

Chemistry A

Advanced GCE

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

Mark Scheme for June 2012

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All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

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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 4a(i), (b)(iii);**

**Question 2(a)(iii);
Question 5(b);**

**Question 3c(ii);
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: $\text{Li}^+(\text{g}) + \text{F}^-(\text{g}) \longrightarrow \text{LiF}(\text{s})$ <i>Question asks for a definition, not an equation</i> |

| Question | Answer | Marks | Guidance |
|----------|--|-------|---|
| 1 | <p>(b) (i)</p> <p>1. Mark Line 1 first as below (right or wrong)</p> <p>2. Mark Line 4 as below (right or wrong)</p> <p>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 $\frac{1}{2}\text{F}_2(\text{g})$ first ionisation energy of Li(g)</p> <p>4. Repeat for differences on Line 2 and Line 3</p> <hr/> <p>4 $\text{Li}^+(\text{g}) + \text{F}(\text{g}) + \text{e}^-$ ✓</p> <p>3 $\text{Li}(\text{g}) + \text{F}(\text{g})$</p> <p>2 $\text{Li}(\text{g}) + \frac{1}{2}\text{F}_2(\text{g})$</p> <p>1 $\text{Li}(\text{s}) + \frac{1}{2}\text{F}_2(\text{g})$ ✓</p> <p>Correct species and state symbols required for all marks IF an electron has formed, it MUST be shown as e^- OR e</p> | | <p>ANNOTATIONS MUST BE USED</p> <p>-----</p> <p>ALLOW marks by ECF as follows: Follow order at top of Answer column</p> <hr/> <p>ALLOW atomisation of $\frac{1}{2}\text{F}_2(\text{g})$ before atomisation of Li(s):</p> <p>ALLOW ionisation of Li(g) before atomisation of $\frac{1}{2}\text{F}_2(\text{g})$:</p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> <p>4 $\text{Li}^+(\text{g}) + \text{F}(\text{g}) + \text{e}^-$ ✓</p> <p>3 $\text{Li}(\text{g}) + \text{F}(\text{g})$</p> <p>2 $\text{Li}(\text{s}) + \text{F}(\text{g})$</p> <p>1 $\text{Li}(\text{s}) + \frac{1}{2}\text{F}_2(\text{g})$ ✓</p> </div> <div style="text-align: center;"> <p>4 $\text{Li}^+(\text{g}) + \text{F}(\text{g}) + \text{e}^-$ ✓</p> <p>3 $\text{Li}^+(\text{g}) + \text{e}^- + \frac{1}{2}\text{F}_2(\text{g})$</p> <p>2 $\text{Li}(\text{g}) + \frac{1}{2}\text{F}_2(\text{g})$</p> <p>1 $\text{Li}(\text{s}) + \frac{1}{2}\text{F}_2(\text{g})$ ✓</p> <p>e^- required for marks involving Line 3 AND Line 4</p> </div> </div> <p>Common errors</p> <p>Line 4: Missing e^- and rest correct 3 marks</p> <p>Line 1: IF $\frac{1}{2}\text{F}_2(\text{g})$ is NOT shown 2 max [Line 4 and $\text{Li}(\text{s}) \rightarrow \text{Li}(\text{g})$] e.g., for F(g), F(s), F(l), F(aq), $\text{F}_2(\text{g})$</p> <p>DO NOT ALLOW F/ when first seen but credit subsequently</p> |

| Question | Answer | Marks | Guidance |
|------------|---|-------|--|
| 1 (b) (ii) | <p>FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = $-1046 \text{ (kJ mol}^{-1}\text{)}$ award 2 marks</p> <hr/> <p>$(-616) = (+159) + (+79) + (+520) + (-328) + \Delta H_{\text{LE}}(\text{LiF})$ OR $\Delta H_{\text{LE}}(\text{LiF}) = (-616) - [(+159) + (+79) + (+520) + (-328)]$ \checkmark</p> <p>$= -616 - 430$ $= -1046 \text{ (kJ mol}^{-1}\text{)} \checkmark$</p> | 2 | <p>IF there is an alternative answer, check the list below for marking of answers from common errors</p> <hr/> <p>ALLOW for 1 mark:</p> <p>+1046 wrong sign -186 +430 instead of -430 +186 +616 instead of -616 -1006.5 (+79) $\Delta H_{\text{at}}(\text{F})$ halved to +39.5 -1702 wrong sign for 328</p> <p>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</p> |
| (c) | <p>$\Delta H < T\Delta S$ 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 $T\Delta S$ \checkmark</p> <hr/> <p>NOTE IGNORE comments about ΔG</p> | 1 | <p>ANNOTATIONS MUST BE USED</p> <p>ALLOW 'exothermic' for negative ALLOW a negative lattice energy value</p> <p>ALLOW ΔH is negative AND magnitude of $\Delta H >$ magnitude of $T\Delta S$</p> <p>IGNORE ONLY magnitude of $\Delta H >$ magnitude of $T\Delta S$</p> |

