

GCE Edexcel GCE Chemistry (6245/01)

January 2006

Mark Scheme (Results)

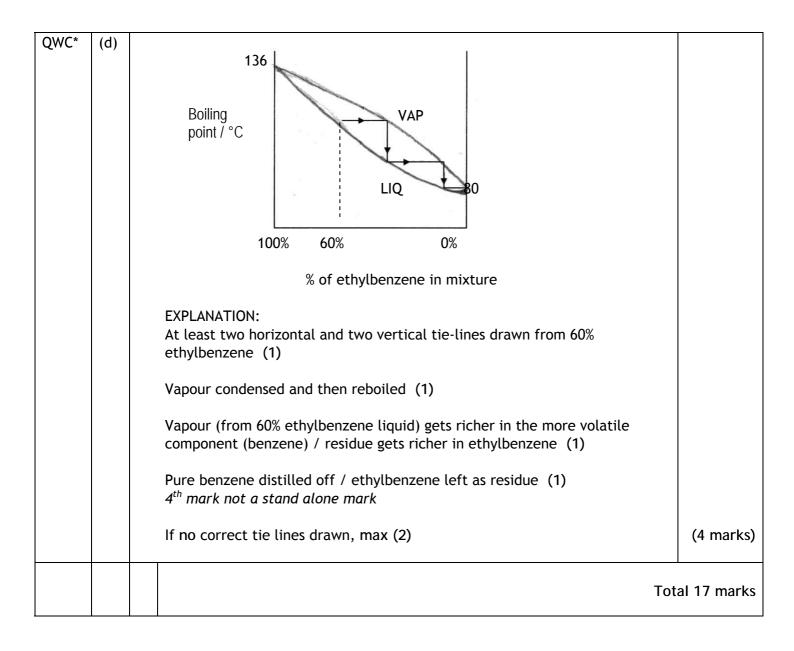
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1.	(a)	The	emf of a half-cell measured relative to the standard hydrogen electrode (1)	
		at a	olutions at 1 mol dm ⁻³ concentration and gases at 1 atm pressure/101kPa and stated temperature / 298K (1) S <i>tandalone mark</i> OW pressure of 100 kPa	(2 marks)
	(b)	(i)	Introducing another metal wire would set up its own p.d. / can only measure a potential difference / need source and sink for electrons / voltmeter requires two connections	(1 mark)
		(ii)	Hydrogen/H ₂ (g) 1 atm / 101kPa (1) Hydrogen ions / H ⁺ _(aq) / hydrochloric acid 1 mol dm ³ (1) (1)	
			H_2 or H^+ with no conditions max (2)	(3 marks)
	(C)	(i)	$2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2^+}(aq) + 4OH(aq) \text{ or multiples}$ OR $2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe(OH)_2(s)$ Species (1)	
			balancing (1) Do not allow species mark if electrons still in equation, but allow balancing mark if 4e on both sides	(2 marks)
		(ii)	$\Delta E_{react}^{\theta} = (+) 0.84 (V) (1)$ Greater than zero therefore feasible (1)	(2 marks)

*	(iii)	Zn oxidises preferentially to Fe/Zinc acts as sacrificial (anode) (1) If Sn used (and damaged), Fe oxidises preferentially (1) <i>Disallow "oxidises more readily"</i> $E^{\theta} Zn^{2+}/Zn$ more negative than for Fe <i>OR</i> $E^{\theta} Zn/Zn^{2+}$ more positive than for Fe <i>OR</i> E^{θ}_{cell} for Zn being oxidised by O ₂ is more positive than for Fe being oxidised by O ₂ <i>OR</i> similar E^{θ} arguments related to preferential oxidation with Sn (1)	
		disallow "higher" or "bigger" for more negative or more positive	(3 marks)
		Tot	al 13 marks
(a)	Delo	calisation / π -system (1)	
	OR		
	bond	Is compared with having three separate π / double bonds / cyclohexatriene,	(3 marks)
(b)	conc Inter 2 nd S	entrated (1) mediate: Nitrobenzene / $C_6H_5NO_2$ (1) tep: Tin / iron and conc HCl (followed by addition of alkali) (1)	(4 marks)
	(a)	(a) Delo due OR Due Conf bond Keku (b) 1 st st conc Inter 2 nd S	If Sn used (and damaged), Fe oxidises preferentially (1) Disallow "oxidises more readily" $E^{\theta} Zn^{2+}/Zn$ more negative than for Fe OR $E^{\theta} Zn/Zn^{2+}$ more positive than for Fe OR E^{θ}_{cell} for Zn being oxidised by O_2 is more positive than for Fe being oxidised by O_2 OR similar E^{θ} arguments related to preferential oxidation with Sn (1) disallow "higher" or "bigger" for more negative or more positive Tot (a) Delocalisation / π -system (1) due to overlap of six <i>p</i> -orbitals OR Due to overlap of p-orbitals around the ring (1) Confers stability/ benzene at a lower energy level / more energy needed to break bonds compared with having three separate π / double bonds / cyclohexatriene, Kekule structure (1) Standalone mark

