RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

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

Mark Scheme for June 2012

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Annotations available in Scoris.

Annotation	Meaning
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore
	Not answered question
	Benefit of doubt not given
	Power of 10 error
	Omission mark
	Rounding error
	Error in number of significant figures
	Correct response

Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

The following questions should be annotated with ticks, crosses, etc. Annotations should be placed to clearly show where they apply within the body of the text (i.e. not in margins)

Question 1(b)(i), (c), (d); **Question 2(a)(iii);** **Question 3c(ii);**
Question 4a(i), (b)(iii); **Question 5(b);** **Question 7(b), (c).**

Question			Answer	Marks	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, product **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** reference to 'constituent elements' **IGNORE**: $Li^+(g) + F^-(g) \longrightarrow LiF(s)$ *Question asks for a definition, not an equation*

Question			Answer	Marks	Guidance
1	(b)	(i)	**1**. Mark **Line 1** first as below (right or wrong) **2**. Mark **Line 4** as below (right or wrong) **3**. Mark difference in species on **Line 1** and **Line 2** **MUST** match one of the enthalpy changes in the table: atomisation of Li(s) atomisation of ½F_2(g) first ionisation energy of Li(g) **4**. Repeat for differences on **Line 2** and **Line 3**		***ANNOTATIONS MUST BE USED*** --- **ALLOW** marks by **ECF** as follows: Follow order at top of Answer column
			4 $Li^+(g) + F(g) + e^-$ ✓ 3 $Li(g) + F(g)$ ✓ 2 $Li(g) + {}^1/_2F_2(g)$ ✓ 1 $Li(s) + {}^1/_2F_2(g)$ ✓ Correct species **and** state symbols required for all marks **IF** an electron has formed, it **MUST** be shown as e^- **OR** e	4	**ALLOW** atomisation of ½F_2(g) before atomisation of Li(s): 4 $Li^+(g) + F(g) + e^-$ ✓ 3 $Li(g) + F(g)$ ✓ 2 $Li(s) + F(g)$ ✓ 1 $Li(s) + {}^1/_2F_2(g)$ ✓ **ALLOW** ionisation of Li(g) before atomisation of ½F_2(g): 4 $Li^+(g) + F(g) + e^-$ ✓ 3 $Li^+(g) + e^- + {}^1/_2F_2(g)$ ✓ 2 $Li(g) + {}^1/_2F_2(g)$ ✓ 1 $Li(s) + {}^1/_2F_2(g)$ ✓ e^- required for marks involving **Line 3 AND Line 4** **Common errors** **Line 4**: Missing e^- and rest correct 3 marks **Line 1**: **IF** ½F_2(g) is **NOT** shown 2 max [**Line 4** and Li(s) → Li(g)] e.g., for F(g), F(s), F(l), F(aq), F_2(g) **DO NOT ALLOW** F*l* when first seen but credit subsequently

Question			Answer	Marks	Guidance
1	(b)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –1046 (kJ mol^{-1}) award 2 marks** --- (–616) = (+159) + (+79) + (+520) + (–328) + ΔH_{LE}(LiF) **OR** ΔH_{LE}(LiF) = (–616) –[(+159) + (+79) + (+520) + (–328)] ✓ = –616 – 430 = –1046 (kJ mol^{-1}) ✓	2	**IF** there is an alternative answer, check **the list below for marking of answers from common errors** --- **ALLOW** for **1 mark**: +1046 wrong sign –186 +430 instead of –430 +186 +616 instead of –616 –1006.5 (+79) ΔH_{at}(F) halved to +39.5 –1702 wrong sign for 328 Any other number: **CHECK** for **ECF** from 1st marking point for expressions with **ONE** error only e.g. one transcription error: e.g. +195 instead of +159
	(c)		$\Delta H < T\Delta S$ ***OR*** $\Delta H - T\Delta S < 0$ **OR** ΔH is more negative than $T\Delta S$ **OR** Negative value of ΔH is more significant than negative value of $T\Delta S$ ✓ ——————— **NOTE** **IGNORE** comments about ΔG	1	***ANNOTATIONS MUST BE USED*** **ALLOW** ‘exothermic’ for negative **ALLOW** a negative lattice energy value **ALLOW** ΔH is negative **AND** magnitude of ΔH > magnitude of $T\Delta S$ **IGNORE ONLY** magnitude of ΔH > magnitude of $T\Delta S$

