GCE

Chemistry A

Advanced GCE

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

Mark Scheme for January 2011

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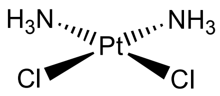
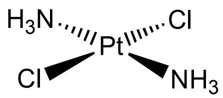
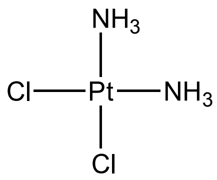
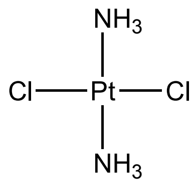
Question			Answer	Mark	Guidance
1	(a)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 8.3×10^4 **OR** 83333 award **2 marks** **THEN IF** units are **dm^6 mol^{-2} s^{-1}**, award 1 further mark $k = \dfrac{rate}{[H_2(g)]\,[NO(g)]^2}$ **OR** $\dfrac{3.6 \times 10^{-2}}{(1.2 \times 10^{-2}) \times (6.0 \times 10^{-3})^2}$ ✓ = 8.3×10^4 **OR** 83000 **OR** 83333 ✓	2	**ALLOW** 1 mark for 8.3×10^x with no working (power of 10 is error) **ALLOW** 2 SF up to calculator value of 8.33333333×10^4 correctly rounded **ALLOW ECF** for calculated answer from incorrectly rearranged *k* expression but **not** for units (Marked independently see below)
			units: dm^6 mol^{-2} s^{-1} ✓	1	**ALLOW** dm^6, mol^{-2} and s^{-1} in any order, ***eg*** mol^{-2} dm^6 s^{-1} **DO NOT ALLOW** other units (Rate equation supplied on paper – **not** derived from data)
	(b)	(i)	*effect on rate* × 2 ✓	1	**ALLOW** 'doubles' **OR** *rate* = 7.2×10^{-2} (mol dm^{-3} s^{-1})
		(ii)	*effect on rate* × ¼ **OR** x 0.25 ✓	1	**ALLOW** 'a quarter' **OR** decrease by ¼ **OR** decrease by 0.25 **OR** rate decreases by 4 **OR** decrease by 75% **OR** *rate* = 0.9×10^{-2} (mol dm^{-3} s^{-1}) **DO NOT ALLOW** just 0.5^2 of rate **OR** rate decreases by 2^2
		(iii)	*effect on rate* × 64 ✓	1	**ALLOW** *rate* = 2.3(04) (mol dm^{-3} s^{-1}) **DO NOT ALLOW** just 'increases by 4 and then by 16 / 4^2 **OR** increases by 4^3

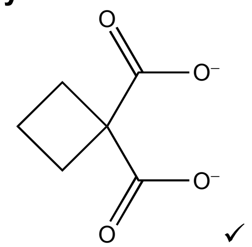
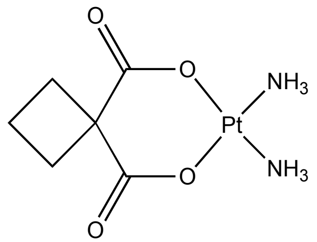
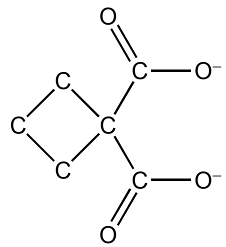
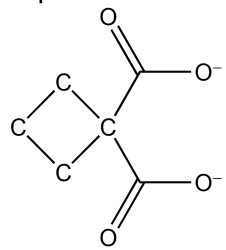
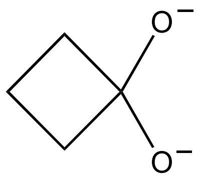
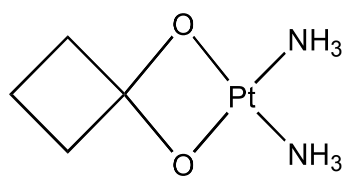
Question			Answer	Mark	Guidance
1	(c)	(i)	(initial) rate increases **AND** more frequent collisions **OR** more collisions **per second/time** ✓	1	**BOTH** points required for mark **ALLOW** rate increases **AND** concentration increases For concentration increases, **ALLOW** particles closer together **OR** less space between particles **DO NOT ALLOW** just more collisions **OR** collisions more likely
		(ii)	rate constant does not change ✓	1	
	(d)		step 1: $H_2(g) + 2\,NO(g) \longrightarrow N_2O(g) + H_2O(g)$ LHS of step one ✓ step 2: $H_2(g) + N_2O(g) \longrightarrow N_2(g) + H_2O(g)$ rest of equations for step 1 **AND** step 2 ✓	2	State symbols **NOT** required For 'rest of equations', This mark can **only** be awarded if 1st mark can be awarded **ALLOW** other combinations of **two** steps that together give the overall equation (shown above part in scoris window), *eg* step 1: $\longrightarrow N_2(g) + ½\,O_2(g) + H_2O(g)$ step 2: $H_2(g) + ½\,O_2(g) \longrightarrow H_2O(g)$ step 1: $\longrightarrow H_2O_2(g) + N_2(g)$ step 2: $H_2(g) + H_2O_2(g) \longrightarrow 2H_2O(l)$ There may be others with species, such as $H_2N_2O_2$ and HNO. Provided the two steps add up to give the overall equation **AND** charges balance, the 2nd mark can be awarded
			Total	**10**	

