OCR
RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

Unit **F325:** Equilibria, Energetics and Elements

Mark Scheme for June 2011

Oxford Cambridge and RSA Examinations

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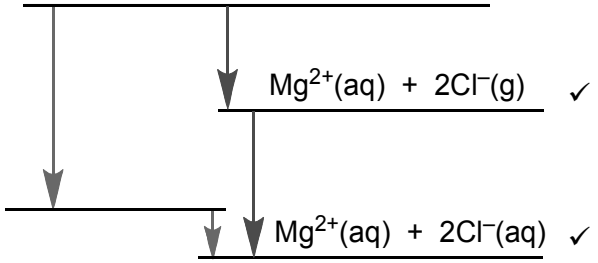
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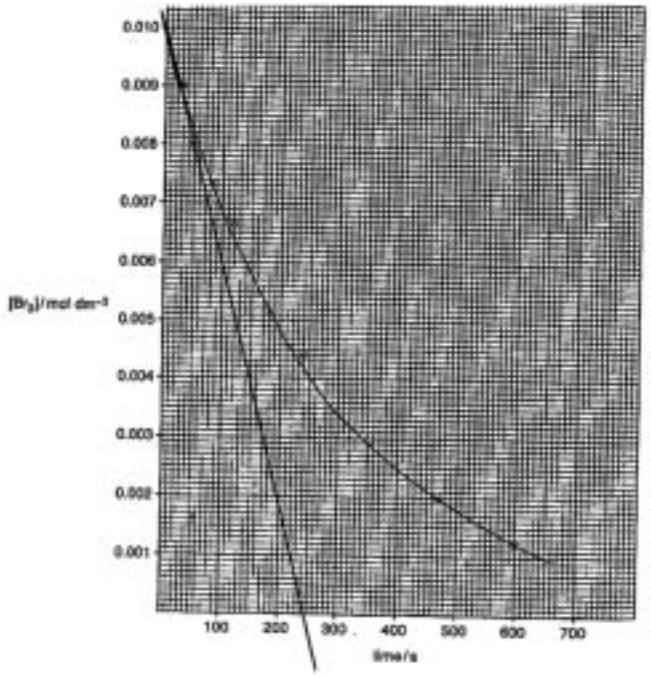
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Question			Answer	Mark	Guidance
1	(a)		(The enthalpy change that accompanies) the formation of **one mole** of a(n ionic) compound ✓ from its **gaseous ions** ✓ (under standard conditions)	2	**IGNORE** 'Energy needed' **OR** 'energy required' **ALLOW** as alternative for compound: lattice, crystal, substance, solid **Note**: 1st mark requires **1 mole** **2nd mark** requires **gaseous ions** **IF** candidate response has '1 mole of gaseous ions', award 2nd mark but **NOT** 1st mark **IGNORE**: $Mg^{2+}(g) + 2Cl^{-}(g) \longrightarrow MgCl_2(s)$ (question asks for words)
	(b)	(i)	Hydration involves bond forming **OR** bonds are made ✓	1	**ALLOW** statement of **any type of bond** being formed **ALLOW** (chloride) ions attract water (molecules) **ALLOW** a response in terms of **hydrogen bonds** breaking **AND** bond making **DO NOT ALLOW** response stating that energy is required **DO NOT ALLOW** response that refers to ions in H_2O, eg H^+
		(ii)		2	Correct species **AND** state symbols required for both marks Mark each marking point independently **ALLOW** response on upper line: $Mg^{2+}(g) + 2Cl^{-}(aq)$ (ie Cl^- hydrated before Mg^{2+}) **ALLOW** $MgCl_2(aq)$

Question			Answer	Mark	Guidance
1	(b)	(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –1921 (kJ mol^{-1}) award 2 marks** --- (–2493) + (–154) = (2 x –363) + $\Delta H_{hyd}(Mg^{2+})$ ✓ $\Delta H_{hyd}(Mg^{2+})$ = (–2493) + (–154) – (2 x –363) = –1921 (kJ mol^{-1}) ✓	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. **See list below for marking of answers from common errors** --- **ALLOW** for **1 mark**: –2284 use of Cl^- rather than 2 x Cl^- (+)1921 signs all reversed **OR** lack of 2 for 363 –1613 sign wrong for 154 (+)3065 sign wrong for 2493 –3373 sign wrong for 2 x 363
	(c)		Magnesium ion **OR** Mg^{2+} is smaller **OR** Mg^{2+} has greater charge density ✓ Mg^{2+} has a stronger attraction to H_2O **OR** Mg^{2+} has a stronger bonding with H_2O ✓	2	**ORA:** Calcium ion **OR** Ca^{2+} is larger **OR** Ca^{2+} has smaller charge density **IGNORE** idea of close packing of ions **IGNORE** 'atomic' and 'atoms' and assume that Mg or Ca refer to ions, ie **ALLOW** Mg has a smaller (atomic) radius **ALLOW** Mg has a stronger attraction to H_2O **ORA:** e.g. Ca^{2+} has less attraction to H_2O **DO NOT ALLOW** Mg **atoms** have a stronger attraction to H_2O **DO NOT ALLOW** stronger attraction/bonding between ions **Note:** Response must refer to attraction/bonding with H_2O or this must be implied from the whole response
			Total	9	