Question			Answer	Marks	Guidance
1	(d)		For **FIRST TWO** marking points, assume that the following refer to 'ions', Mg^{2+}, etc. For 'ions', **ALLOW** 'atoms' For Mg^{2+}, Na^+, Cl^- and F^-, **ALLOW** symbols: Mg, Na, Cl and F **ALLOW** names: magnesium, sodium, chlorine, chloride, fluorine, fluoride *i.e.* **ALLOW** Mg has a smaller (atomic) radius For **THIRD** marking point, **IONS** must be used		**DO NOT ALLOW** molecules **ALLOW** F*l* for F
			Comparison of size of anions Chloride ion **OR** Cl^- is larger (than F^-) **OR** Cl^- has smaller charge density (than F^-) ✓ ***Comparison of size AND charge of cations*** Mg^{2+} is smaller (than Na^+) **AND** Mg^{2+} has a greater charge (than Na^+) ✓ ***Comparison of attraction between ions*** F^- has greater attraction for Na^+ / + ions **AND** Mg^{2+} has greater attraction for F^- / – ions ✓ **Quality of Written Communication**: --- Third mark needs to link ionic size and ionic charge with the attraction that results in lattice enthalpy	3	***ANNOTATIONS MUST BE USED*** --- **ORA** F^- is smaller **OR** F^- has a larger charge density ✓ **IGNORE** just Cl^- is large *comparison required* **ORA**: Na^+ is larger **AND** Na^+ has a smaller charge ✓ **IGNORE** just Mg^{2+} is small *comparison required* **ALLOW** 'greater charge density' for 'greater charge' but **NOT** for smaller size + ***AND*** – ***IONS must be used for this mark*** **IGNORE** greater attraction between **ions** in NaF **AND** MgF_2 + ***AND*** – *ions* ***OR*** *oppositely charged ions are required* **ASSUME** attraction to be electrostatic unless stated otherwise: e.g. **DO NOT ALLOW** nuclear attraction **ALLOW** pull for attraction **ALLOW** 'attracts with more force' for greater attraction **IGNORE** just 'greater force' (*could be repulsion*) **IGNORE** comparison of bond strength/energy to break bonds **IGNORE** comparisons of numbers of ions **IGNORE** responses in terms of packing
			Total	**12**	

Question			Answer	Marks	Guidance
2	(a)	(i)	(K_c =) $\frac{[CO_2]^2\ [N_2]}{[CO]^2\ [NO]^2}$ ✓	1	Square brackets required for **ALL** four concentrations
		(ii)	$dm^3\ mol^{-1}$ ✓	1	**ALLOW** $mol^{-1}\ dm^3$

Question			Answer	Marks	Guidance
2	(a)	(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 0.95 award **4 marks** --- ***Equilibrium amounts:*** $n(CO) = 0.46 - 0.20 = 0.26$ mol ✓ $n(CO_2) = 0.2(0)$ mol ✓ $n(N_2) = 0.1(0)$ mol ✓ **K_c calculation** **Must** use calculated equilibrium amounts **AND** 0.25 $(K_c =) \frac{0.20^2 \times 0.10}{0.26^2 \times 0.25^2} = 0.95$ (dm^3 mol^{-1}) ✓	4	***ANNOTATIONS MUST BE USED*** **IF** there is an alternative answer, apply **ECF** by checking working for intermediate marks --- **APPLY ECF** from incorrect starting $n(CO)$ By **ECF**, $n(N_2) = n(CO_2)/2$ For **all** parts, **ALLOW** numerical answers from 2 significant figures up to the calculator value **Correct numerical answer with no working scores 4 marks** **ALLOW** calculator value: 0.946745562 down to 0.95 (2SF), correctly rounded, e.g. 0.947 **IGNORE** units, even if incorrect --- **Common errors** 1.89 3 marks use of $n(N_2) = 0.2(0)$ mol $(K_c =) \frac{0.20^2 \times 0.20}{0.26^2 \times 0.25^2} = 1.893491124$ (dm^3 mol^{-1}) ✓ 1.29 3 marks 0.45 and 0.46 swapped over $n(CO) = 0.45 - 0.21 = 0.24$ mol ✓ $n(CO_2) = 0.21$ mol ✓ $n(N_2) = 0.105$ mol ✓ $(K_c =) \frac{0.21^2 \times 0.105}{0.24^2 \times 0.25^2} = 1.28625$ (dm^3 mol^{-1}) ✓ 1.024 3 marks 0.45 used twice $n(CO) = 0.45 - 0.20 = 0.25$ mol ✓ $n(CO_2) = 0.2(0)$ mol ✓ $n(N_2) = 0.1(0)$ mol ✓ $(K_c =) \frac{0.20^2 \times 0.10}{0.25^2 \times 0.25^2} = 1.024$ (dm^3 mol^{-1}) ✓ 1.185 3 marks 0.46 used twice $n(CO) = 0.46 - 0.21 = 0.25$ mol ✓ $n(CO_2) = 0.21$ mol ✓ $n(N_2) = 0.105$ mol ✓ $(K_c =) \frac{0.21^2 \times 0.105}{0.25^2 \times 0.25^2} = 1.185408$ (dm^3 mol^{-1}) ✓

