H

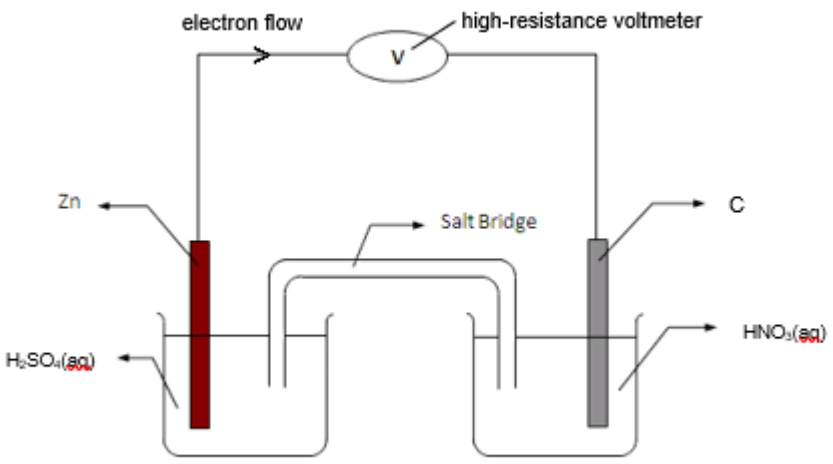
millennia institute

2022 Preliminary Examination
Pre-University 3

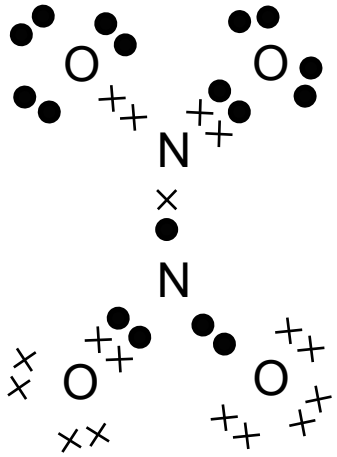
H2 CHEMISTRY **9729/03**

Paper 3 Free Response

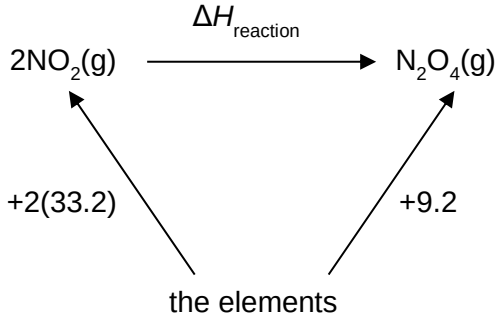
Section A

1	**(a)**	**(i)**			*[3] 7 / 7* *[2] 5 / 7* *[1] 3 / 7* *max [1]: battery or mixing of solutions* *salt bridge*
		(ii)		anode: $Zn \longrightarrow Zn^{2+} + 2e^-$ cathode: $NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$ [1] sum: $Zn + 2NO_3^- + 4H^+ \longrightarrow Zn^{2+} + 2NO_2 + 2H_2O$ or $Zn + 2HNO_3 + H_2SO_4 \longrightarrow ZnSO_4 + 2NO_2 + 2H_2O$ [1]	
		(iii)		E_{cell} = + 0.81 – (- 0.76) = +1.57 V	
		(iv)		concentration of H^+ / NO_3^- higher than 1.00 mol dm^{-3} / temperature higher and reaction is endothermic / NO_2 gas formed escapes the solution [1] equilibrium position of cathode half-equation shifts right, higher E_{cell} [1]	

(b) (i)



(ii)



$\Delta H_{reaction}$ = –2(33.2) + 9.2 = –57.2 kJ mol^{-1}

(iii)

bond is formed between two NO_2
energy released / exothermic

(iv)

decrease in number of moles of gases [1]
decreased ways to arrange molecules (1) and distribute energy (2)
decreased disorder (3) hence decreased entropy (4) [1]

(v)