Question			Answer	Mark	Guidance
2	(a)		Fe: $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^6 4s^2$ ✓ Fe^{2+}: $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^6$ ✓	2	**ALLOW** 4s before 3d, i.e. $(1s^2 2s^2 2p^6) 3s^2 3p^6 4s^2 3d^6$ **ALLOW** $4s^0$ **ALLOW** subscripts **IGNORE** $1s^2 2s^2 2p^6$ is written out a second time
	(b)		coloured (compound/complex/precipitate/ions) **OR** catalyst ✓	1	**IGNORE** 'variable oxidation states' **….** but **ALLOW** the idea that Fe^{2+} can react to form an **ion** with a different charge/oxidation state. '**ion**' is essential: 'atom' or 'metal' is **not** sufficient **IGNORE** partially filled d sub-shell/d orbital (question refers to property of Fe^{2+})
	(c)		Fe oxidised from +2 to +3 ✓ Cr reduced from +6 to +3 ✓	2	**CHECK** and credit oxidation numbers on equation **ALLOW** Fe^{2+} oxidised to Fe^{3+} **ALLOW** Cr^{6+} reduced to Cr^{3+} **ALLOW** + sign after number in oxidation number, *ie* 2+, etc **ALLOW** 1 mark only if oxidation numbers given with no identification of which species has been oxidised or reduced, *ie* Fe goes from +2 to +3 **AND** Cr goes from +6 to +3 Fe reduced from +2 to +3 **AND** Cr oxidised from +6 to +3 (*oxidation and reduction the wrong way around*) **DO NOT ALLOW** just 'Fe is oxidised **and** Cr reduced' **IGNORE** other oxidations numbers (even if wrong) **IGNORE** any references to electrons

Question			Answer	Mark	Guidance
2	(d)		(K_{stab} =) $\dfrac{\left[[Fe(NH_3)_6]^{2+}\right]}{\left[[Fe(H_2O)_6]^{2+}\right]\left[NH_3\right]^6}$ On **top**, **ONLY** $[Fe(NH_3)_6]^{2+}$ shown **AND** on bottom, $[Fe(H_2O)_6]^{2+}$ **AND** $[NH_3]^6$ shown ✓ correct use of square brackets and double square brackets in expression ✓	2	**IGNORE** state symbols **ALLOW** 1 mark if complete expression with correct use of double brackets is shown but upside down **DO NOT ALLOW** round brackets for concentrations and complex ions **ALLOW for 1 mark** (K_{stab} =) $\dfrac{\left[[Fe(NH_3)_6]^{2+}\right]\left[H_2O\right]^6}{\left[[Fe(H_2O)_6]^{2+}\right]\left[NH_3\right]^6}$
	(e)	(i)	O_2/oxygen bonds to Fe^{2+}/Fe(II)/Fe ✓ When required, O_2 substituted **OR** O_2 released ✓	2	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** O_2 binds to Fe^{2+} **OR** O_2 donates electron pair to Fe^{2+} **ALLOW** O_2 bonds to metal ion/metal **DO NOT ALLOW** just O_2 bonds to haemoglobin **OR** O_2 bonds to complex **ALLOW** bond breaks between O_2 and Fe^{2+} when O_2 required **OR** O_2 replaces H_2O **OR** vice versa **ALLOW** O_2 replaces CO_2 **OR** vice versa **ALLOW** O_2 replaces a ligand **OR** vice versa **IGNORE** just ‘by ligand substitution’ (in the question)