Question			Answer	Marks	Guidance
2	(a)	(iv)	Mark **ECF** from **(iii)** **IF** K_c from **(iii)** < 1 equilibrium to left/towards reactants **OR** **IF** K_c from **(iii)** > 1 equilibrium to right/towards products ✓	1	**First look at K_c value for (iii) at bottom of cut** **----------** **ALLOW** favours reverse reaction For correct K_c value in **(iii)** of 0.95, **ALSO ALLOW** equilibrium position near to centre ✓
	(b)	**(i)**	K_c has decreased **AND** ΔH is negative **OR** (forward) reaction is exothermic ✓	1	Statement **AND** reason required for mark **ALLOW** for reason: reverse reaction is endothermic
		(ii)	**Effect of *T* and *P* on equilibrium** (increased) temperature shifts equilibrium to left **AND** (increased) pressure shifts equilibrium to right **AND** fewer (gaseous) moles on right-hand side ✓ **Overall effect on equilibrium** Difficult to predict relative contributions of two opposing factors ✓	2	**Reason ONLY** required for pressure Temperature and ΔH had been *required in (i)* **ALLOW** ratio of (gas) moles is 4:3 **ALLOW** opposing effects may not be the same size **ALLOW** effects could cancel each other out **ALLOW** effects oppose one another **DO NOT ALLOW** just 'it is difficult to predict equilibrium position' (*in question*) *For the 2nd mark, we are assessing the idea that we don't know which factor is dominant*
			Total	**10**	

Question			Answer	Marks	Guidance
3	(a)	(i)	$(K_a =)\ \dfrac{[H^+][CH_3(CH_2)_2COO^-]}{[CH_3(CH_2)_2COOH]}$ ✓	1	**ALLOW** $CH_3CH_2CH_2COOH$ **OR** C_3H_7COOH in expression **DO NOT ALLOW** use of HA and A^- in this part. **DO NOT ALLOW**: $\dfrac{[H^+][CH_3(CH_2)_2COO^-]}{[CH_3(CH_2)_2COOH]} = \dfrac{[H^+]^2}{[CH_3(CH_2)_2COOH]}$: **CON**
		(ii)	$pK_a = -\log K_a = 4.82$ ✓	1	**ALLOW** 4.82 up to calculator value of 4.821023053 **DO NOT ALLOW** 4.8
		(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 2.71 award **3 marks** --- $[H^+] = \sqrt{[K_a][CH_3(CH_2)_2COOH]}$ **OR** $\sqrt{1.51\times10^{-5}\times0.250}$ ✓ $[H^+] = 1.94 \times 10^{-3}$ (mol dm^{-3}) ✓ $pH = -\log[H^+] = 2.71$ ✓	3	**IF** alternative answer to more or fewer decimal places, check calculator value and working for 1st and 2nd marks --- **ALLOW** use of HA and A^- in this part **Calculator**: $1.942935923 \times 10^{-3}$ **ALLOW** use of calculated K_a value, either calculator value or rounded on script. pH **must** be to 2 decimal places **ALLOW ECF** from incorrectly calculated $[H^+]$ and pH **ONLY** when values for both K_a **AND** $[CH_3CH_2CH_2COOH]$ have been used, i.e. 1.5×10^{-5} **AND** 0.250. e.g.: pH = 5.42 2 marks $-\log(1.51 \times 10^{-5} \times 0.250)$ *No* √ pH = 2.11 2 marks $-\log(\sqrt{\dfrac{1.51\times10^{-5}}{0.250}})$ pH = 4.22 1 mark $-\log(\dfrac{1.51\times10^{-5}}{0.250})$ *No* √ **DO NOT ALLOW** just $-\log(1.51 \times 10^{-5}) = 4.82$ **NO MARKS**

Question			Answer	Marks	Guidance
3	(b)	(i)	$Mg + 2H^+ \longrightarrow Mg^{2+} + H_2$ ✓	1	**IGNORE** state symbols **ALLOW** $Mg + 2\ CH_3(CH_2)_2COOH \longrightarrow 2CH_3(CH_2)_2COO^- + Mg^{2+} + H_2$ **DO NOT ALLOW** on RHS: $(CH_3(CH_2)_2COO^-)_2Mg^{2+}$ ***Ions must be shown separately***
		(ii)	$CO_3^{2-} + 2H^+ \longrightarrow H_2O + CO_2$ ✓	1	**IGNORE** state symbols **ALLOW** $CO_3^{2-} + 2\ CH_3(CH_2)_2COOH \longrightarrow 2\ CH_3(CH_2)_2COO^- + H_2O + CO_2$ **ALLOW** as product H_2CO_3
	(c)	(i)	$CH_3(CH_2)_2COONa$ **OR** $CH_3(CH_2)_2COO^-$ forms **OR** $CH_3(CH_2)_2COOH + OH^- \rightarrow CH_3(CH_2)_2COO^- + H_2O$ ✓ $CH_3(CH_2)_2COOH$ is in excess **OR** acid is in excess **OR** some acid remains ✓	2	**ALLOW names throughout** **ALLOW** '**sodium** salt of **butanoic acid**' **ALLOW** $CH_3(CH_2)_2COOH + NaOH \rightarrow CH_3(CH_2)_2COONa + H_2O$ **DO NOT ALLOW** just 'forms a salt/conjugate base' i.e. identity of product is required