$\Delta G = \Delta H - T\Delta S$

at high T, $-T\Delta S$ (positive) has larger magnitude than ΔH (negative)
$\Delta G > 0$ / more positive

at low T, $-T\Delta S$ (positive) has smaller magnitude than ΔH (negative)
$\Delta G < 0$ / more negative

(vi)

	$2NO_2(g)$	⇌	$N_2O_4(g)$
$p_{initial}$ / bar	1.00		0
p_{change} / bar	**–0.702**		**+0.351**
p_{final} / bar	**0.298**		0.351

$K_p = \frac{p_{NO_2}}{p_{N_2O_4}{}^2} = \frac{0.351}{(0.298)^2}$ = 3.95 bar^{-1}

2	**(a)**	**(i)**		octahedral, 90° [1] 6 electron domains maximise distance from one another to minimise repulsion [1]	
		(ii)		ligands approach at 3 axes () z^2 and x^2-y^2 point at 3 axes, greater electronic repulsion, higher energy xy, yz and xz point away from the 3 axes / diagonal, less electronic repulsion, lower energy	*[2] 6 / 6* *[1] 3 / 6*
		(iii)		less electronic repulsion as z^2 is further away from the ligand / z^2 points directly at axial ligands	
		(iv)		Co^{2+}: [Ar] $3d^7$ yes, decreased energy of z^2 electron Ni^{2+}: [Ar] $3d^8$ no net energy change, decreased z^2 electron energy, increased x^2-y^2 electron energy or even number of electrons	*[2] 4 / 4* *[1] 2 / 4*
		(v)		Cu^+: [Ar] $3d^{10}$ Since the d orbitals are fully-filled, there is no d-d transition. Hence, the complex ions are not coloured.	
	(b)			$Cu^{2+} + 2e^- \longrightarrow Cu$ E = +0.34 V $Cu + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+} + 2e^-$ E = +0.05 V [1] E_{cell} = +0.34 + 0.05 = +0.39 V [1] $\Delta G = -nF\Delta E_{cell} = -(2)(96500)(+0.39)$ = –75.3 kJ mol^{-1} < 0, hence feasible [1]	

3 (a) (i) Buffer solutions are solutions which resist pH changes when small amounts of acids or bases are added to it.

(ii) H^+ (that tries to leave) are more strongly attracted to the more negatively-charged ion more difficult dissociation

(iii) $\eta_{H_2PO_4^-} = \frac{2.00\ g}{136.1\ g/mol}$ = 0.0147 mol
hence $[H_2PO_4^-]$ = 0.0147 mol dm^{-3} [1]
$\eta_{HPO_4^{2-}} = \frac{1.42 g}{142.0\ g/mol}$ = 0.0100 mol
hence $[HPO_4^{2-}]$ = 0.0100 mol dm^{-3} [1]

$K_a(H_2PO_4^-) = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 10^{-7.20}$
$\frac{[H^+](0.0100)}{(0.0147)} = 10^{-7.20}$
hence $[H^+] = 9.275 \times 10^{-8}$ mol dm^{-3}
hence pH = 7.03 [1]

(iv) $H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

(v) **I**: 10.0 cm^3

	$H_2PO_4^-$	+	OH^-	→	HPO_4^{2-}	+	H_2O	
Before rxn /mol	0.00147		0.0001		0.001			[1]
Change	-0.0001		-0.0001		+0.0001			
After rxn /mol	0.00137		0		0.0011			[1]

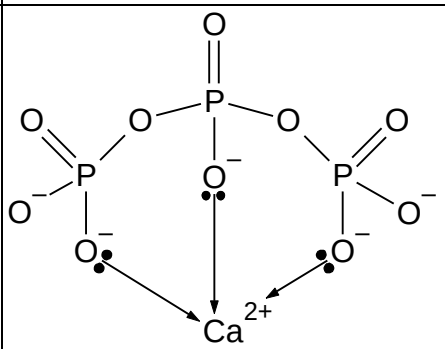
pH = 7.20 + log $\frac{(0.0011/V)}{(0.00137/V)}$ = 7.10 [1]