Question			Answer	Mark	Guidance
2	(e)	(ii)	(For complex) with CO, stability constant is greater (than with complex in O_2) **OR** with CO, stability constant is high ✓ (Coordinate) bond with CO is stronger (than O_2) **OR** bond with CO is strong ✓	2	**ANNOTATE WITH TICKS AND CROSSES, etc** **Comparison** of CO and O_2 is **NOT** required **ALLOW** stability constant with/of CO is greater **IGNORE** (complex with) CO is more stable **ALLOW** bond with CO is less likely to break **OR** bond with CO more likely to form **OR** 'CO cannot be removed' **OR** idea that attachment of CO is irreversible **OR** CO is a stronger ligand (than O_2) **OR** CO has greater affinity for ion/metal/haemoglobin (than O_2) **IGNORE** CO bonds more easily
	(f)	(i)	Pt^{2+}/Pt is +2/2+, 2 x Cl^- –2 ✓	1	**DO NOT ALLOW** response in terms of Cl_2 rather than Cl^- **DO NOT ALLOW** 'charges cancel' without the charges involved being stated

Question			Answer	Mark	Guidance
2	(f)	(ii)	  **OR**   ✓✓ For each structure Ligand donates an electron pair to metal (ion)/Pt^{2+}/Pt **OR** forms a coordinate bond to the metal (ion)/Pt^{2+}/Pt ✓	3	**IGNORE** any charge, ie Pt^{2+} **OR** Cl^{-}, even if wrong **IGNORE** any angle, even if wrong **ACCEPT** bonds to H_3N (does not need to go to 'N') Assume that a solid line is in plane of paper Each structure **must** contain 2 'out wedges' **AND** 2 'in wedges' or **dotted** lines **OR** 4 **solid** lines at right angles (all in plane of paper) **DO NOT ALLOW any** structure that cannot be in one plane **DO NOT ALLOW any** structure with Cl_2 as a ligand **DO NOT** apply **ECF** from one structure to the other **ALLOW** coordinate bonds shown on diagrams provide that they start from a lone pair **ALLOW** 'dative covalent bond' or 'dative bond' as alternative for 'coordinate bond **IGNORE** *cis* and *trans* labels (even if incorrect) **IGNORE** incorrect connectivity to NH_3, ie **ALLOW** NH_3—
		(iii)	platin binds to DNA (of cancer cells) **OR** platin stops (cancer) cells dividing/replicating ✓	1	

Question			Answer	Mark	Guidance
2	(g)		**1,1-cyclobutanedicarboxylate ion**  ✓ **Correct charge required** **(could also be 2– outside square brackets)** **carboplatin** (*cis* isomer shown below)  ✓	2	Must show cyclobutane ring with both COO^- groups bonded to same carbon **ALLOW** COO^- **OR** CO_2^- for each carboxylate ion **ALLOW** structures showing CH_2 or C atoms provided it is clear that C skeleton is shown, **Note**: H atoms are not required if C atoms shown, *ie*   **DO NOT ALLOW** circle inside cyclobutane ring Two bonds from Pt to O atoms Any bonds from ligand **MUST** come from O **OR** from atom with lone pair **IGNORE** any charge shown **Note**: H atoms are not required if C atoms shown, (see ion in 1st structure) **ALLOW ECF** from 1st structure provided that the attached atoms are capable of forming coordinate bonds (*ie* they contain a lone pair of electrons) ***Example*** if 1st structure is as below, then **ALLOW** 1 mark **ECF**   X ECF ✓
			Total	**18**	