(c)	(i)	AlBr ₃ /FeBr ₃ / AlCl ₃ / Al ₂ Cl ₆ / FeCl ₃ / Fe ₂ Cl ₆	(1 mark)
	(ii)	AlBr ₃ + CH ₃ CH ₂ Br CH ₃ CH ₂ ⁺ + AlBr ₄ ⁻ (1) ALLOW C ₂ H ₅ ⁺ in this equation only	
		EITHER	
		(1) for arrow $CH_2 CH_3 \longrightarrow (+)$ (1) for arrow Internediate (1)	
		$(H_{1}^{CH_{2}CH_{3}}) \rightarrow (O)^{CH_{2}CH_{3}} + HB_{r} + AlB_{r_{3}}$	
		(1) for Arrow from C-H bond	
		OR	
		(1) for a mow Intermediate (1)	
		$(1) \text{ for arrow} \qquad \qquad$	
		$\frac{\text{Arrows}}{\text{Do not allow to } C_2 H_5^+}$ (3)	
		ALLOW to point/go to + charge	(4 marks)
		ALLOW C_2H_5 in intermediate	
	(iii)	Electrophilic substitution	(1 mark)



3	(a)	(i)	Forms ions which have partially filled <i>d</i> -orbitals <i>OR</i>	
			Forms ions which have a partially filled <i>d</i> -subshell	(1 mark)
		(ii)	Scandium / Sc and Zinc / Zn	(1 mark)
	(b)	(i)	Fe^{2^+} [Ar] $3d^6$	
			Mn ^{2⁺} [Ar] 3d ⁵ (1) for both correct	(1 mark)
		(ii)	Fe^{3+} is $3d^5$ / half filled <i>d</i> -subshell which is more stable than $3d^6$ (1)	
			Mn^{2^+} is (already) $3d^5$ (which is more stable than $3d^4$) (1)	(2 marks)
	(c)		Shape (1) Bonding to correct atoms (1)	
			$\left(\begin{array}{c} NC \\ NC \\ NC \\ NC \\ CN \\ CN \\ CN \\ CN $	(2 marks)
	(d)		Two As atoms oxidised from +3 to +5 per mole of As_2O_3 (loss of 4e ⁻) (1)	
			\therefore if 5 moles oxidised, total 20e ⁻ lost / change in oxidation no. = 20 (1)	
			\therefore 4 moles MnO ₄ reduced, total 20e gained / change in oxidation no. 20 \therefore each Mn(VII) gains 5e /change in oxidation no. 5 (1)	
			Mn(II) / Mn ²⁺ (1) NOT standalone mark	(4 marks)
	(e)	(i)	$VO_3^- + 2H^+ / 2H_3O^+ \rightarrow VO_2^+ + H_2O / 3H_2O$	(1 mark)
		(ii)	No because oxidation no. of V is +5 in VO_2^+ / Oxidation no. of V unchanged (at +5)	(1 mark)
		(iii)	First green colour : VO_2^+ and VO^{2+} (1) Second green colour : V^{3+} / $[V(H_2O)_6]^{3+}$ (1)	
			Violet colour : $V^{2^+} / [V(H_2O)_6]^{2^+}$ (1)	(3 marks)
			Tot	al 16 marks