II: 200 cm^3

	$H_2PO_4^-$	+	OH^-	→	HPO_4^{2-}	+	H_2O	
Before rxn /mol	0.00147		0.002		0.001			
Change	-0.00147		-0.00147		+0.00147			
After rxn /mol	0		0.000530	[1]	0.00247			

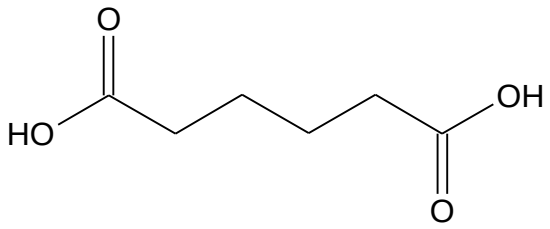
$[OH^-] = \frac{0.000530}{0.3}$ = 0.001768 [1]

pOH = 2.75
pH = 14 – 2.75 = 11.2 [1]

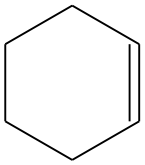
	(b)	**(i)**		$2Na_2HPO_4 + NaH_2PO_4 \longrightarrow Na_5P_3O_{10} + 2H_2O$	
		(ii)		tetrahedral	
		(iii)			*overall 3– charge okay*
		(iv)		$[Ca^{2+}]$ present = $\frac{5.06 \times 10^{-5}\ g/dm^3}{40.1\ g/mol}$ = 1.2618 × 10^{-6} mol dm^{-3} [1] $K_{sp}(Ca_3(PO_4)_2) = [Ca^{2+}]^3[PO_4^{3-}]^2$ = 2.07 × 10^{-33} mol^5 dm^{-15} $[Ca^{2+}]^3(6.53 \times 10^{-8})^2 = 2.07 \times 10^{-33}$ hence maximum $[Ca^{2+}]$ allowed in solution = 7.859254 × 10^{-7} mol dm^{-3} [1] hence $\eta_{Ca^{2+}}$ to remove = $\eta_{Na_5P_3O_{10}}$ to add = 1.2618 × 10^{-6} – 7.859254 × 10^{-7} = 4.7587 × 10^{-7} mol mass of $Na_5P_3O_{10}$ to add = 4.7587 × 10^{-7} mol × 368.0 g/mol = 1.75 × 10^{-4} g [1]	

4 **(a)**

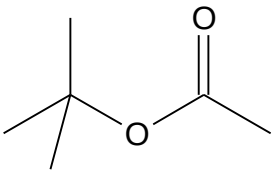
I



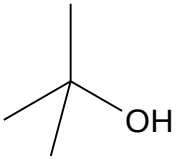
H



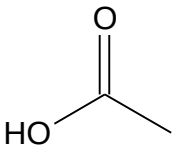
J



K

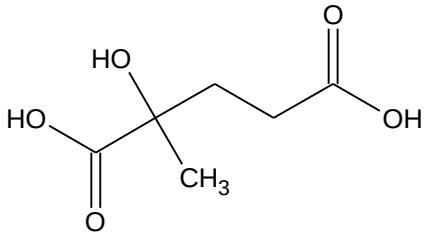


L

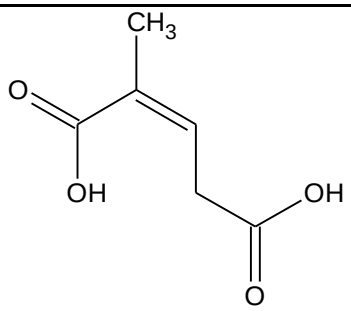


(b)