Question			Answer	Mark	Guidance
2	(a)		**Temperature**: (Forward) reaction is exothermic **OR** gives out heat **OR** reverse reaction is endothermic **OR** takes in heat ✓ **Pressure**: Right-hand side has fewer number of (gaseous) moles ✓ **ORA** **Equilibrium** Lower temperature/cooling **AND** increasing pressure shifts (equilibrium position) to the right ✓	3	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** K_c increases at lower temperatures **3rd mark** is for stating that **BOTH** low temperature and high pressure shift equilibrium to the right (Could be separate statements) **Note: ALLOW** suitable alternatives for 'to right', e.g.: towards NO_2 **OR** towards products **OR** in forward direction **OR** increases yield of NO_2/products **ALLOW** 'favours the right', as alternative for 'shifts equilibrium to right' **IGNORE** responses in terms of rate
	(b)		$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$ ✓ $2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$ ✓	2	**ALLOW** multiples, e.g. $2NH_3 + 2½O_2 \longrightarrow 2NO + 3H_2O$ **ALLOW** $\rightleftharpoons$ **OR** $\rightarrow$ in equations
	(c)	(i)	$(K_c =) \frac{[NO_2]^2}{[NO]^2\,[O_2]}$ ✓	1	Square brackets are **essential**

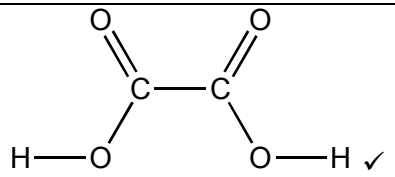
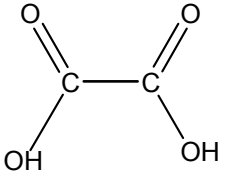
Question			Answer	Mark	Guidance
2	(c)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 45 dm^3 mol^{-1}, award **5 marks** **IF** answer = 45 with incorrect units, award **4 marks** --- **Equilibrium moles** 0.60 mol NO_2 ✓ 0.20 mol NO **AND** 0.40 mol O_2 ✓ **Equilibrium concentrations (equilibrium moles ÷ 2)** $[NO_2]$ = 0.30 mol dm^{-3} **AND** [NO] = 0.10 mol dm^{-3} **AND** $[O_2]$ = 0.20 mol dm^{-3} ✓ **Calculation of K_c and units** $K_c = \frac{0.30^2}{0.10^2 \times 0.20}$ = 45 ✓ dm^3 mol^{-1} ✓	**5**	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW ECF** throughout ***Alternative route if concs NO and O_2 calculated at start:*** **initial concentrations:** 0.40 mol dm^{-3} NO **AND** 0.35 mol dm^{-3} O_2 ✓ **Equilibrium concentrations:** $[NO_2]$ = 0.30 mol dm^{-3} ✓ [NO] = 0.10 mol dm^{-3} **AND** $[O_2]$ = 0.20 mol dm^{-3} ✓ For units, **ALLOW** mol^{-1} dm^3 **ALLOW ECF** using any incorrect values for **concentrations OR moles** of NO, O_2 AND NO_2 For **ECF**, **ALLOW** 2 significant figures up to calculator value correctly rounded **ALLOW ECF** from incorrect K_c expression for both calculation and units **Common ECFs worth less than 5 marks:** **22.5** not ÷2 3 marks + unit mark **1.61** 0.6 for NO_2 but 0.8 for NO and 0.7 for O_2 No mark for moles NO and O_2 3 marks + unit mark **0.804** As above but also no ÷2 No mark for moles NO and O_2 **AND** ÷2 2 marks + unit mark
			Total	**11**	

Question			Answer	Mark	Guidance
3			Evidence of at least two half-lives measured on graph **OR** within text (would need evidence of two half-lives) ✓ Any half-life value stated in range 180–220 s **OR** constant half-life ✓ 1st order ✓ **Note**: This is only correct response for order (ie no **ECF**). If not stated separately, this mark can be awarded from a rate equation, e.g. *rate* = $k[Br_2]^1$ **OR** *rate* = $k[Br_2]$ Evidence of tangent on graph drawn to line at t = 0 s ✓ e.g.  	4	**ANNOTATE ALL Q3 WITH TICKS AND CROSSES, etc** **MARK ON GRAPH OR IN TEXT** **LOOK FOR STATEMENT ON GRAPH OR WITHIN TEXT** **ALLOW** almost constant half-life --- **Note:** Response may use an alternative approach from half-life for the 1st two marks based on gradients of tangents**:** **1st mark** would be awarded for evidence of two tangents drawn on graph **2nd mark** would be awarded for stating that ratio of concentrations = ratio of rates, e.g. gradient of tangent at 0.010 mol dm^{-3} has twice the value of gradient of tangent at 0.005 mol dm^{-3} --- **MARK TANGENTS ON GRAPH** **ALLOW** some leeway but tangent must coincide with part of curve that is 'straight' (ie between $[Br_2]$ = 0.010–0.009 and **MUST NOT** cross the curve

