MARK SCHEME

1	**(a)**	**W**: Si $SiCl_4 + 2H2O \rightarrow SiO_2 + 4HCl$ **X**: P $PCl_5 + CH_3COOH \rightarrow POCl_3 + CH_3COCl$ *OR* $3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$	**[4]**
	(b) (i)	$Al_2O_3(s) + 2NaOH(aq) \rightarrow 2Na[Al(OH)_4](aq) + H_2O(l)$ OR $Al_2O_3(s) + 2OH^-(aq) \rightarrow 2[Al(OH)_4]^-(aq) + H_2O(l)$	**[3]**
	(b) (ii)	On addition of $HCl(aq)$, a white ppt is formed. Ppt would dissolve in excess $HCl(aq)$ to give a colourless solution.	
	(c)	$BaCO_3$ has a higher thermal decomposition temperature. Ba^{2+} has a larger ionic radius compared to $\mathbf{Z}^{2+}$/Mg^{2+}. Ba^{2+} hence has a lower charge density, and polarise the CO_3^{2-} anion to a lower extent (compared to $\mathbf{Z}^{2+}$/Mg^{2+}), and the C–O bonds are weakened to a smaller extent, resulting in a higher thermal decomposition temperature.	
	(d)	The 3p electron to be removed from Al is at a higher energy level compared to the 3s electron to be removed from Mg, hence the p electron is less strongly attracted to the nucleus and require less energy to remove.	**[1]**
			[Total: 9]

2	**(a)**	For pH = 3.5 $[H^+] = 10^{-3.5} = \underline{3.16 \times 10^{-4}\ moldm^{-3}}$ Let the number of moles of C_5H_5NHCl be Y mol Since $pK_a = 5.25$, $K_a = 10^{-5.25} = \underline{5.62 \times 10^{-6}}$ $(3.16 \times 10^{-4})^2$ / Y – $(3.16 \times 10^{-4}) = 5.62 \times 10^{-6}$ Y = $[(3.16 \times 10^{-4})^2 / 5.62 \times 10^{-6}] + (3.16 \times 10^{-4})$ = <u>0.0181 mol</u> ***Or*** $(3.16 \times 10^{-4})^2$ / Y = 5.62×10^{-6} Y = $[(3.16 \times 10^{-4})^2 / 5.62 \times 10^{-6}]$ = <u>0.0178 mol</u> Mass to be added = $(0.0181 \times (12.0 \times 5 + 1.0 \times 6 + 14.0 + 35.5)) \div 0.98$ = <u>2.13 g (or 2.10 g)</u>	**[3]**
	(b)	$[C_5H_5N] = [(0.100 \times 0.025) – (0.0125 \times 0.005)] / 0.03 = \underline{0.0813\ mol\ dm^{-3}}$ [pyridinium chloride] = $(0.0125 \times 0.005) / 0.03 = \underline{2.08 \times 10^{-3}\ mol\ dm^{-3}}$ $pK_b = 14 – pK_a = \underline{8.75}$ pOH = pK_b + lg [salt]/[base] pOH = 8.75 + lg $(2.08 \times 10^{-3} / 0.0813) = 7.16$ pH = 14 – 7.16 = <u>6.84</u>	**[3]**
	(c)	On addition of a <u>small amount of acid</u> (H^+) to the buffer solution, nearly all the <u>added H^+ ions are neutralised</u> by the large amount of C_5H_5N. Hence $[H^+]$ does not increase appreciably and the <u>pH is kept approximately constant</u>. $C_5H_5N\ (aq) + H^+(aq) \rightarrow C_5H_5NH^+(aq)$ On addition of a <u>small amount of base</u> (OH^-) to the buffer solution, nearly all the <u>added OH^- ions are neutralised</u> by the large amount of $C_5H_5NH^+$. Hence $[OH^-]$ does not increase appreciably and the pH is kept approximately constant. $C_5H_5NH^+\ (aq) + OH^-(aq) \rightarrow C_5H_5NH\ (aq) + H_2O(l)$	**[3]**
			[Total: 9]