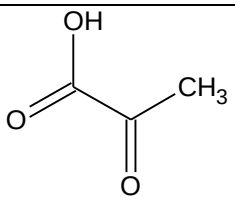
Information	**Deduction**
A, $C_6H_{10}O_5$, is a chiral compound	**A** has a carbon with 4 different groups / atoms attached to it
When 1 mol of **A** is reacted with excess solid sodium carbonate at room temperature and pressure, 24 dm^3 of CO_2 is formed.	Acid-carbonate reaction **A** has 2 -COOH groups
A does not react with hot acidifed potassium dichromate(VI)	**A** cannot be oxidised
A reacts with excess hot concentrated H_2SO_4 to form **B**, $C_6H_8O_4$	elimination **A** has a tertiary alcohol (since cannot be oxidised but can undergo elimination) **B** has an alkene group
1 mol of **B** reacts completely with 2 mol of NaOH(aq)	**B** has 2 -COOH groups acid-base reaction
When **B** is heated with acidified $KMnO_4$(aq), **C**, $C_3H_4O_3$, and **D**, $C_3H_4O_4$, are formed.	**o**xidative cleavage / oxidation
C gives a yellow precipitate with warm aqueous alkaline iodine	**C** has CH_3CO- oxidation
Both **C** and **D** reacts with magnesium to give effervescence	Both **C** and **D** have -COOH group