Question			Answer	Marks	Guidance
3	(c)	(ii)	**Moles (2 marks)** amount $CH_3(CH_2)_2COOH$ = 0.0100 (mol) ✓ amount $CH_3(CH_2)_2COO^-$ = 0.0025 (mol) ✓ **Concentration (1 mark)** $[CH_3(CH_2)_2COOH]$ = 0.100 mol dm^{-3} **AND** $[CH_3(CH_2)_2COO^-]$ = 0.025 mol dm^{-3} ✓ **$[H^+]$ and pH (2 marks)** $[H^+] = 1.51\times10^{-5} \times \frac{0.100}{0.025}$ = 6.04 x 10^{-5} (mol dm^{-3}) ✓ pH = –log 6.04 x 10^{-5} = 4.22 ✓ **pH to 2 DP**	2 1 2	***ANNOTATIONS MUST BE USED*** --- **ALLOW** HA and A^- throughout **Mark** by **ECF** throughout **ONLY** award final 2 marks via a correct pH calculation via $K_a \times \frac{[CH_3(CH_2)_2COOH]}{[CH_3(CH_2)_2COO^-]}$ using data derived from that in the question (i.e. not just made up values)
			ALLOW alternative approach based on Henderson–Hasselbalch equation for final 2 marks pH = $pK_a + \log\frac{0.025}{0.100}$ **OR** $pK_a - \log\frac{0.100}{0.025}$ ✓ pH = 4.82 – 0.60 = 4.22 ✓ **ALLOW** $-\log K_a$ for pK_a		
			TAKE CARE with awarding marks for pH = 4.22 There is a mark for the concentration stage. If this has been omitted, the ratio for the last 2 marks will be 0.0100 and 0.0025. **4 marks max.** **Common errors** **pH = 5.42** As above for 4.22 but with acid/base ratio inverted. Award 4 **OR** 3 marks **Award zero marks for:** 4.12 from no working or random values pH value from K_a square root approach (weak acid pH) pH value from K_w /10^{-14} approach (strong base pH)		**Common errors** **pH = 4.12** use of initial concentrations: 0.250 and 0.050 given in question. **Award last 3 marks for:** 0.250/2 **AND** 0.050/2 = 0.125 **AND** 0.025 ✓ $1.51\times10^{-5} \times \frac{0.125}{0.025}$ = 7.55 x 10^{-5} (mol dm^{-3}) ✓ pH = $-\log[H^+]$ = 4.12 ✓ **Award last 2 marks for:** $1.51\times10^{-5} \times \frac{0.250}{0.050}$ = 7.55 x 10^{-5} (mol dm^{-3}) ✓ pH = $-\log[H^+]$ = 4.12 ✓ **pH = 5.52** As above for 4.12 but with acid/base ratio inverted. Award 2 **OR** 1 marks as outlined for 4.12 above

Question			Answer	Marks	Guidance
3	(d)		$HCOOH + CH_3(CH_2)_2COOH \rightleftharpoons HCOO^- + CH_3(CH_2)_2COOH_2^+$ ✓ acid 1 base 2 base 1 acid 2 ✓ **CARE:** Both + and – charges are required for the products in the equilibrium **DO NOT AWARD** the 2nd mark from an equilibrium expression that omits either charge	2	State symbols **NOT** required **ALLOW** 1 **and** 2 labels the other way around. **ALLOW** 'just acid' and 'base' labels throughout if linked by lines so that it is clear what the acid-base pairs are For 1st mark, **DO NOT ALLOW** $COOH^-$ (i.e. H at end rather than start) but within 2nd mark **ALLOW** $COOH^-$ by **ECF** **IF** proton transfer is wrong way around then **ALLOW** 2nd mark for idea of acid–base pairs, i.e. $HCOOH + CH_3(CH_2)_2COOH \rightleftharpoons HCOOH_2^+ + CH_3(CH_2)_2COO^-$ × base 2 acid 1 acid 2 base 1 ✓ For H_2COOH^+ shown with wrong proton transfer, **DO NOT ALLOW** an **ECF** mark for acid–base pairs
			Total	**16**	