3 (a)

Initial P of NO(g) = $\frac{1}{4} \times 5 = 1.25$ atm

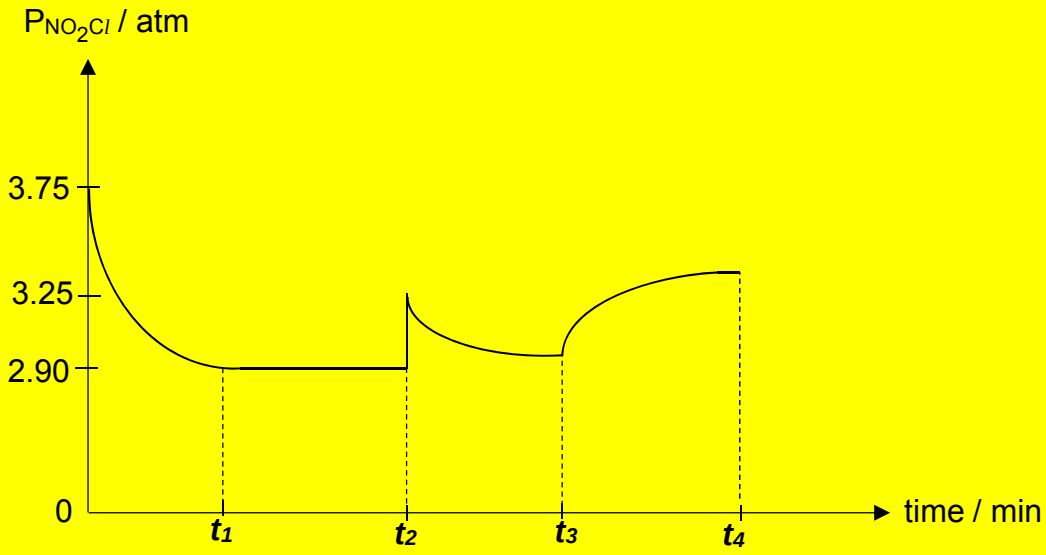
Initial P of NO_2Cl(g) = 5 – 1.25 = 3.75 atm

	NO_2Cl	+	NO	⇌	NOCl	+	NO_2
Initial P / atm	3.75		1.25		0		0
Δ in P / atm	–0.85		–0.85		+0.85		+0.85
Eqm P / atm	2.90		0.40		0.85		0.85

$K_p = \frac{(0.85)(0.85)}{(2.90)(0.40)}$ = 0.623 (no units)

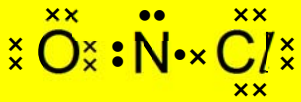
[2]

(b)



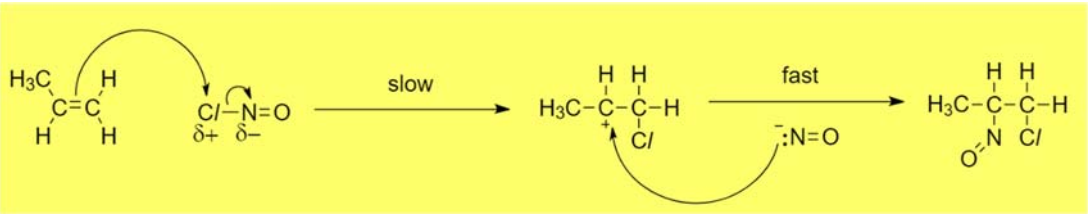
[2]

(c)