Question	Answer	Mark	Guidance
3	*rate* = $\frac{0.010}{250}$ = 0.000040 **OR** 4.0 x 10^{-5} ✓ units: mol dm^{-3} s^{-1} ✓	2	**ALLOW** values from 1 SF (0.00004 **OR** 4 x 10^{-5}) up to calculator value, correctly rounded **ALLOW** range ~ $\frac{0.010}{160}$ to $\frac{0.010}{300}$: i.e. **ALLOW** a calculated gradient in the range 6 x 10^{-5} – 3 x 10^{-5} from a tangent drawn at t = 0 **IF** tangent is drawn on graph at a different time or incorrectly (e.g. crossing curve), then mark rate calculation by **ECF** using the gradient of the tangent drawn by the candidate (*ie* not the range above). **IF** no tangent is drawn **ALLOW** a value in the range above **ONLY** Credit **only** attempts at tangents, not just a random straight line **IGNORE** a '– sign'
	rate = $k[Br_2]$ **OR** $k = \frac{rate}{[Br_2]}$ ✓ k = calculated result from $\frac{\text{calculated value for rate}}{0.010}$ ✓ units: s^{-1} ✓	3	**DO NOT ALLOW** *rate* = k[Br], *ie* Br instead of Br_2 **DO NOT ALLOW** just $k[Br_2]$, *ie* '*rate* =' **OR** '*r* =' must be present **Calculation of *k* is from candidate's calculated initial rate** From 0.00004, $k = \frac{0.000040}{0.010}$ = 4 x 10^{-3} s **Note:** **IF** order with respect to Br_2 has been shown as 2nd order, then mark this part by **ECF,** e.g. if Br_2 shown to be 2nd order, rate = $k[Br_2]^2$ k = calculated result from $\frac{\text{calculated value for rate}}{0.010^2}$ **units**: dm^3 mol^{-1} s^{-1} **OR** mol^{-1} dm^3 s^{-1} **Note:** Units mark must correspond to the candidate's stated rate equation, **NOT** an incorrectly rearranged k expression
	Total	9	

Question			Answer	Mark	Guidance
4	(a)	(i)	proton donor ✓	1	**ALLOW** H^+ donor
		(ii)	(the proportion of) dissociation ✓ Correct equation for **any** of the four acids: $C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$ **OR** $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ **OR** $CH_3COCOOH \rightleftharpoons H^+ + CH_3COCOO^-$ **OR** $CH_3CHOHCOOH \rightleftharpoons H^+ + CH_3CHOHCOO^-$ ✓	2	**ALLOW** a weak acid partly dissociates **ALLOW** a strong acid totally dissociates **ALLOW** ionisation for dissociation **ALLOW** the ability to donate a proton Equilibrium sign **required** **ALLOW** equilibria involving H_2O and H_3O^+ e.g. $C_6H_5COOH + H_2O \rightleftharpoons H_3O^+ + C_6H_5COO^-$, etc **DO NOT ALLOW** $HA \rightleftharpoons H^+ + A^-$
		(iii)	weakest: CH_3COOH acetic acid C_6H_5COOH benzoic acid $CH_3CHOHCOOH$ lactic acid strongest: $CH_3COCOOH$ ✓ pyruvic acid	1	**ALLOW** correct order using **any** identifier from the table, *ie*, common name, systematic name, structural formula **OR** pK_a value
		(iv)	$C_6H_5COOH_2^+ + CH_3CHOHCOO^-$ ✓	1	**BOTH** products **AND** correct charges required for mark Mark **ECF** from incorrect order in **(iii)** See response from **(iii)** below response to **(iv)**

Question			Answer	Mark	Guidance
4	(b)	(i)	$2CH_3COCOOH + Ca(OH)_2 \rightarrow (CH_3COCOO)_2Ca + 2H_2O$ ✓ **Note:** pyruvic acid must have been used here and formula of pyruvic acid and pyruvate **must** be correct	1	All species **AND** balancing required for the mark **ALLOW** $(CH_3COCOO^-)_2Ca^{2+}$ **ALLOW** equation showing $2CH_3COCOO^- + Ca^{2+}$ **IF** charges shown, charges **must** balance, e.g. **DO NOT ALLOW** $(CH_3COCOO^-)_2Ca$ **IGNORE** state symbols if shown **ALLOW** multiples **ALLOW** equilibrium sign
		(ii)	$H^+ + OH^- \longrightarrow H_2O$	1	**ALLOW** multiples but **not** same species on both sides **ALLOW** equilibrium sign **IGNORE** state symbols if shown **ALLOW** $H_3O^+ + OH^- \longrightarrow 2H_2O$ **ALLOW** $CH_3COCOOH + OH^- \longrightarrow CH_3COCOO^- + H_2O$
	(c)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 2.11, award **4 marks** --- $K_a = 10^{-pKa}$ $= 10^{-2.39}$ **OR** 0.00407 ✓ $K_a = \frac{[H^+]\,[CH_3COCOO^-]}{[CH_3COCOOH]}$ (**ALLOW** use of HA,H^+ and A^-) **OR** $[H^+] = \sqrt{(K_a \times [HA])}$ **OR** $[H^+] = \sqrt{0.00407 \times 0.0150}$ ✓ (subsumes 1st marking point) $[H^+] = 0.00782$ (mol dm^{-3}) ✓ pH = –log 0.00782 = **2.11** ✓	4	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **IF ECF, ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** 0.0041 to calculator value: 0.004073802 **IF** the pK_a of a different weak acid has been used use **ECF** from 2nd marking point **ALLOW** 0.0078 to calculator value (depending on previous rounding) **ALLOW ONLY 2.11** **(This is to take into account poor previous rounding)** **IF** candidate has used 0.0150 mol dm^{-3} (*ie* assumes strong acid) **ALLOW** final mark **ONLY** by **ECF** for a pH of 1.82 **IF** no square root used, pH = 4.21 3 marks