Question			Answer	Mark	Guidance
3	(a)	(i)	$HOCH_2COOH + NaOH \rightarrow HOCH_2COONa + H_2O$ ✓	1	**ALLOW:** $HOCH_2COOH + OH^- \rightarrow HOCH_2COO^- + H_2O$ **ALLOW:** $H^+ + OH^- \rightarrow H_2O$ **DO NOT ALLOW** molecular formulae (cannot see which OH has reacted)
		(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **0.142** (mol dm^{-3}), award **2 marks** -- amount of $HOCH_2COOH = 0.125 \times \frac{25.0}{1000}$ = 0.003125 (mol) ✓ concentration NaOH = $0.003125 \times \frac{1000}{22.00}$ = 0.142 (mol dm^{-3}) ✓ --	2	**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** 3.125×10^{-3} mol **ALLOW ECF**: answer above × $\frac{1000}{22.00}$ **ALLOW** 2 SF: 0.14 to calculator value: 0.142045454 -- If candidate has written in **(a)(i)**: $HOCH_2COOH$ + **2**NaOH, mark by **ECF**: concentration NaOH = **2** × $0.003125 \times \frac{1000}{22.00}$ = 0.284 (mol dm^{-3})
		(iii)	Vertical section matches the (pH) range (of the indicator) **OR** colour change (of the indicator) **OR** end point (of the indicator) ✓	1	**ALLOW** stated pH range for vertical section at about 7–10, 6–10, etc ie **ALLOW** 'pH range must be about 7–10' **ALLOW** 'pH changes rapidly' for vertical section **ALLOW** 'equivalence point' for vertical section, *ie* **ALLOW** equivalence point matches the (pH) range, *etc* **DO NOT ALLOW** just 'end point matches (pH) range' **DO NOT ALLOW** just 'indicator matches vertical section' Response **must** link either the pH range or colour change or end point with the vertical section / pH range ~ 7–10

Question			Answer	Mark	Guidance
3	(b)	(i)	(K_a =) $\frac{[H^+]\,[HOCH_2COO^-]}{[HOCH_2COOH]}$ ✓	1	**IGNORE** state symbols **IGNORE** $\frac{[H^+]^2}{[HOCH_2COOH]}$ in **(i)** but **ALLOW** in **(ii)**
		(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **1.46 x 10^{-4}**, award **2 marks** **THEN IF** units are **mol dm^{-3}**, award 1 **further mark** -- $[H^+] = 10^{-2.37} = 0.00427$ (mol dm^{-3}) ✓ $K_a = \frac{0.00427^2}{0.125} = 1.46 \times 10^{-4}$ ✓ units: mol dm^{-3} ✓	2 1	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below **UNITS** can be credited with no numerical answer -- **ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** 4.27 x 10^{-3} (mol) **ALLOW** 2 SF: 0.0043 up to 0.004265795188 (calc value) **IF** candidate has rounded to 0.00427 (mol dm^{-3}) in 1st response, credit **EITHER** 2 SF: 1.5 x 10^{-4} up to 1.458632 × 10^{-4} (from 0.00427) **OR** 2 SF: 1.5 x 10^{-4} up to 1.455760687 × 10^{-4} (from unrounded calculator value of 0.004265795188) **ALLOW** calculation based on equilibrium conc of glycolic acid as 0.125 – $[H^+]$: Using $[H^+]$ = 0.00427, $K_a = \frac{0.00427^2}{0.125 - 0.00427} = 1.51 \times 10^{-4}$ For **UNITS** this is the **ONLY** correct answer
		(iii)	% dissociation = $\frac{0.00427}{0.125} \times 100$ = 3.4 (%) ✓ Assume working from **EITHER** from a rounded $[H^+]$ **OR** unrounded calculator value of **b(ii)** $[H^+]$	1	**ALLOW** ECF using calculated $[H^+]$ from **b(ii),** **ALLOW** 2 SF: 3.4 % up to calculator value ***Note:*** $[H^+]$ from **b(ii)** displayed *at top of answer window* ***DO NOT MARK THIS TWICE!***