4	(a)	(i)	Correct points (1) Smooth curve (1)	
			$\frac{100}{0.90}$	(2 marks)
		(ii)	First half life 15 min (± 1 min) (1) Second half life 15 min (± 1 min) (1)	(2 marks)
			If not shown on graph max (1)	
		(iii)	1 st order (1) t _{1/2} is constant (1)	(2 marks)
	(b)	(i)	Zero	(1 mark)
		(ii)	Rate = k [2-bromo-2-methylbutane] ALLOW a formula Mark consequentially on (a)(iii) and (b) (i)	(1 mark)
		(iii)	$\begin{array}{c} CH_{3} \\ H_{5}C_{2}-C-CH_{3} \\ H_{5}C_{2}-C-CH_{3} \\ H_{5}C_{2} \\ H_{5}C_{2} \\ H_{5}C_{2} \\ (1) \\ H_{5}C_{2} \\ (1) \\ (+Br^{-}) \end{array}$	
			$\begin{array}{c} CH_{3} & CH_{3} \\ I \oplus & (\longrightarrow) & H_{S}C_{2} - C - CH_{3} \\ H_{S}C_{2} & I \\ (I) & OH \end{array}$ $\begin{array}{c} H_{S}C_{2} & CH_{3} \\ I \oplus & OH \\ I \oplus & OH \end{array}$ $\begin{array}{c} H_{S}C_{2} & CH_{3} \\ I \oplus & OH \\ I \oplus & OH \end{array}$ $\begin{array}{c} H_{S}C_{2} & CH_{3} \\ I \oplus & OH \\ I \oplus & OH \end{array}$ $\begin{array}{c} H_{S}C_{2} & CH_{3} \\ I \oplus & OH \\ I \oplus & OH \end{array}$ $\begin{array}{c} H_{S}C_{2} & CH_{3} \\ I \oplus & OH \\ I \oplus & OH \end{array}$ $\begin{array}{c} H_{S}C_{2} & CH_{3} \\ I \oplus & OH \\ I \oplus & OH \end{array}$ $\begin{array}{c} H_{S}C_{2} & CH_{3} \\ I \oplus & OH \\ I \oplus & OH \end{array}$ $\begin{array}{c} H_{S}C_{2} & CH_{3} \\ I \oplus & OH \\ I \oplus & OH \\ I \oplus & OH \end{array}$ $\begin{array}{c} H_{S}C_{2} & CH_{3} \\ I \oplus & OH $	
			mark for each arrow (2) and transition state including sign (1)	(3 marks)
	(C)	The	intermediate /carbocation / _{C2H5} is planar (1)	
			intermediate /carbocation / _{C2H5} is planar (1)	
			al) attack from either side (1)	
		(the	refore) racemic mixture (produced) (1) Standalone mark	(3 marks)
	1			tal 14 marks

5	(a)	(i)	Elimination / dehydration	(1 mark)
		(ii)	Concentrated sulphuric acid / concentrated phosphoric acid / aluminium	
			oxide ACCEPT correct formula	(1 mark)
		(iii)	Hydrolysis	(1 mark)
		(iv)	Esterification	(1 mark)
		(v)	CH ₃ OH / methanol	(1 mark)
	(b)	(i)	EITHER EITHER $H_{3}C$ $C = 0$ $H_{3}C - \frac{1}{C} - CN$ $[1] for H_{3}C (1) H = CNH_{3}C - \frac{1}{C} - CN H_{3}C - \frac{1}{C} - CN H_{3}C - \frac{1}{C} - CNH_{3}C - \frac{1}{C} - CN H_{3}C - \frac{1}{C} - CN H_{3}C - \frac{1}{C} - CNH_{3}C - \frac{1}{C} + \frac{1}{C}$	
			Lone pairs not essential Arrows may start from minus of O ⁻ ALLOW CN ⁻ OR ⁻ CN	(4 marks)
		(ii)	High [H ⁺] insufficient CN ⁻ (available for nucleophilic attack) (1) Low [H ⁺] insufficient H ⁺ / HCN for the second stage (1)	
			High $[[H^{\dagger}]$ surpresses ionisation / shifts equilibrium to left and low $[H^{\dagger}]$ shifts equilibrium to right max (1)	(2 marks)

(c)	(i)	(Free) radical / peroxide	(1 mark)
	(ii)	$ \begin{array}{ccc} H & CH_3 \\ -C - C - C \\ H & COOCH_3 \end{array} $	
		Correct repeating unit (1) Continuation bonds dependent on a 2 carbon skeleton unit (1)	(2 marks)
	(iii)	The polymer chain lengths are different (due to different termination steps) / different size molecules/ different numbers of monomer (units)	(1 mark)
		Tot	al 15 marks
		TOTAL FOR PAPER	R: 75 MARKS