Question			Answer	Mark	Guidance
4	(d)	(i)	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** recognisable mixture of formulae **DO NOT ALLOW** molecular formula but **ALLOW** $(COOH)_2$ **OR** $(CO_2H)_2$  **ALLOW** OH **BUT not** O–H–C
		(ii)	$C_2H_2O_4 \rightleftharpoons H^+ + C_2HO_4^-$ ✓ $C_2HO_4^- \rightleftharpoons H^+ + C_2O_4^{2-}$ ✓	2	**ALLOW** in **either** order **ALLOW** arrow instead of equilibrium sign **ALLOW** molecular formulae for this part **ALLOW** equilibria involving H_2O and H_3O^+ **ALLOW** equations using structures

Question			Answer	Mark	Guidance
4	(e)		***Chemicals (1 mark)*** lactic acid / $CH_3CHOHCOOH$ **AND** (sodium) lactate / $CH_3CHOHCOO^-$ (Na^+) ✓	6	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** any lactate salt **ALLOW** lactic acid **AND** NaOH **OR** lactic acid **AND** OH^- --- **FOR ALTERNATIVE** using Henderson–Hasselbalch equation, **SEE PAGE 11** --- If another weak acid has been selected and salt has been selected, allow **ECF** for remainder of question **SEE PAGE 12** ---
			Concentrations (4 marks) **EITHER** $[H^+(aq)] = 10^{-3.55}$ **OR** 2.8×10^{-4} **OR** 2.82×10^{-4} (mol dm^{-3})✓ *separate marking point* $K_a = 10^{-3.86}$ **OR** 1.4×10^{-4} **OR** 1.38×10^{-4} (mol dm^{-3}) ✓ *separate marking point* $\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_a}$ **OR** $\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$ ✓ $\frac{[HA]}{[A^-]} = \frac{2.8\times10^{-4}}{1.4\times10^{-4}}$ **OR** $\frac{2}{1}$ **OR** 2 **OR** $\frac{[A^-]}{[HA]} = \frac{0.5}{1}$ **OR** 0.5✓ This marking point subsumes previous marking point **ONLY**		**ALLOW** 2.8×10^{-4} up to calculator value of 2.81838×10^{-4} **ALLOW** 0.00028, etc **ALLOW** 1.4×10^{-4} up to calculator value of 1.38038×10^{-4} **ALLOW** 0.00014, etc **ALLOW** use of $CH_3CHOHCOOH$ **AND** $CH_3CHOHCOO^-(Na^+)$ **ALLOW** use of acid **AND** salt **ALLOW** value from $\frac{\text{calculated value of } [H^+]}{\text{calculated value of } K_a}$ **ALLOW** 2SF up to calculator value of 2.041742129 correctly rounded but **ALLOW** 2 if 2.8×10^{-4} and 1.4×10^{-4} used **ALLOW** 2 mol dm^{-3} HA **AND** 1 mol dm^{-3} A^- **OR** any concentration ratio of 2(acid) : 1(salt) **ALLOW** 2SF up to calculator value of 0.489778819 correctly rounded but **ALLOW** 0.5 if 2.8×10^{-4} and 1.4×10^{-4} used
			Comment (1 mark) Magic tang/taste could come from other chemicals/substances in the sweet **OR** The buffer would have the same taste/tang as the magic tang ✓		