Question			Answer	Mark	Guidance
3	(c)		**ONE mark for equilibrium expression** equilibrium: $HOCH_2COOH \rightleftharpoons H^+ + HOCH_2COO^-$✓	1	**ANNOTATE WITH TICKS AND CROSSES, etc** **DO NOT ALLOW** H^+, A^- and HA **ALLOW** < – > as alternative for equilibrium sign
			Four marks for action of buffer $HOCH_2COOH$ reacts with added alkali **OR** $HOCH_2COOH + OH^- \rightarrow$ **OR** added alkali reacts with H^+ **OR** $H^+ + OH^- \rightarrow$ ✓ $\rightarrow HOCH_2COO^-$ **OR** Equilibrium $\rightarrow$ right ✓ $HOCH_2COO^-$ reacts with added acid ✓ $\rightarrow HOCH_2COOH$ **OR** Equilibrium $\rightarrow$ left ✓	4	**ALLOW** response in terms of H^+, A^- and HA Equilibrium responses **must** refer back to a written equilibrium: **IF** more than one equilibrium shown, assume correct one **ALLOW** weak acid reacts with added alkali **DO NOT ALLOW** acid reacts with added alkali **ALLOW** conjugate base reacts with added acid **DO NOT ALLOW** salt/base reacts with added acid
			Two marks for preparation of buffer Ammonia reacted with an **excess** of glycolic acid **OR** some glycolic acid remains ✓ $HOCH_2COOH + NH_3 \rightarrow HOCH_2COONH_4$ ✓	2	**ALLOW** as products $HOCH_2COO^- + NH_4^+$ **ALLOW** $\rightleftharpoons$ sign instead of $\rightarrow$
	(d)		Base 1 + Acid 2 $\rightleftharpoons$ Acid 1 + Base 2 1st mark for identifying acids and bases. ✓ 2nd mark for correct pairing (ie numbers) ✓	2	**ALLOW**: Base 2 + Acid 1 $\rightleftharpoons$ Acid 2 + Base 1

Question			Answer	Mark	Guidance
3	(e)		$2HSCH_2COO^- + R\text{–}S\text{–}S\text{–}R \longrightarrow {}^-OOCCH_2S\text{–}SCH_2COO^- + 2R\text{–}SH$ ✓ $2R\text{–}SH + H_2O_2 \longrightarrow R\text{–}S\text{–}S\text{–}R + 2H_2O$ ✓	2	**ALLOW** $(SCH_2COO^-)_2$ **ALLOW** equation with ammonium salt, ie: $2HSCH_2COONH_4$ + ……… $\longrightarrow H_4NOOCCH_2S\text{–}SCH_2COONH_4$ + ………
			Total	**20**	

Question			Answer	Mark	Guidance
4	(a)	(i)	Complete circuit with electrodes to voltmeter **AND** salt bridge between solutions ✓ Sn^{4+}/Sn^{2+} half cell with Pt electrode **AND** both solutions labelled as 1 mol dm^{-3} / 1M H^+/H_2 half cell with Pt electrode **AND** H^+ solution labelled as 1 mol dm^{-3} / 1M ✓	3	**ANNOTATE WITH TICKS AND CROSSES, etc** circuit shown **must** be complete, *ie* must be capable of working salt bridge **must** be labelled and must dip into both solutions **ALLOW** concentration label of 'equimolar' or similar wording for Sn^{4+}/Sn^{2+} half cell **ALLOW** any strong acid **IF** both half cells are correct with no concentrations, **ALLOW** 1 out of the 2 marks available for the 2 half cells **IGNORE** any stated temperature or pressure, even if wrong
		(ii)	$2Cr + 3Sn^{4+} \rightarrow 2Cr^{3+} + 3Sn^{2+}$ ✓ $Cr + 3Cu^+ \rightarrow Cr^{3+} + 3Cu$ ✓ $Sn^{2+} + 2Cu^+ \rightarrow Sn^{4+} + 2Cu$ ✓ Conditions not standard **OR** concentrations not 1 mol dm^{-3} ✓ High activation energy **OR** slow rate ✓	5	**ANNOTATE WITH TICKS AND CROSSES, etc** Correct species **AND** balancing needed for each mark **ALLOW** equations as shown with equilibrium sign **ALLOW multiples** but **electrons** must not be shown **IF** three equations have correct species but no balancing, **AWARD** 1 mark **ALLOW** not favoured kinetically
	(b)	(i)	$CH_3OH + 1½O_2 \rightarrow CO_2 + 2H_2O$ ✓	1	Correct species **AND** balancing needed **ALLOW** multiple, *ie* $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$ **ALLOW** CH_4O for formula of methanol
		(ii)	$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$ ✓	1	
		(iii)	less CO_2 **OR** less greenhouse gases ✓ greater efficiency ✓	2	**ALLOW** no CO_2 **OR** no greenhouse gases **ALLOW** (very) efficient **IGNORE** less pollution **OR** 'renewable fuels'
		(iv)	methanol is a **liquid** **AND** methanol is easier to store/transport ✓	1	**Both points required for mark** Response **MUST** state that methanol is a **liquid** **IGNORE** methanol has a higher boiling point Assume that '**it**' refers to methanol **IGNORE** safety issues, *eg* H_2 leakage, flammability, explosive
			Total	**13**	