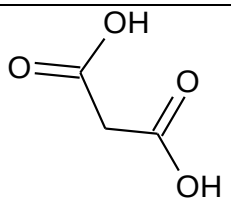
A



B

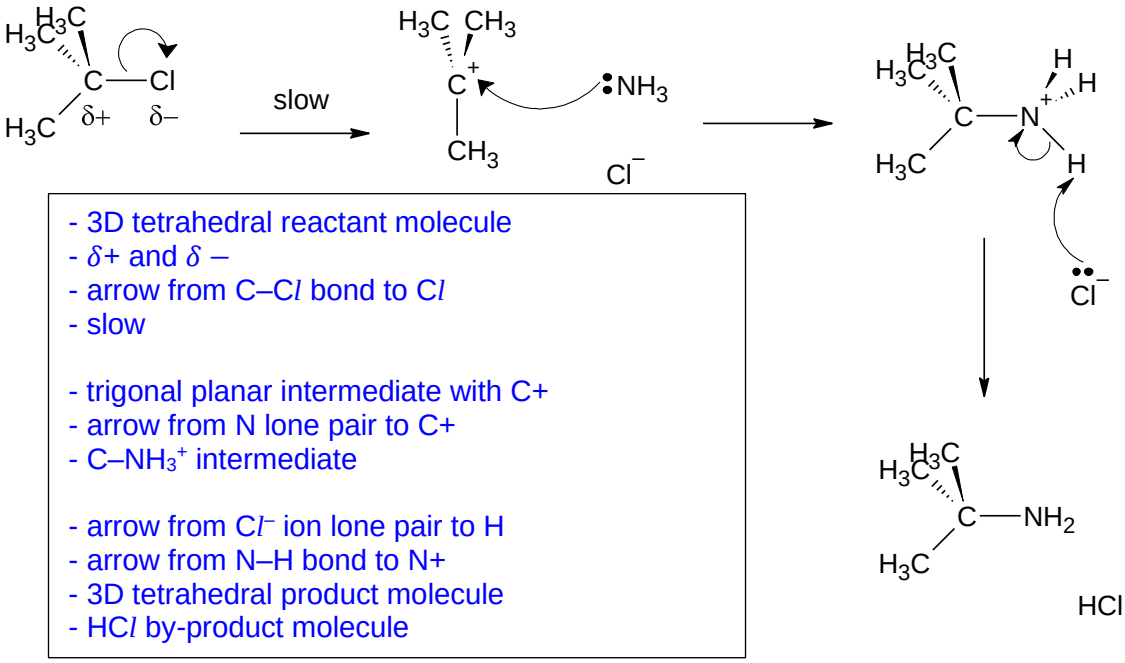


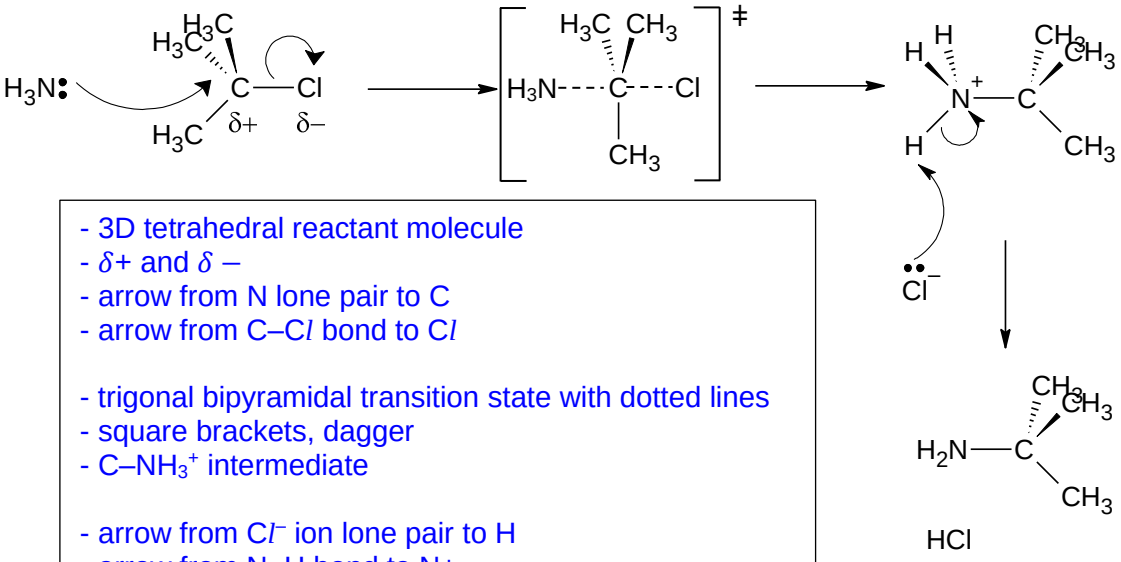
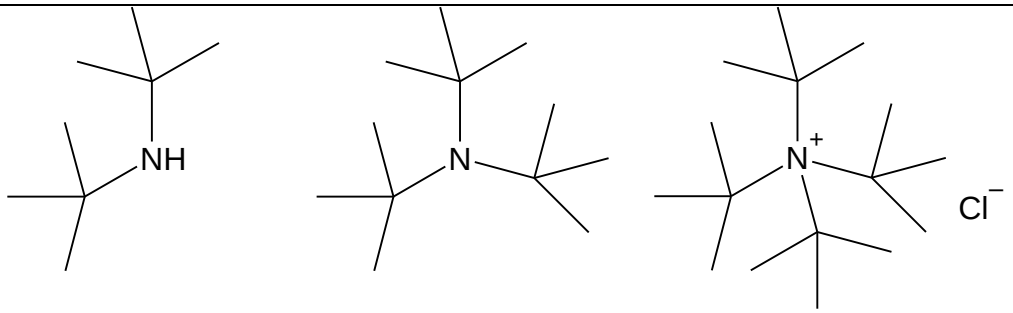
C