Question	Answer	Mark	Guidance
	ALTERNATIVE approach for concentrations using Henderson–Hasselbalch equation ***(4 marks)***		**ALLOW** use of $CH_3CHOHCOOH$ **AND** $CH_3CHOHCOO^-(Na^+)$ **ALLOW** use of acid **AND** salt
	$pH = pK_a + \log\frac{[A^-]}{[HA]}$ **OR** $-\log K_a + \log\frac{[A^-]}{[HA]}$ ✓		**ALLOW** $pH = pK_a - \log\frac{[HA]}{[A^-]}$ **OR** $-\log K_a - \log\frac{[HA]}{[A^-]}$
	$\log\frac{[A^-]}{[HA]} = 3.55 - 3.86$ ✓ (subsumes previous mark)		**ALLOW** $\log\frac{[HA]}{[A^-]} = 3.86 - 3.55$ (subsumes previous mark)
	$\log\frac{[A^-]}{[HA]} = -0.31$ ✓ (subsumes previous mark)		**ALLOW** $\log\frac{[HA]}{[A^-]} = 0.31$ (subsumes previous mark)
	$\frac{[A^-]}{[HA]} = 10^{-0.31} = \frac{0.490}{1}$ **OR** 0.490 ✓		**ALLOW** $\frac{[HA]}{[A^-]} = 10^{0.31} = \frac{2.04}{1}$ **OR** $\frac{2}{1}$ **OR** 2 For $\frac{[A^-]}{[HA]}$, **ALLOW** 2 SF up to calculator value of 0.48978819 For $\frac{[HA]}{[A^-]}$, **ALLOW** 2 SF up to calculator value of 2.041737945 but **ALLOW** 2 if $10^{-0.31}$ used

Question	Answer	Mark	Guidance

4 (e)

SUMMARY OF 4(e) MARKING POINTS FOR EACH POSSIBLE ACID CHOSEN
FIRST, CHECK THE ANSWER ON ANSWER LINE: IF answer is correct for weak acid chosen, award MP2–MP5
IF there is an alternative answer, check to see if there is any **ECF** credit possible using working below

	lactic	**pyruvic**	**acetic**	**benzoic**
pK_a	3.86	2.39	4.76	4.19
MP1	lactic **AND** lactate **OR** lactic acid **AND** OH^-	No mark	No mark	No mark
MP2: $[H^+]$	$10^{-3.55}$ **OR** 2.82×10^{-4} (**calc**: 2.81838×10^{-4})			
MP3: K_a	$10^{-3.86}$ **OR** 1.38×10^{-4}	$10^{-2.39}$ **OR** 4.07×10^{-3}	$10^{-4.76}$ **OR** 1.74×10^{-5}	$10^{-4.19}$ **OR** 6.46×10^{-5}
calc:	$1.380384265 \times 10^{-4}$	$4.073802778 \times 10^{-3}$	$1.737800829 \times 10^{-5}$	$6.45654229 \times 10^{-5}$
MP4: ratio expression	$\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_a}$ **OR** $\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$			
MP5: $\frac{[HA]}{[A^-]}$	$\frac{2.82\times10^{-4}}{1.38\times10^{-4}}$ **OR** 2.04	$\frac{2.82\times10^{-4}}{4.07\times10^{-3}}$ **OR** 0.0693	$\frac{2.82\times10^{-4}}{1.74\times10^{-5}}$ **OR** 16.2	$\frac{2.82\times10^{-4}}{6.46\times10^{-5}}$ **OR** 4.37
calc:	2.041737945	**calc:** 0.069183097	**calc:** 16.21810097	**calc:** 4.365158322
OR $\frac{[A^-]}{[HA]}$	$\frac{1.38\times10^{-4}}{2.82\times10^{-4}}$ **OR** 0.489	$\frac{4.07\times10^{-3}}{2.82\times10^{-4}}$ **OR** 14.4	$\frac{1.74\times10^{-5}}{2.82\times10^{-4}}$ **OR** 0.0617	$\frac{6.46\times10^{-5}}{2.82\times10^{-4}}$ **OR** 0.229
calc:	0.489778819	14.45439771	0.0616595	0.229086765

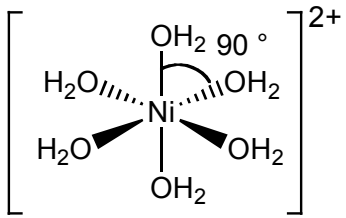
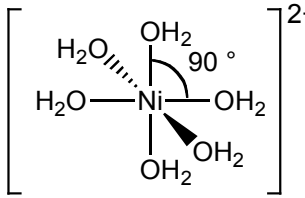
TAKE CARE: Calc values are completely unrounded and may differ between brands of calculator
Use **actual** candidate values at each stage using rounding to 2 or more SF.
MP5: calculated using 3 SF from MP2 and MP3
calc values for MP5 are completely unrounded (using calculator values from MP2 and MP3)

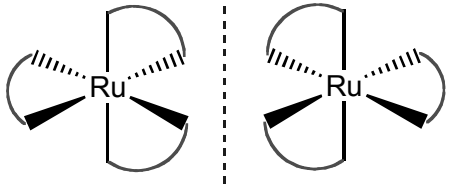
Be slightly flexible as candidates may have written down rounded values but carried on with calculator values – This approach is **ACCEPTABLE**