Question			Answer	Mark	Guidance
5	(a)		**A**: **forms** fewer **moles**/**molecules** of gas ✓ **B**: **forms** gas from a liquid ✓ **C**: **forms** liquid from gases ✓ **D**: **forms** more **moles**/**molecules** of gas ✓	4	**Note**: Responses must imply the key difference between the sides of the equation **IGNORE** comments about C(s)
	(b)		$\Delta S = \Sigma S$(products) – ΣS(reactants) = 40 + 214 – 89 = 165 ($J\ K^{-1}\ mol^{-1}$) **=** 0.165 ($kJ\ K^{-1}\ mol^{-1}$) ✓	1	**ANNOTATE WITH TICKS AND CROSSES, etc** *Mark is for the working line:* 40 + 214 – 89 = 165
			At 25 ˚C, ΔG = +178 – 298 × 0.165 ✓ = (+)129 ✓ units: $kJ\ mol^{-1}$ ✓ **OR** (+)129,000 ✓ units: $J\ mol^{-1}$ ✓ As $\Delta G > 0$, reaction is **not** feasible **OR** as $\Delta G > 0$, $CaCO_3$ is stable ✓	4	**UNITS** have a separate mark **ALLOW** 129 to calculator value of 128.83 **DO NOT ALLOW** 128 (incorrect rounding) **IF** 25 ºC used rather than 298 K, credit by **ECF**, calculated ΔG = 174 to calculator value of 173.875 ***ENTROPY APPROACH***--------------------- **ALLOW** At 25 ˚C, $\Delta S_{total} = 0.165 - \frac{178}{298}$ ✓ = –0.432 ✓ $kJ\ K^{-1}\ mol^{-1}$ ✓ **OR** –432 ✓ $J\ K^{-1}\ mol^{-1}$ ✓ As $\Delta S < 0$, reaction is **not** feasible ✓ ***ENTROPY APPROACH***---
			Minimum temperature for feasibility when $0 = \Delta H - T\Delta S$ **OR** $\Delta H = T\Delta S$ **OR** $T = \frac{\Delta H}{\Delta S}$ ✓ $= \frac{178}{0.165}$ = 1079 K **OR** 806 °C ✓ The units **must** be with the stated temperature	2	Minimum temperature for feasibility when $0 = \Delta S_{system} + \Delta S_{surroundings}$ **OR** $\Delta S_{system} = \frac{\Delta H}{T}$ **ALLOW** 1080 K up to calculator value of 1078.787879, correctly rounded, eg 1078.79 is correct value to 6SF **DO NOT ALLOW** 1078 (incorrect rounding) **IF** 1079 K is given and additional temperature in ºC is incorrect, **IGNORE** ºC temperature (and vice versa)
			Total	**11**	