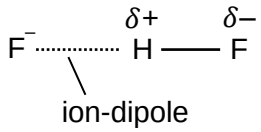


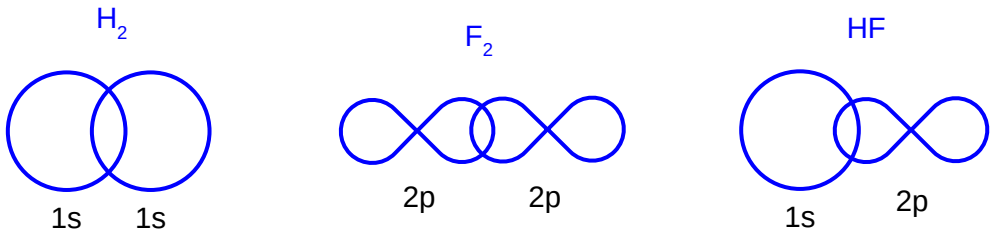
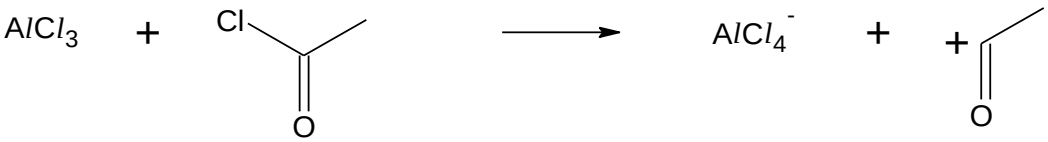
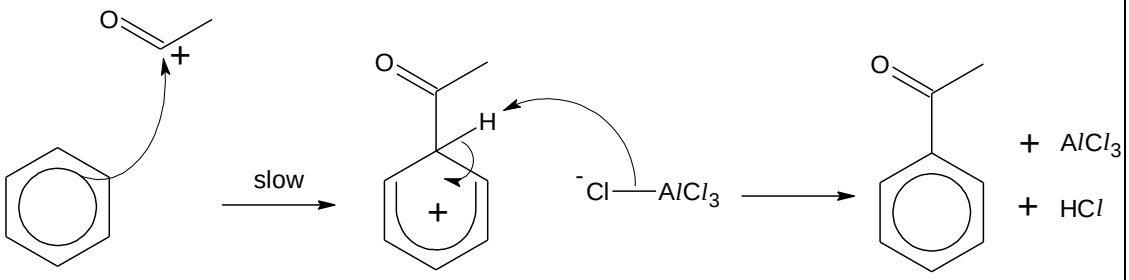
D

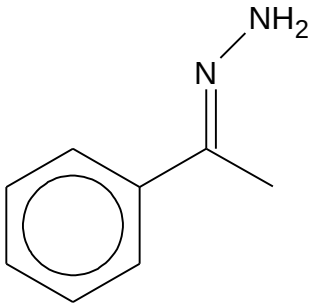
Section B

5	**(a)**	**(i)**	$p_T V_T = p_1 V_1 + p_2 V_2$ $p_T(200) = 155(150) + 80(120)$ [1] sub p_T = 164 kPa [1] ans		
		(ii)	nucleophilic substitution, S_N1 3 electron-donating methyl groups disperse positive charge stabilising the carbocation	3 methyl groups sterically hinder nucleophile approach from opposite C–C*l*	*[2] 4 / 4* *[1] 2 / 4*
		(iii)	S_N1:  - 3D tetrahedral reactant molecule - δ+ and δ – - arrow from C–C*l* bond to C*l* - slow - trigonal planar intermediate with C+ - arrow from N lone pair to C+ - C–NH_3^+ intermediate - arrow from Cl^- ion lone pair to H - arrow from N–H bond to N+ - 3D tetrahedral product molecule - HC*l* by-product molecule		*no need to name again* *[3] 10 / 11* *[2] 7 / 11* *[1] 4 / 11*

				S_N2 (accept only if **(ii)** is S_N2):  - 3D tetrahedral reactant molecule - $\delta+$ and $\delta-$ - arrow from N lone pair to C - arrow from C–C*l* bond to C*l* - trigonal bipyramidal transition state with dotted lines - square brackets, dagger - C–NH_3^+ intermediate - arrow from Cl^- ion lone pair to H - arrow from N–H bond to N+ - 3D tetrahedral product molecule - HC*l* by-product molecule	*no need to name again* *[3] 10 / 11* *[2] 7 / 11* *[1] 4 / 11*
		(iv)		 use limiting amount of $(CH_3)_3CCl$ / use excess NH_3 OR HC*l* (if HC*l* given as answer, no possible method to limit the formation)	*any one*