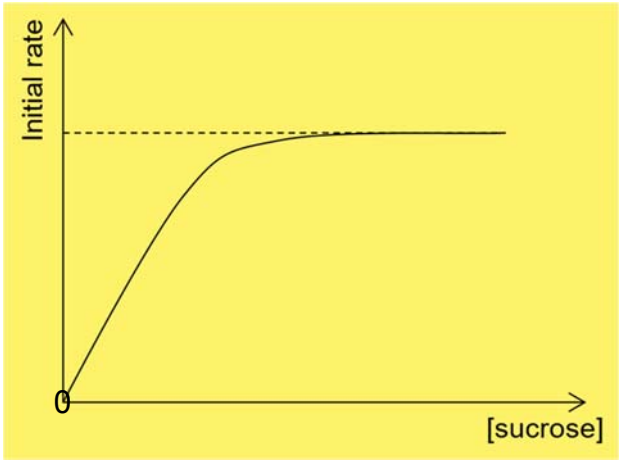
[1]

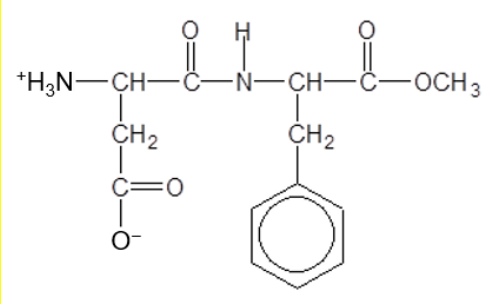
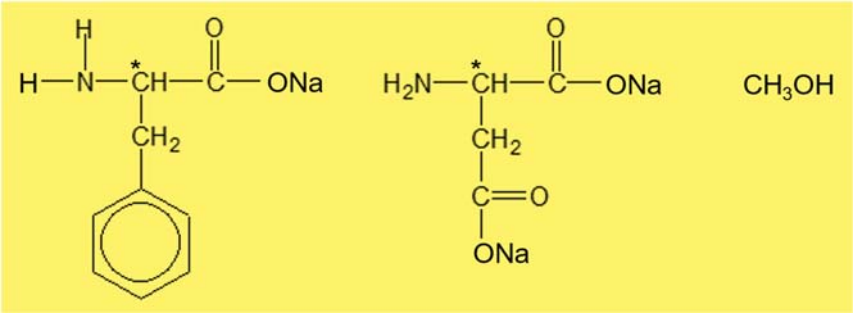
(d) Electrophilic addition

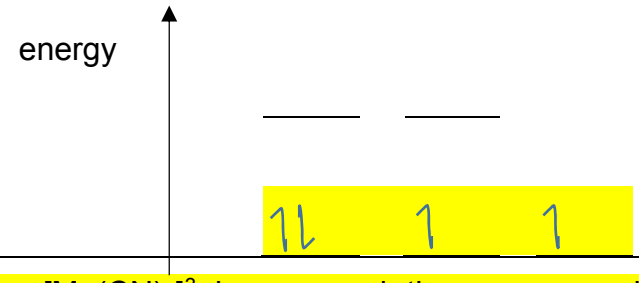


[3]

[Total: 8]