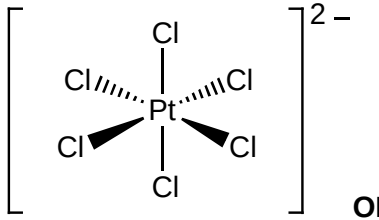
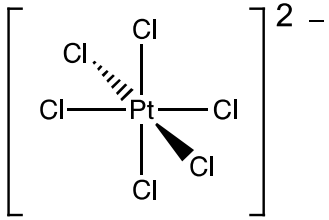
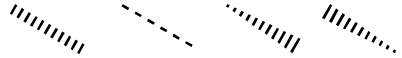
Question			Answer	Marks	Guidance
4	(a)	(i)	***initial rates data:*** **From Experiment 1** to **Experiment 2** **AND** $[NO_2]$ x 1.5, rate x 1.5 ✓ 1st order with respect to NO_2 ✓ **From Experiment 2** to **Experiment 3** **AND** $[O_3]$ is doubled, rate x 2 ✓ 1st order with respect to O_3 ✓ ***rate equation and rate constant:*** *rate* = $k[NO_2]\,[O_3]$ ✓ $k = \frac{rate}{[NO_2][O_3]}$ **OR** $\frac{4.80 \times 10^{-8}}{0.00150 \times 0.00250}$ ✓ = 0.0128 ✓ $dm^3\ mol^{-1}\ s^{-1}$ ✓	8	***ANNOTATIONS MUST BE USED*** **Quality of Written Communication**: --- Changes **MUST** be linked to Experiment numbers **in writing** (*Could be described unambiguously)* **IGNORE** annotations in the table --- For 2nd condition, **ALLOW** 'when $[NO_2]$ increases by half, rate increases by half **NOTE**: Orders may be identified within a rate equation **ALLOW**: working from any of the Experiments : All give the same calculated answer 0.0128 subsumes previous rearrangement mark **ALLOW**: $mol^{-1}\ dm^3\ s^{-1}$ ✓ **DO NOT ALLOW** 0.013 *over-rounding* --- **ALLOW ECF** from inverted *k* expression: $k = \frac{[NO_2][O_3]}{rate}$: *k* = 78.125 ✓ **ALLOW** 3 SF or more **NOTE** units must be from rate equation ✓

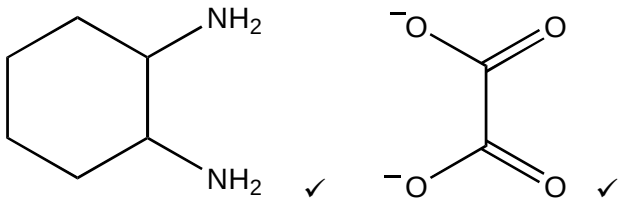
Question			Answer	Marks	Guidance
4	(a)	(ii)	**step 1**: $NO_2 + O_3$ LHS of step one ✓ $\longrightarrow NO_3 + O_2$ **step 2**: $NO_2 + NO_3 \longrightarrow N_2O_5$ rest of equations for step 1 **AND** step 2 ✓ **CHECK** that each equation is balanced **CARE:** **Step 1 AND Step 2** must add up to give overall equation In **Step 2**, **IGNORE** extra species shown on both sides, e.g. $NO_2 + NO_3 + O_2 \longrightarrow N_2O_5 + O_2$ **Step 2** can only gain a mark when **Step 1** is correct	2	State symbols **NOT** required For 'rest of equations', **ALLOW** other combinations that together give the overall equation, *e.g.*: $\longrightarrow NO_5$ $NO_2 + NO_5 \longrightarrow N_2O_5 + O_2$ *e.g.*: $\longrightarrow NO + 2O_2$ $NO + NO_2 + O_2 \longrightarrow N_2O_5$ **DO NOT ALLOW** use of algebraic species, e.g. X
	(b)	(i)	3 **gaseous** moles $\longrightarrow$ 2 **gaseous** moles ✓ Less randomness **OR** becomes more ordered ✓	2	**ALLOW** products have fewer **gaseous** moles **ORA** **ALLOW** 'molecules' instead of 'moles' **ALLOW** fewer ways of distributing energy **OR** fewer degrees of freedom **OR** fewer ways to arrange
		(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = –148 award **3 marks** --- $\Delta G = \Delta H - T\Delta S$ ✓ = –198 – (298 x –168/1000) ✓ = –148 (kJ mol^{-1}) ✓	3	**IF** there is an alternative answer, check calculator value and working for intermediate marks by **ECF** --- 2nd mark subsumes 1st mark for $\Delta G = \Delta H - T\Delta S$ **ALLOW** –148 to calculator value of –147.936 **ALLOW for 2 marks:** 49866 (kJ mol^{-1})*: not converting ΔS from J to kJ (no ÷ 1000)* –193.8 (kJ mol^{-1}) *use of 25 instead of 298*