Question			Answer	Mark	Guidance
6	(a)	(i)	(K_w =) $[H^+(aq)]\ [OH^-(aq)]$ ✓	1	**IGNORE** state symbols **ALLOW** $[H_3O^+(aq)]\ [OH^-(aq)]$
		(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **2.3×10^{-10}** (mol dm^{-3}), award **2 marks** **IF** answer = **2.34×10^{-10}** (mol dm^{-3}) , award **1 mark** -- $[H^+] = 10^{-pH} = 4.27 \times 10^{-5}$ (mol dm^{-3}) ✓ $[OH^-] = \frac{1.0 \times 10^{-14}}{4.27 \times 10^{-5}}$ $= 2.34 \times 10^{-10}$ $= 2.3 \times 10^{-10}$ (mol dm^{-3}) ✓	2	**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** 4.3×10^{-5} up to calculator: $4.265795188 \times 10^{-5}$ **ALLOW** 0.0000427 Answer **MUST** be to 2 SF (in question) **ALLOW** = 2.3×10^{-x} (mol dm^{-3}) for 1 mark (must be a negative power) **ALLOW** alternative approach based on pOH: pOH = 14 – 4.27 = 9.63 ✓ (**DO NOT ALLOW** 9.6) $[OH^-] = 10^{-pOH} = 10^{-9.63} = 2.3 \times 10^{-10}$ (mol dm^{-3}) ✓
	(b)	(i)	Endothermic **because** K_w increases with temperature ✓	1	Endothermic **AND** reason required for the mark **ALLOW** Endothermic **because** increasing temperature shifts equilibrium/reaction to the right
		(ii)	K_w value from graph from 2.2 to 2.6×10^{-14} (mol^2 dm^{-6})✓ Using 2.4×10^{-14}, $[H^+] = \sqrt{2.4 \times 10^{-14}}$ **OR** 1.55×10^{-7} ✓ pH = –log (1.55×10^{-7}) = 6.81 (using $K_w = 2.4 \times 10^{-14}$) ✓	3	**ANNOTATE WITH TICKS AND CROSSES, etc** Actual $K_w = 2.38 \times 10^{-14}$ mol^2 dm^{-6} For this mark, candidate **must** use a value between 2.0 and 3.0×10^{-14} (mol^2 dm^{-6}), *ie* from the approximately correct region of the graph, **ALLOW** 6.8 up to calculator value **Note**: You will need to calculate the pH value from the candidate's estimate of K_w at 37 ºC before awarding the 3rd marking point **ONLY** award an **ECF** pH mark if candidate has generated a value of $[H^+]$ by attempting to take a square root of a value between 2.0 and 3.0×10^{-14}

Question			Answer	Mark	Guidance
6	(b)	(iii)	(Work is) inaccurate **OR** invalid **because** K_w varies with temperature ✓	1	Response requires **reason** for inaccuracy/invalidity in terms of K_w **ALLOW** incorrect with reason **IGNORE** unreliable **ALLOW** inaccurate because wrong K_w was used For K_w varies with temperature, **ALLOW** equilibrium shifts with temperature
	(c)		Acid and alkali mixed ✓ Amounts of acid **AND** alkali stated ✓ Temperature taken at start **AND** finish ✓ energy, $Q = mc\Delta T$ **OR** in words **AND** meaning of m, c **AND** ΔT given ✓ Energy scaled up to form 1 mol of water ✓ ΔH_{neut} = –energy change ✓	6	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** 'base' for 'alkali throughout **ALLOW** if mentioned anywhere which could be within a definition for enthalpy change of neutralisation Amounts could be expressed as amounts, moles, volumes **OR** concentrations **ALLOW** temperature change m = mass/volume of solution/reactants/mixture, etc (but **NOT** surroundings) c = (specific) heat capacity (of solution/water) **OR** 4.18/4.2 ΔT = temperature change **ALLOW** divide energy by moles **ALLOW** '–' sign shown in earlier part, ie $\Delta H_{neut} = -\frac{Q}{n}$ **ALLOW** a statement linking ΔH with temperature change, *ie*: **IF** temperature increases, ΔH_{neut} is **–ve** **OR IF** temperature decreases, ΔH_{neut} is +ve