	(b)	**(i)**		 ion-dipole	*[1] correct 2 species* *[1] dipoles on HF, correctly labelled*
		(ii)		HF is a Brønsted acid as it lost / released H^+	
		(iii)		anode: $2F^- \longrightarrow F_2 + 2e^-$ cathode: $2H^+ + 2e^- \longrightarrow H_2$	*electrode labels required*
		(iv)		$\eta_{KHF_2} = \frac{355\ g}{78.1\ g/mol}$ = 4.545 mol $\eta_{HF} = \frac{145\ g}{20.0\ g/mol}$ = 7.25 mol [1] from KHF_2:	

				η_{H^+} discharged = η_{F^-} discharged = 4.545 mol from HF: η_{H^+} discharged = η_{F^-} discharged = 7.25 mol hence total η_{H^+} discharged = total η_{F^-} discharged = 4.545 mol + 7.25 mol = 11.795 mol [1] since $\frac{\eta_{H_2}}{\eta_{H^+}} = \frac{\eta_{F_2}}{\eta_{F^-}} = \frac{1}{2}$, $\eta_{H_2} = \eta_{F_2} = \frac{11.795\ mol}{2}$ = 5.8977 mol pV = nRT volume of each gas H_2 and F_2, $V = \frac{nRT}{p} = \frac{(5.8977)(8.31)(223)}{101325}$ = 0.108 m^3 [1]	
		(v)		H_2 less electrons weaker instantaneous dipole – induced dipole forces of attraction between molecules more ideal gas	***[0]*** *wrong gas* *[2] 4 / 4* *[1] 2 / 4*
		(vi)			*[1] correct orbital overlaps for all 3 molecules* *[1] correct orbital labels × 6*
6	**(a)**	**(i)**		name of mechanism: electrophilic substitution electrophile generation:  1m for correct name and correct generation of electrophile (ignore arrows) benzene attack electrophile: deprotonation:  - arrow from circle to C+ - slow - positive charge with break - side chain attached - arrow from Cl^- lone pair / bond pair to H - arrow from C–H bond to ring - restored delocalisation - HCl [2] 7 / 8 [1] 3 / 8	
		(ii)		hydrocarbon substituent is electron-donating increasing electron density of delocalised π electrons in benzene	*[2] 4 / 4* *[1] 2 / 4*

				more reactive towards (subsequent) electrophilic substitution / benzene becomes a stronger nucleophile to attack electrophile (again)	
		(iii)		**M:**  **N:** N_2	

	(b)	**(i)**		increasing atomic radii down Group 2 [1] although nuclear charge and shielding increases distance of valence electrons from nucleus increases weaker electrostatic forces of attraction between them [1]	
		(ii)		more thermally-stable carbonates down Group 2 [1] lower charge density of Group 2 ions polarises carbonate ion less stronger C–O bond, require more energy to break [1]	
		(iii)		mass of CO_2 = 1.02 g – 0.505 g = 0.515 g $\eta_{CO_2} = \frac{0.515\ g}{44.0\ g/mol}$ = 0.0117 mol = $\eta_{\boldsymbol{X}CO_3}$ [1] M_r of **X**CO_3 = $\frac{1.02}{0.0117}$ = 87.1 M_r of $\mathbf{X}^{2+}$ = 87.1 – 60.0 = 27.1 [1] nearest Group 2 element is Mg [1]	

	(c)	**(i)**		$UO_2 + 4HF \longrightarrow UF_4 + 2H_2O$ [1] $UF_4 + F_2 \longrightarrow UF_6$ $UO_2 + 4HF + F_2 \longrightarrow UF_6 + 2H_2O$ [1]	*Award 2m if only correct final equation shown.*
		(ii)		UO_2 was oxidised to UF_6 the oxidation state of U increased from +4 (in UO_2) to +6 (in UF_6) [1] F_2 was reduced to UF_6 the oxidation state of F decreased from 0 (in F_2) to –1 (in UF_6) [1]	
		(iii)		M_r of $^{235}UF_6$ = 349 M_r of $^{238}UF_6$ = 352 let abundance of $^{235}UF_6$ = x $349x + 352(1 - x) = 351.95$ $x \times 100\%$ = 1.67% [1]	
		(iv)		Since % abundance is less than 2% it cannot be used. [1]	