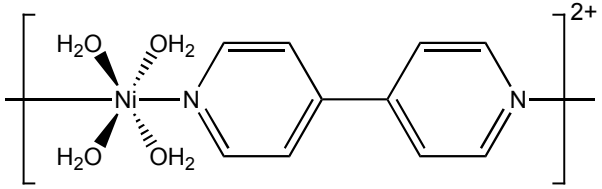
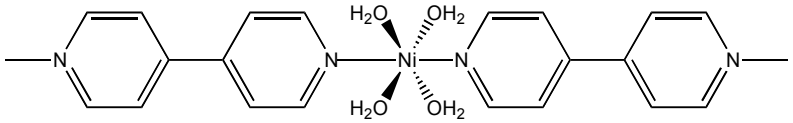
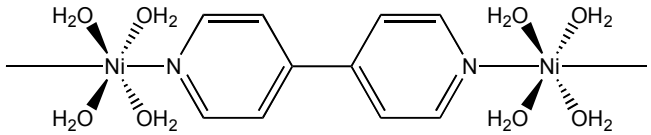
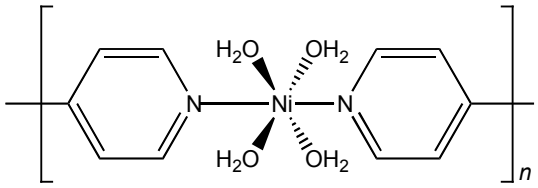
		Total	**20**	

Question			Answer	Mark	Guidance
5	(a)		**process** **increase** **decrease** $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$ ✓ $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$ ✓ $NH_4Cl(s) + aq \rightarrow NH_4Cl(aq)$ ✓ $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$ ✓ $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$ ✓ **All 5 correct ⟶ 2 marks** **4 correct ⟶ 1 mark**	**2**	
	(b)		ΔH: + **AND** bonds broken ✓ ΔS: + **AND** more random/more disorder/more ways of arranging energy ✓	**2**	**Sign and reason required for each mark** **ALLOW** forces of attraction/hydrogen bonds are overcome **DO NOT ALLOW** response in terms of bonds breaking **AND** bond making (for melting bonds are just broken) **DO NOT ALLOW** responses implying that bonds within H_2O molecules are broken **IGNORE** comments related to ΔG **IGNORE** comments related to ΔG
	(c)	**(i)**	$\Delta S = (3 \times 131 + 198) - (186 + 189)$ ✓ $\Delta S = (+)216$ (J K^{-1} mol^{-1}) ✓	**2**	**ALLOW** 1 mark for –216 (wrong sign) **ALLOW** 1 mark for –46 (131 instead of 3 x 131) **ALLOW** 1 mark for 594 (sign of 189)

Question			Answer	Mark	Guidance
5	(c)	(ii)	Two from points below: 1. fuel **OR** fuel cells 2. manufacture of margarine **OR** hydrogenation of alkenes/unsaturated fats 3. manufacture of ammonia **OR** 'Haber process' ✓ 4. manufacture of HCl/hydrochloric acid 5. reduction of metal ores/metal oxides	1	**2 uses for one mark** **IGNORE** hydrogenation of margarine
	(d)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = –109, award first **3 marks** for calculation --- At 298 K, 91.2 = 176 – $T\Delta S$ ✓ ΔS (= $\frac{176-91.2}{298}$) = 0.285 (kJ K^{-1} mol^{-1}) **OR** ΔS (= $\frac{176000-91200}{298}$) = 285 (J K^{-1} mol^{-1}) ✓ *subsumes 1st marking point* At 1000 K, ΔG = 176 – 1000 x 0.285 = –109 (kJ mol^{-1}) ✓ Reaction **does** take place (spontaneously) because ΔG < 0 **OR** ΔG is -ve ✓ **Note**: If no value of ΔG, this mark **cannot** be awarded.	4	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** 0.285 (3 SF) up to calculator value of 0.284563758 **ALLOW** 285 (3 SF) up to calculator value of 284.563758 **ALLOW** –109 up to calculator value correctly rounded, i.e. –108.6, –108.56, etc **ALLOW ECF** from incorrect ΔS, *ie* calculated value of ΔG from ΔG = 176 – 1000 x calculated value of ΔS Answer and reason **BOTH** needed for mark **ALLOW** reaction is feasible for 'reaction does take place' **Note**: If candidate has a + ΔG value, mark **ECF**, ie reaction does not take place because ΔG > 0 **OR** ΔG is +ve
			Total	**11**	

Question			Answer	Mark	Guidance
6	(a)		Ni $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$ ✓ d block: (Ni:) 'd' is **highest energy** sub-shell/orbital ✓ Ni^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ ✓ Transition element: has **an ion** with an incomplete/partially-filled d **sub-shell/orbital** ✓ --- A ligand donates an electron pair to Ni^{2+} **OR** metal ion **OR** metal ✓ A complex ion is an ion bonded to ligand(s)/surrounded by ligands ✓ Coordinate bond/dative covalent mentioned at least once in the right context ✓	4 3	**ANNOTATE WITH TICKS AND CROSSES, etc** **Note:** Examples must be for Ni, not other d block elements **ALLOW** 4s before 3d, ie $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$ **ALLOW** $[Ar]4s^2 3d^8$ **OR** $[Ar]3d^8 4s^2$ **ALLOW** upper case D, etc and subscripts, e.g. $[Ar]4S_2 3D_8$ **DO NOT ALLOW** highest energy shell is 'd' **OR** 'd is the outer sub-shell' (4s as well) **ALLOW** $[Ar]3d^8$ **ALLOW** electron configurations with $4s^0$ **ALLOW** for example Ni^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ **OR** $[Ar]3d^7$ ***No other Ni ions are acceptable*** **ALLOW** lone pair forms a coordinate bond to Ni^{2+} (which will also collect the coordinate bond mark) **ALLOW** diagram of $[Ni(H_2O)_6]^{2+}$ complex ion for 2nd marking point
	(b)	(i)	 3D diagram ✓ 90º bond angle ✓	2	Must contain 2 'out wedges', 2 'in wedges' and 2 lines in plane of paper **OR** 4 lines, 1 'out wedge' and 1 'in wedge':  **ALLOW** dotted line **OR** unfilled wedge as alternatives for dotted wedge Accept bonds to H_2O (does not need to go to 'O') Accept 90 ° written by diagram. Charge **NOT** needed. Square brackets **NOT** needed