Question			Answer	Marks	Guidance
4	(b)	(iii)	**CARE: responses involve changes of negative values** --- **Feasibility with increasing temperature** Reaction becomes less feasible/not feasible **AND** ΔG increases **OR** ΔG becomes less negative **OR** $\Delta G = 0$ **OR** $\Delta G > 0$ **OR** ΔG is positive **OR** ΔG approaches zero ✓ *****IF** a candidate makes a correct statement about the link between ΔG and feasibility, **IGNORE** an incorrect ΔH and $T\Delta S$ relationship **IF** there is no ΔG statement, then mark any ΔH and $T\Delta S$ relationship in line with the mark scheme --------------------- **Effect on $T\Delta S$** $T\Delta S$ becomes more negative **OR** $T\Delta S$ decreases **OR** $-T\Delta S$ increases **OR magnitude** of $T\Delta S$ increases ✓ ---	2	***ANNOTATIONS MUST BE USED*** --- As alternative for 'not feasible' **ALLOW 'not** spontaneous' **OR** a comment that implies 'reaction does not take place' **ALLOW for ΔG increases** $\Delta H = T\Delta S$ **OR** $\Delta H > T\Delta S$ **OR** $\Delta H - T\Delta S$ is positive **OR** $T\Delta S$ becomes more significant than ΔH **OR** $T\Delta S$ becomes the same as ΔH **OR** $T\Delta S$ becomes more negative than ΔH **NOTE Last statement will also score 2nd mark** ------------------- **DO NOT ALLOW** $T\Delta S$ increases --- ***APPROACH BASED ON TOTAL ENTROPY:*** **Feasibility with increasing temperature** Reaction becomes less feasible/not feasible **AND** $\Delta S - \Delta H/T$ **OR** ΔS_{total} decreases/ less positive **OR** ΔS outweighs/ is less significant than $\Delta H/T$ ✓ **Effect on $\Delta H/T$** $\Delta H/T$ is less negative **OR** $\Delta H/T$ increases **OR** $-\Delta H/T$ decreases **OR** magnitude of $\Delta H/T$ decreases ✓
			Total	**17**	

Question			Answer	Marks	Guidance
5	(a)		(A transition element) has (at least) one **ion** with a partially filled d sub-shell/ d orbital ✓ Fe **AND** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ ✓ Fe(II) / Fe^{2+} **AND** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ ✓ Fe(III) / Fe^{3+} **AND** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ ✓	4	**ALLOW** incomplete for partially filled **DO NOT ALLOW** d shell **ALLOW** 4s before 3d, i.e. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ **IF** candidate has used subscripts **OR** caps **OR** [Ar], **DO NOT ALLOW** when first seen but credit subsequently, i.e. $1s_2 2s_2 2p_6 3s_2 3p_6 3d_6 4s_2$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3D^6$ $[Ar]4s^2 3d^6$ For Fe^{2+} and Fe^{3+}, **ALLOW** $4s^0$ in electron configuration **IGNORE** electron configurations of elements other than Fe
	(b)		**EXAMPLES MUST REFER TO Cu^{2+} FOR ALL MARKS** **PRECIPITATION** **Reagent** NaOH(aq) **OR** KOH(aq) ✓ States not required **Transition metal product AND observation** $Cu(OH)_2$ **AND** blue precipitate/solid ✓ **Correct balanced equation** $Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$ ✓ state symbols **not** required **IF more than one example shown, mark example giving lower mark**	3	***ANNOTATIONS MUST BE USED*** **ALLOW** NaOH in equation if 'reagent' not given in description **ALLOW a small amount** of NH_3/ammonia **DO NOT ALLOW** concentrated NH_3 **DO NOT ALLOW** just OH^- **ALLOW** $Cu(OH)_2(H_2O)_4$ **ALLOW** any shade of blue **ALLOW** (s) as state symbol for ppt (may be in equation) **ALLOW** $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2(H_2O)_4 + 2H_2O$ For NH_3, also **ALLOW:** $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow Cu(OH)_2(H_2O)_4 + 2NH_4^+$ **ALLOW** full equation, e.g. $CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$ $CuCl_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaCl$

Question			Answer	Marks	Guidance
5	(b)		**LIGAND SUBSTITUTION – 2 likely** **Reagent** NH_3(aq)/ammonia ✓ State not required **Transition metal product AND observation** $[Cu(NH_3)_4(H_2O)_2]^{2+}$ **AND** deeper/darker blue (solution) ✓ **Correct balanced equation** $[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$ ✓ **OR** ---------- **Reagent** Concentrated HCl **OR** (dilute) HCl(aq) **OR** NaCl(aq) ✓ State not required **Transition metal product AND observation** $[CuCl_4]^{2-}$ **AND** yellow (solution) ✓ **Correct balanced equation** $[Cu(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CuCl_4]^{2-} + 6H_2O$ ✓	3	**IF more than one example shown, mark example giving lower mark** **ALLOW** NH_3 in equation if 'reagent' not given in description **DO NOT ALLOW** precipitate **ALLOW** royal blue, ultramarine blue or any blue colour that is clearly darker than for $[Cu(H_2O)_6]^{2+}$ ✓ ---------- **ALLOW** $CuCl_4^{2-}$ i.e. no brackets **ALLOW** any shades of yellow, e.g. yellow–green **DO NOT ALLOW** precipitate **ALLOW other correct ligand substitutions using same principles for marking as in two examples given**
	(c)	**(i)**	Pt oxidised from 0 +4 ✓ N reduced from +5 to +4 ✓	2	**ALLOW** 1 mark for Pt from 0 to +4 **AND** N from +5 to +4 i.e. oxidation and reduction not identified or wrong way round **DO NOT ALLOW** Pt is oxidised and N reduced with no evidence **DO NOT ALLOW** responses using other incorrect oxidation numbers **(CON)**