Question			Answer	Mark	Guidance
6	(d)		**Ionic radius** Potassium ion **OR** K^+ **OR** K ion is smaller **OR** K^+ has greater charge density ✓ **Lattice enthalpy** Lattice enthalpy of KF is more negative than RbF ✓ **OR** K^+ has greater attraction for F^- **Hydration enthalpy** ΔH(hydration) of K^+ is more negative than Rb^+ ✓ **OR** K^+ has greater attraction for H_2O **Enthalpy change of solution** Idea that ΔH(solution) is affected more by lattice enthalpy than by hydration enthalpy ✓	4	**ANNOTATE WITH TICKS AND CROSSES, etc** **Throughout question, ORA** in terms of Rb^+ **Throughout question, ALLOW** energy for enthalpy **DO NOT ALLOW** potassium **OR** K **OR** reference to atoms (*ie* reference to ions is required throughout a response) **ALLOW** lattice enthalpy of KF > lattice enthalpy of RbF **ALLOW** more energy needed to separate K^+ **AND** F^- **IGNORE** KF has stronger bonds **ALLOW** ΔH(hydration) of K^+ > ΔH(hydration) of Rb^+ **ALLOW** more energy needed to separate K^+ **AND** H_2O **IGNORE** K^+ has a stronger bond to H_2O **ALLOW** a correct attempt to link the contribution of lattice enthalpy and hydration enthalpy to ΔH(solution), *ie* lattice enthalpy is a more important factor than hydration enthalpy
	(e)		(During dissolving,) entropy/disorder increases **OR** disorder increases ✓ $T\Delta S > \Delta H$ **OR** $T\Delta S$ is more positive than ΔH **OR** $\Delta H - T\Delta S$ is negative ✓	2	**ALLOW** entropy change is positive **OR** ΔS is positive **OR** $T\Delta S$ is positive **ALLOW** ΔS(system) > $\Delta H/T$ **ALLOW** ΔS(system) is more positive than $\Delta H/T$ ✓ **ALLOW** ΔS(system) + ΔS(surroundings) is positive **ALLOW** Energy contribution from increase in entropy is greater than decrease in energy from enthalpy change **OR** entropy change outweighs enthalpy change **IGNORE** ΔG is negative
			Total	**20**	

Question			Answer	Mark	Guidance
7	(a)	(i)	**amount $S_2O_3^{2-}$ used** $= 0.00100 \times \frac{24.6}{1000} = 2.46 \times 10^{-5}$ mol ✓ **amount O_2 in 25 cm^3 sample** $= \frac{2.46 \times 10^{-5}}{4} = 6.15 \times 10^{-6}$ mol ✓ **Concentration of O_2 in sample** $= 6.15 \times 10^{-6} \times \frac{1000}{25} = 2.46 \times 10^{-4}$ (mol dm^{-3}) ✓ **mass concentration of O_2 in mg dm^{-3}** $= 2.46 \times 10^{-4} \times 32$ g $= 7.872 \times 10^{-3}$ (g dm^{-3}) = 7.872 (mg dm^{-3}) ✓	4	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** 0.0000246 (mol) **ECF** = $\frac{\text{answer above}}{4}$ **ALLOW** 0.00000615 g **ECF** answer above × $\frac{1000}{25}$ **ALLOW** 0.000246 g **ECF** = answer above × 32 x 1000 **ALLOW** 7.9 **OR** 7.87 **ALLOW** 2 SF up to calculator value **Must be in mg for mark** **Note:** Candidate may work out steps 3 and 4 in the opposite order, *ie* **mass of O_2 in sample** $= 6.15 \times 10^{-6} \times 32 \times 1000 = 1.968 \times 10^{-1}$ mg **mass concentration of O_2 in mg dm^{-3}** $= 1.968 \times 10^{-1} \times \frac{1000}{25} = 7.872$ (mg dm^{-3})
		(ii)	**Comment** 7.872 > 5 so fish can survive ✓	1	**ECF** If final answer > 5 fish **can** survive If final answer < 5 fish **cannot** survive
	(b)	(i)	NO ✓	1	**ALLOW** N_2H_2

Question			Answer	Mark	Guidance
7	(b)	(ii)	$2H_2O + 2I^- + 2NO_2^- \longrightarrow 2NO + I_2 + 4OH^-$ **OR** $2H^+ + 2I^- + 2NO_2^- \longrightarrow 2NO + I_2 + 2OH^-$ **species** ✓ **balance** ✓	2	**IGNORE** state symbols **ALLOW** multiples **For species ONLY, IGNORE** any extra H_2O or e^- on either side of the equation **ALLOW** on LHS: $2HI + 2NO_2^-$ **OR** $2I^- + 2HNO_2$ **ALLOW** species and equation involving N_2H_2: $6H_2O + 8I^- + 2NO_2^- \longrightarrow N_2H_2 + 4I_2 + 10OH^-$ **OR** $6H^+ + 8I^- + 2NO_2^- \longrightarrow N_2H_2 + 4I_2 + 4OH^-$ **species** ✓ **balance** ✓
			Total	**8**	

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