Question			Answer	Mark	Guidance
6	(b)	(ii)	**A:** $NiCl_4^{2-}$ ✓ **B**: $Ni(OH)_2$ ✓	2	**ALLOW** $[NiCl_4]^{2-}$ **DO NOT ALLOW** $Ni(Cl^-)_4^{2-}$ **ALLOW** $Ni(OH)_2(H_2O)_4$ **OR** $[Ni(OH)_2(H_2O)_4]$
		(iii)	**C**: $[Ni(NH_3)_6]^{2+}$ ✓	1	**Square** brackets essential 2+ charge must be outside square brackets **ALLOW** $[Ni(OH)_6]^{4-}$
		(iv)	$[Ni(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$ ✓ ✓	2	**1 mark for each side of equation** **ALLOW** equilibrium sign **ALLOW ECF** from **(iii)** for the following: $[Ni(NH_3)_4]^{2+}$ (wrong number of NH_3) **Any** 6 coordinate Ni^{2+} complex with NH_3 and H_2O ligands, e.g. $[Ni(NH_3)_4(H_2O)_2]^{2+}$, $[Ni(NH_3)_5(H_2O)]^{2+}$, etc **ALLOW** from $[Ni(OH)_6]^{4-}$, $[Ni(H_2O)_6]^{2+} + 6OH^- \longrightarrow [Ni(OH)_6]^{4-} + 6H_2O$ **OR** $[Ni(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Ni(OH)_6]^{4-} + 6NH_4^+$
	(c)	(i)	$C_{10}H_8N_2$ ✓	1	**ALLOW** atoms in any order
		(ii)	4 ✓	1	
		(iii)	 ✓ ✓ One mark for each structure *2nd structure must be correct mirror image of 1st structure*	2	Charge and N atom labels **NOT** needed **ALLOW** any attempt to show bipy. Bottom line is the diagram on the left. 1 mark for 3D diagram with ligands attached for ONE stereoisomer. Must contain 2 out wedges, 2 in wedges and 2 lines in plane of paper: **ALLOW** structures with Ni in centre

Question			Answer	Mark	Guidance
6	(c)	(iv)	**3 marks available** **1st mark** Correct 4,4'-bipy structure shown separately or within attempted structure with Ni^{2+} ✓ **2 marks** The remaining 2 marks are available for a section of the polymer with repeat unit identified as follows: **IF** Ni is bonded to 4 H_2Os (bond to O) with a bond to N end **of two** 4,4'-bipy structure **OR** **IF each N of** 4,4'-bipy is bonded to a Ni bonded to 4 H_2Os (bond to O), award 1 mark ✓ **IF** correct repeat unit is shown, award 2 marks ✓✓ 	3	**ALLOW** aromatic rings   Charge **NOT** needed. Square brackets **NOT** needed Bonds around Ni do **NOT** need to be shown 3D Accept bonds to H_2O (does **NOT** need to go to 'O') **ALLOW** the following structure for repeat unit for all 2nd and 3rd marks: 
			Total	**21**	