Question			Answer	Marks	Guidance
5	(c)	(ii)	$Pt + 6HCl + 4HNO_3 \longrightarrow H_2PtCl_6 + 4NO_2 + 4H_2O$ ✓✓	2	**1st mark for ALL species correct and no extras:** i.e: $Pt + HCl + HNO_3 \longrightarrow H_2PtCl_6 + NO_2 + H_2O$ **DO NOT ALLOW** charge on Pt, e.g. Pt^{2+} **2nd mark** for correct balancing **ALLOW** correct multiples
	(d)		 **OR**  **3-D Shape 1 mark** Correct 3-D diagram of Pt surrounded by 6Cl **ONLY** ✓ **Bond angle 1 mark** bond angle of 90º on diagram or stated ✓ **Charge 1 mark** 2– charge shown outside of brackets ✓	3	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' For bond into paper, **ALLOW**:  **IGNORE** charges on Pt and Cl for this mark The 2 marks for charge **AND** bond angle are **ONLY** available from a diagram showing Pt bonded to 6 Cl **ONLY** **ALLOW ONLY** if diagram has Pt surrounded by 6Cl **ONLY** **BUT** 3-D shape may not be correct **DO NOT ALLOW** if **ANY** charges shown on Pt or Cl within brackets

Question			Answer	Marks	Guidance
5	(e)	(i)	Donates **two** electron pairs to a **metal** (ion) ✓ forms **two** coordinate bonds ✓	2	**ALLOW** lone pairs for electron pairs **ALLOW** dative (covalent) bond for coordinate bond **ALLOW** 1 mark for a full definition of a ligand (without reference to 2: **i.e.** Donates **an** electron pair to a metal (ion) forming **a** coordinate bond ✓
		(ii)	 ✓ ✓	2	**ALLOW** displayed formulae '– charges' essential in $(COO^-)_2$ structure **DO NOT ALLOW** $–H_2N$
			Total	**21**	

Question			Answer	Marks	Guidance
6	(a)	(i)	complete circuit with **voltmeter** and **salt bridge** linking two half-cells ✓ Pt electrode in Fe^{3+}/Fe^{2+} half-cell with **same** concentrations ✓ Cr electrode in 1 mol dm^{-3} Cr^{3+} half-cell ✓	3	Salt bridge **MUST** be labelled **ALLOW** Fe^{2+} and Fe^{3+} with concentrations of 1 mol dm^{-3} **ALLOW** 1 M but **DO NOT ALLOW** 1 mol
		(ii)	$Cr + 3Fe^{3+} \longrightarrow Cr^{3+} + 3Fe^{2+}$ ✓	1	**ALLOW** $\rightleftharpoons$ sign **DO NOT ALLOW** if e^- shown uncancelled on both sides, e.g. $Cr + 3Fe^{3+} + 3e^- \longrightarrow Cr^{3+} + 3Fe^{2+} + 3e^-$
		(iii)	1.51 V ✓	1	**IGNORE** sign
	(b)		$Cr_2O_7^{2-}$ **AND** H^+ ✓	1	**ALLOW** acidified dichromate
	(c)		$Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3HCOOH(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3CO_2(l)$ ✓✓ State symbols **not** required	2	**1st mark for ALL species correct and no extras:** $Cr_2O_7^{2-}$, H^+, HCOOH, Cr^{3+}, H_2O **AND** CO_2 **NOTE**: H^+ may be shown on both sides **ALLOW** $\rightleftharpoons$ sign **2nd mark** for correct balancing with H^+ cancelled down
	(d)	(i)	$E^{\ominus}$ for chromium (redox system) is more negative/lower/less (than copper redox system) **ORA** ✓ chromium system shifts to the left / $Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$ **AND** copper system shifts to the right / $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ ✓	2	**ALLOW** E_{cell} is +1.08 V (sign required) **ALLOW** Cr loses electrons more readily/more easily oxidised **OR** Cr is a stronger reducing agent **OR** Cu loses electrons less readily **OR** Cu is a weaker reducing agent