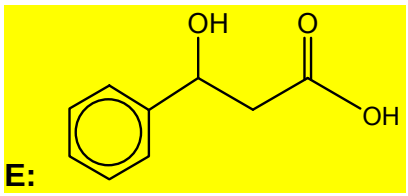
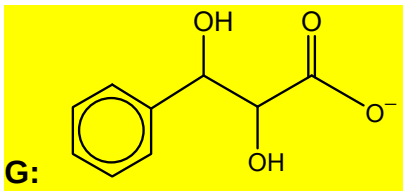
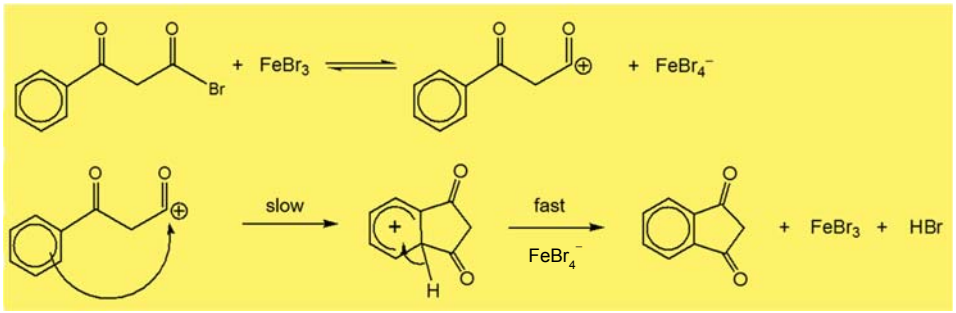
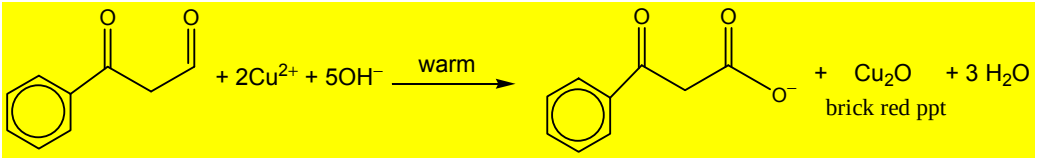
4	**(a)**	**(i)**	Comparing Experiments 1 and 2, When the volume/concentration of HC*l* increases to 1.5 times, rate increases to 1.5 times. Hence, reaction is first order with respect to HC*l*. Comparing Experiments 1 and 3, When the volume/concentration of sucrose doubles, rate doubles. Hence, reaction is first order with respect to sucrose.	**[2]**
		(ii)	Rate = k [sucrose] [HC*l*] From Experiment 1, [sucrose] = $0.850 \times \frac{20}{50} = 0.340$ mol dm^{-3} [HC*l*] = $1.23 \times \frac{30}{50} = 0.738$ mol dm^{-3} $k = \frac{1.77 \times 10^{-3}}{(0.340)(0.738)} = 7.05 \times 10^{-3}$ mol^{-1} dm^3 min^{-1}	**[2]**
		(iii)	[sucrose] = $0.850 \times \frac{40}{70} = 0.486$ mol dm^{-3} [HC*l*] = $1.23 \times \frac{20}{70} = 0.351$ mol dm^{-3} Both concentrations for Initial rate of reaction = $7.05 \times 10^{-3} \times 0.486 \times 0.351$ $= 1.20 \times 10^{-3}$ mol dm^{-3} min^{-1}	**[2]**
	(b)	**(i)**		**[1]**

		(ii)	When [sucrose] is low, reaction is first order with respect to sucrose due to the availability of active sites on the enzyme molecules for binding. When [sucrose] is high, all active sites on the enzyme molecules are occupied. The rate of reaction then is independent of [sucrose] and the reaction is zero order with respect to sucrose.	**[2]**
	(c)	**(i)**		**[1]**
		(ii)	The zwitterions of aspartame form ion-dipole interactions with water.	**[1]**
		(iii)		**[3]**
				[Total: 14]

5	**(a)**		Due to the similar energy/ close proximity of the 3d and 4s electrons in the transition elements, transtion element can form ions of approximately the similar stability by losing different number of electrons.	**[1]**
	(b)		In the presence of octahedral ligand field, the degenerate d-orbitals in the metal complex were spilt into two energy levels. The colour observed is due to the difference in energy levels, ΔE. The difference in electronic configuration due to different oxidation state affect ΔE. Light of different energies/ different wavelengths are absorbed for the promoion of electrons from the lower energy orbital to the vacant/partially filled higher energy orbital/ d-d transition, different complementary colour is observed.	**[2]**
	(c)		$E^{\ominus}(Mn^{3+}/Mn^{2+})$ is more positive than $E^{\ominus}([Mn(CN)_6]^{3-}/[Mn(CN)_6]^{4-})$, which shows that Mn^{3+} is more readily reduced, hence a weaker oxidising agent in cynaide solution than in water. More energy is required to add an electron to the negatively charged $[Mn(CN)_6]^{3-}$ due to repulsion.	**[2]**
	(d)	**(i)**	Figure 1.1  	**[1]**
		(ii)	Since $[Mn(CN)_6]^{3-}$ ions are red, the energy gap between the 2 sets of d-orbitals in $[Mn(CN)_6]^{3-}$ is bigger. This suggests that $[Mn(CN)_6]^{3-}$ is the low spin complex, as its energy gap, ΔE, is greater than the pairing energy/ Coulombic repulsion/ repulsion energy, electrons in $[Mn(CN)_6]^{3-}$ would pair up.	**[1]**
	(e)	**(i)**	[O] $HMnO_4^- \rightarrow MnO_4^- + H^+ + e$ [R] $3H^+ + 2e + HMnO_4^- \rightarrow MnO_2 + 2H_2O$ Overall equation: $3HMnO_4^- + H^+ \rightarrow MnO_2 + 2\ MnO_4^- + 2H_2O$	**[1]**
		(ii)	$E_{cell} = +2.10 - (+0.90) = +1.20$ V $\Delta G = -nFE_{cell} = -(2)(96500)(1.20) = -232$ kJ mol^{-1}	**[2]**
	(f)		In acidic condition, $O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ $\quad E^{\ominus} = +1.23$ V $Mn^{3+} + e \rightleftharpoons Mn^{2+}$ $\quad E^{\ominus} = +1.54$ V $E^{\ominus}_{cell} = +1.23 - (+1.54) = -0.31$ V	**[2]**

