8 g mol^{-1} [1]

hence A_r of X = 211.8 – 124.0 = 87.8
X is Sr [1]</td></tr>
<tr><td></td><td></td><td></td><td></td><td colspan="3">Marker's comment
- A common mistake was students combining the M_r of the 2 product gases as the "total M_r", which does not make sense (mathematically they could have arrived at same numerical answer).
- An alternative method was to equate $\eta_{M(NO_3)_2} = \eta_{MO}$.</td></tr>
</table>

	(b)			$AlCl_3 + 6H_2O \longrightarrow Al(H_2O)_6^{3+} + 3Cl^-$ water coordinates to Al^{3+} [1] $Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H^+$ $AlCl_3$ / $Al(H_2O)_6^{3+}$ / Al^{3+} dissociate / hydrolyses partially [1] Al^{3+} has high charge density polarises H_2O break / weaken O–H bond release H^+ ion [1] Marker's comment - A significant number of students could not recall the 2 reaction equations.	
	(c)	**(i)**		 Marker's comment - Many students did not label the coordinate / dative bond, losing the mark - A significant number of students could not recall how to draw the dimer. - Some students incorrectly drew an Al–Al bond, which does not make sense as the Al atom does not have any more valence e^-.	
		(ii)		the forward reaction is endothermic due to bond-breaking [1] equilibrium position shifts right to offset temperature increase by absorbing excess heat energy hence average M_r decreases [1] Marker's comment - Many students could not recognise that it was an equilibrium reaction, and that they had to deduce the ΔH in order to apply LCP.	
		(iii)		ΔS is positive due to increased number of moles of gas molecules [1] since $\Delta G = \Delta H - T\Delta S$ and ΔH is positive at high T $\lvert\Delta H\rvert$ (positive term) $<$ $\lvert -T\Delta S\rvert$ (negative term) hence ΔG is negative and the dissociation reaction is spontaneous [1] at low T $\lvert\Delta H\rvert$ (positive term) $>$ $\lvert -T\Delta S\rvert$ (negative term) hence ΔG is positive and the dissociation reaction is not spontaneous [1] Marker's comment - Poorly done. Many students did not phrase the second section of their answers well.	

	(d)	(i)		$pV = nRT$ $(101325)\left(\frac{268}{10^6}\right) = n_{gas}(8.31)(673)$ n_{gas} = 0.0048555 mol [1] $n_{gas} = \frac{m}{M_r}$ M_r of gas mixture = $\frac{0.84\ g}{0.0048555\ mol}$ = 173.0 [1] Marker's comment - Many students did not realise that the ICE table will not work for this question.	
		(ii)		$n_{Al_2Cl_6} = \frac{0.84\ g}{267.0\ g\ mol^{-1}}$ = 0.00315 mol $n_{AlCl_3} = \frac{0.84\ g}{133.5\ g\ mol^{-1}}$ = 0.00629 mol	
		(iii)		$n_{Al_2Cl_6}$ that have dissociated = 0.0048555 mol – 0.003146 mol = 0.001709 mol %Al_2Cl_6 that have dissociated = $\frac{0.001709\ mol}{0.003146\ mol} \times 100\%$ = 54.3% Marker's comment - A majority of students were unable to solve this difficult question.	