Question			Answer	Marks	Guidance
6	(d)	(ii)	Cr reacts with H^+ ions/acid to form H_2 gas ✓	1	**ALLOW** equation: $2Cr + 6H^+ \longrightarrow 2Cr^{3+} + 3H_2$ (**ALLOW** multiples) **DO NOT ALLOW** just 'hydrogen forms', i.e. Cr, H^+/acid **AND** H_2 must **all** be included for the mark
	(e)	(i)	1.45 V ✓	1	**IGNORE** sign
		(ii)	**2 marks**, ✓ ✓, for **two** points from the following list: **1.** Methanoic acid is a liquid **AND** easier to store/transport **OR** hydrogen is a gas **AND** harder to store/transport **OR** hydrogen as a liquid is stored under pressure **2.** Hydrogen is explosive/more flammable **3.** HCOOH gives a greater cell potential/voltage **4**. HCOOH has more public/political acceptance than hydrogen as a fuel	2	**ASSUME** 'it' refers to HCOOH **DO NOT ALLOW** 'produces no CO_2' **IGNORE** comments about biomass and renewable *HCOOH and H_2 are **both** manufactured from natural gas*
			Total	**14**	

Question			Answer	Marks	Guidance
7	(a)		$MnO_2 + 4OH^- \longrightarrow MnO_4^{2-} + 2H_2O$ **+ 2e⁻** ✓ $3H_2O + ClO_3^-$ **+ 6e⁻** ✓ $\longrightarrow 6OH^- + Cl^-$	2	**ALLOW** 'e': i.e. – sign not required
	(b)		**Role of CO_2** CO_2 reacts with H_2O forming an acid **OR** carbonic acid/H_2CO_3 forms **OR** CO_2 is acidic ✓ **Equation involving OH^-** $H_2CO_3 + OH^- \longrightarrow H_2O + HCO_3^-$ **OR** $H_2CO_3 + 2OH^- \longrightarrow 2H_2O + CO_3^{2-}$ **OR** $CO_2 + OH^- \longrightarrow CO_3^{2-} + H^+$ **OR** $CO_2 + OH^- \longrightarrow HCO_3^-$ **OR** $CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O$ **OR** $H^+ + OH^- \longrightarrow H_2O$ ✓ **Effect on equilibrium with reason** equilibrium shifts to right **AND** to restore OH^- ✓	3	***ANNOTATIONS MUST BE USED*** --- **ALLOW** equation: $CO_2 + H_2O \longrightarrow H_2CO_3$ **OR** $CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$ **OR** $CO_2 + H_2O \longrightarrow 2H^+ + CO_3^{2-}$ **ALLOW** for 'restores OH^-' the following: 'makes more OH^-', 'OH^- has been used up' **DO NOT ALLOW** just 'equilibrium shifts to right'

Question			Answer	Marks	Guidance
7	(c)		**FOLLOW through stages to mark** --- **Moles in titration** $n(KMnO_4) = 0.0200 \times \frac{26.2}{1000} = 5.24 \times 10^{-4}$ mol ✓ $n(SO_3^{2-}) = 1.31 \times 10^{-3}$ mol ✓ **Scaling** $n(SO_3^{2-})$ in original 100 cm^3 $= 4 \times 1.31 \times 10^{-3} = 5.24 \times 10^{-3}$ mol ✓ **Mass** Mass of Na_2SO_3 in sample $= 126.1 \times 5.24 \times 10^{-3}$ g = 0.660764 g ✓ **Percentage** % $Na_2SO_3 = \frac{0.660764}{0.720} \times 100 = 91.8\%$ ✓	5	***ANNOTATIONS MUST BE USED*** ***AT LEAST 3 SF for each step*** --- **ECF** 2.5 x answer above **ECF** 4 x answer above **ECF** 126.1 x answer above **ALLOW** 0.661 g up to calculator value **ECF** $\frac{\text{calculated mass above}}{0.720} \times 100$ **ALLOW** 91.8% (1 DP) up to calculator value of 91.77277778 i.e. **DO NOT ALLOW** 92%
			ALLOW alternative approach based on theoretical content of Na_2SO_3 for last 2 marks **Theoretical amount, in moles, of Na_2SO_3 in sample** $n(Na_2SO_3) = \frac{0.720}{126.1} = 5.71 \times 10^{-3}$ mol ✓ **Percentage** % $Na_2SO_3 = \frac{5.24 \times 10^{-3}}{5.71 \times 10^{-3}} \times 100 = 91.8\%$ ✓		**COMMON ERRORS**: 36.8(1)% 4 marks no 2.5 factor 22.9(4)% 4 marks no scaling by 4 9.18% 3 marks no 2.5 and no x 4 Watch for random ECF %s for % from incorrect $M(Na_2SO_3)$, e.g. use of $M(SO_3^{2-})$ = 80.1 giving 58.3%
			Total	**10**	

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