		In alkaline solution, $O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$ $E^\ominus = +0.40$ V $E^\ominus_{cell} = +0.40 - (+0.18) = +0.22$ V Since the $E^\ominus_{cell} > 0$ in alkaline environment and $E^\ominus_{cell} < 0$ in acidic environment, Mn(II) is more stable in acidic environment than in alkaline environment.	
			[Total: 12]

6	**(a)**	**(i)**	CO_2: Carbon in CO_2 has attained maximum oxidation state. N_2: N≡N is very strong resulting high activation energy.	**[2]**
		(ii)	Methane: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ Hydrogen sulfide: $H_2S(g) + 1½\ O_2(g) \rightarrow SO_2(g) + H_2O(l)$ Hydrogen: $H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$	**[2]**
		(iii)	Energy evolved = $200 \times 4.18 \times (64.7 - 29.6) = 29.34$ kJ mass of biogas used = $1000 \times 6.44 \times 10^{-4} = 0.644$ g Fuel value of biogas = $29.34 \div 0.644 = 45.6$ kJ g^{-1}	**[2]**
		(iv)	Amount of methane in 1 dm^3 biogas = $0.644 \times 0.722 \div (12.0 + 4.0)$ = 0.0291 mol Amount of H_2S in 1 dm^3 biogas = $0.644 \times 0.012 \div (2.0 + 32.1)$ = 0.000227 mol Amount of H_2 in 1 dm^3 biogas = $0.644 \times 0.027 \div 2.0$ = 0.00869 mol Energy evolved = 29.34 kJ $= (0.0291 \times \lvert\Delta H_c(CH_4)\rvert) + (0.000227 \times 482) + (0.00869 \times 386)$ $\Delta H_c(CH_4) = -890$ kJ mol^{-1}	**[2]**
	(c)	• Longer time for hot flue gas to pass through spiral copper coil • Spiral copper coil increase the surface area for energy transfer • copper is a good conductor of heat • the combustion takes place inside the apparatus, not affected by draught.		**[1]**
	(d)	To **<u>remove sulfur dioxide</u>** gas as low concentration of this gas can also irritates the respiratory system.		**[1]**
				[Total: 10]

7	(a)	(i)	Reaction **I**: $H_2N–NH_2$ Reaction **II**: PBr_3	[2]
		(ii)	**E:**  **G:** 	[2]
		(iii)	Electrophilic substitution 	[3]
	(b)		1) Test: Add Br_2(aq). Compound **F**: Orange Br_2(aq) decolourises. Compounds **B** and **C**: Br_2(aq) remains orange. 2) Test: Add $AgNO_3$(aq) Compound **B**: No ppt forms. Compound **C**: Cream ppt (AgBr) forms.	[4]
	(c)		Brick-red precipitate forms. 	[2]
				[Total: 13]

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