Question			Answer	Mark	Guidance
7	(a)		**Definition** The e.m.f. (of a half-cell) compared with a standard hydrogen half-cell/standard hydrogen electrode ✓ **Standard conditions** Temperature of 298 K / 25ºC **AND** (solution) concentrations of 1 mol dm^{-3} **AND** pressure of 101 kPa **OR** 100 kPa ✓	**2**	**ALLOW** voltage **OR** potential difference **OR** p.d. **OR** electrode potential **OR** reduction potential **OR** redox potential as alternative for e.m.f. **IGNORE** S.H.E. (as abbreviation for standard hydrogen electrode) **ALLOW** 1 atmosphere/1 atm **OR** 10^5 Pa **OR** 1 bar
	(b)		1.25 (V) ✓	**1**	**IGNORE** any sign
	(c)	(i)	$Cd + 2NiO(OH) + 2H_2O \longrightarrow Cd(OH)_2 + 2Ni(OH)_2$ LHS: correct species and correctly balanced ✓ RHS: correct species and correctly balanced ✓	**2**	**2 marks for correct equation** **ALLOW** NiOOH OR NiO_2H **ALLOW** ⇌ sign for equation (*ie* assume reaction goes from left to right) **ALLOW** 1 mark for correctly balanced equation with e^- and/or OH^- shown e.g.: $Cd + 2NiO(OH) + 2H_2O + 2OH^- + 2e^- \longrightarrow Cd(OH)_2 + 2Ni(OH)_2 + 2OH^- + 2e^-$ **ALLOW** 1 mark for balanced correct reverse equation with OH^- **AND** e^- cancelled: $Cd(OH)_2 + 2Ni(OH)_2 \longrightarrow Cd + 2NiO(OH) + 2H_2O$
		(ii)	oxidation: Cd from 0 to +2 ✓ '+' sign **not** required reduction: Ni from +3 to +2 ✓'+' sign **not** required	**2**	**ALLOW** $Cd^0 \rightarrow Cd^{2+}$ (shows 0 and 2+) **ALLOW** $Ni^{3+} \rightarrow Ni^{2+}$ (shows 3+ and 2+) **ALLOW ECF** from **(c)(i)** equation written 'wrong way around'.
	(d)	(i)	reverse reactions to charging **OR** $Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$ $Ni(OH)_2 + OH^- \longrightarrow NiO(OH) + H_2O + e^-$ **OR** reaction that is reverse to reaction given in **c(i):** $Cd(OH)_2 + 2Ni(OH)_2 \longrightarrow Cd + 2NiO(OH) + 2H_2O$ ✓	**1**	If half-equations are given, then **BOTH** equations required **ALLOW** ⇌ sign for equation (*ie* assume reaction goes from left to right)

Question			Answer	Mark	Guidance
7	(d)	(ii)	$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$ ✓ $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ ✓	2	**ALLOW** multiples; **ALLOW** ⇌ sign for each equation **Note**: These are the **only** correct responses
			Total	10	

Question			Answer	Mark	Guidance
8			**step 1** $Cu + 4HNO_3 \longrightarrow Cu^{2+} + 2NO_3^- + 2NO_2 + 2H_2O$ **OR** $Cu + 2H^+ + 2HNO_3 \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$ **OR** $Cu + 4H^+ + 2NO_3^- \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$ ✓ **step 2** **2 equations with 1 mark for each** $Cu^{2+} + CO_3^{2-} \longrightarrow CuCO_3$ ✓ $2H^+ + CO_3^{2-} \longrightarrow H_2O + CO_2$ ✓ **step 4** $2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$ ✓	4	**ANNOTATE ALL Q8 WITH TICKS AND CROSSES, etc** **ALLOW** multiples throughout **IGNORE** state symbols throughout **ALLOW** $Cu(NO_3)_2$ for $Cu^{2+} + 2NO_3^-$ **AWARD 2 MARKS for a combined equation:** $Cu^{2+} + 2H^+ + 2CO_3^{2-} \longrightarrow CuCO_3 + H_2O + CO_2$ ✓✓ **DO NOT ALLOW** $2H^+ + CO_3^{2-} \longrightarrow H_2CO_3$ **ALLOW** $2Cu^{2+} + 4KI \longrightarrow 2CuI + I_2 + 4K^+$ **ALLOW** $Cu^{2+} + I^- \longrightarrow Cu^+ + ½I_2$

Question			Answer	Mark	Guidance
8			**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 67.6%, award **5 marks.** **Ignore any attempted equation in step 4** **IF** answer = **33.8% AND IF** Cu^{2+}/I_2 in **step 4** equation shown with 1:1 molar ratio, award 5 marks for **ECF** --- amount $S_2O_3^{2-}$ used = 0.100 x $\frac{29.8}{1000}$ = 2.98 x 10^{-3} mol ✓ amount I_2 = 1.49 x 10^{-3} mol **OR** amount Cu^{2+} = 2.98 x 10^{-3} mol ✓ amount Cu^{2+} in original 250 cm^3 = **10 x** 2.98 x 10^{-3} = 2.98 x 10^{-2} mol ✓ Mass of Cu/Cu^{2+} in brass = 63.5 x 2.98 x 10^{-2} g = 1.8923 g ✓ percentage Cu in brass = $\frac{1.8923}{2.80} \times 100$ = 67.6% ✓ **MUST** be to **one** decimal place (in the question)	**5**	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **Working must be to 3 SF throughout until final % mark** BUT ignore trailing zeroes, ie for 0.490 allow 0.49 **ECF** answer above **ECF** 10 x answer above **ECF** 63.5 x answer above **ALLOW** 1.88 g **ECF** $\frac{\text{answer above}}{2.80} \times 100$ Answer **must** be to one decimal place **ALLOW** % Cu = 67.5 % **IF** mass of Cu has been rounded to 1.89 g in previous step **Common ECFs:** **6.76%** x10 missing 3/5 marks for calculation 2 d.p. MS states 1 d.p. **33.8%** **IF** Cu^{2+}/I_2 in **step 4** equation with 2:1 ratio **OR** not attempted, response, 4/5 marks for calculation (moles Cu^{2+} incorrect)
			Total	**9**	

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