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

| Question | | | Answer | Marks | Guidance |
|----------|-----|------|--|-------|---|
| 2 | (a) | (i) | $(K_c =) \frac{[\text{CO}_2]^2 [\text{N}_2]}{[\text{CO}]^2 [\text{NO}]^2} \checkmark$ | 1 | Square brackets required for ALL four concentrations |
| | | (ii) | $\text{dm}^3 \text{ mol}^{-1} \checkmark$ | 1 | ALLOW $\text{mol}^{-1} \text{ dm}^3$ |

| Question | Answer | Marks | Guidance |
|----------|-----------|-------|---|
| 2 | (a) (iii) | 4 | <p>ANNOTATIONS MUST BE USED IF there is an alternative answer, apply ECF by checking working for intermediate marks</p> <hr/> <p>APPLY ECF from incorrect starting $n(\text{CO})$ By ECF, $n(\text{N}_2) = n(\text{CO}_2)/2$</p> <p>For all parts, ALLOW numerical answers from 2 significant figures up to the calculator value</p> <p>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</p> <hr/> <p>Common errors</p> <p>1.89 3 marks use of $n(\text{N}_2) = 0.2(0)$ mol</p> $(K_c =) \frac{0.20^2 \times 0.20}{0.26^2 \times 0.25^2} = 1.893491124 \text{ (dm}^3 \text{ mol}^{-1}) \checkmark$ <hr/> <p>1.29 3 marks 0.45 and 0.46 swapped over</p> $n(\text{CO}) = 0.45 - 0.21 = 0.24 \text{ mol } \checkmark$ $n(\text{CO}_2) = 0.21 \text{ mol } \checkmark$ $n(\text{N}_2) = 0.105 \text{ mol } \checkmark$ $(K_c =) \frac{0.21^2 \times 0.105}{0.24^2 \times 0.25^2} = 1.28625 \text{ (dm}^3 \text{ mol}^{-1}) \checkmark$ <hr/> <p>1.0243 marks 0.45 used twice</p> $n(\text{CO}) = 0.45 - 0.20 = 0.25 \text{ mol } \checkmark$ $n(\text{CO}_2) = 0.2(0) \text{ mol } \checkmark$ $n(\text{N}_2) = 0.1(0) \text{ mol } \checkmark$ $(K_c =) \frac{0.20^2 \times 0.10}{0.25^2 \times 0.25^2} = 1.024 \text{ (dm}^3 \text{ mol}^{-1}) \checkmark$ <hr/> <p>1.1853 marks 0.46 used twice</p> $n(\text{CO}) = 0.46 - 0.21 = 0.25 \text{ mol } \checkmark$ $n(\text{CO}_2) = 0.21 \text{ mol } \checkmark$ $n(\text{N}_2) = 0.105 \text{ mol } \checkmark$ $(K_c =) \frac{0.21^2 \times 0.105}{0.25^2 \times 0.25^2} = 1.185408 \text{ (dm}^3 \text{ mol}^{-1}) \checkmark$ |

| 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 <i>required in (i)</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' (<i>in question</i>) <i>For the 2nd mark, we are assessing the idea that we don't know which factor is dominant</i> |
| Total | | | 10 | |

| Question | Answer | Marks | Guidance |
|-----------|---|-------|---|
| 3 (a) (i) | $(K_a =) \frac{[H^+][CH_3(CH_2)_2COO^-]}{[CH_3(CH_2)_2COOH]}$ ✓ | 1 | <p>ALLOW CH₃CH₂CH₂COOH OR C₃H₇COOH in expression</p> <p>DO NOT ALLOW use of HA and A⁻ in this part.</p> <p>DO NOT ALLOW:</p> $\frac{[H^+][CH_3(CH_2)_2COO^-]}{[CH_3(CH_2)_2COOH]} = \frac{[H^+]^2}{[CH_3(CH_2)_2COOH]}: \text{CON}$ |
| | (ii) $pK_a = -\log K_a = 4.82$ ✓ | 1 | <p>ALLOW 4.82 up to calculator value of 4.821023053</p> <p>DO NOT ALLOW 4.8</p> |
| | <p>(iii) FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 2.71 award 3 marks</p> <p>-----</p> $[H^+] = \sqrt{K_a}[CH_3(CH_2)_2COOH] \text{ OR } \sqrt{1.51 \times 10^{-5} \times 0.250}$ <p>✓</p> $[H^+] = 1.94 \times 10^{-3} \text{ (mol dm}^{-3}\text{)} \text{ ✓}$ $pH = -\log[H^+] = 2.71 \text{ ✓}$ | 3 | <p>IF alternative answer to more or fewer decimal places, check calculator value and working for 1st and 2nd marks</p> <p>-----</p> <p>ALLOW use of HA and A⁻ in this part</p> <p>Calculator: 1.942935923 x 10⁻³</p> <p>ALLOW use of calculated K_a value, either calculator value or rounded on script.</p> <p>pH must be to 2 decimal places</p> <p>ALLOW ECF from incorrectly calculated [H⁺] and pH ONLY when values for both K_a AND [CH₃CH₂CH₂COOH] have been used, i.e. 1.5 x 10⁻⁵ AND 0.250. e.g.:</p> <p>pH = 5.42 2 marks $-\log(1.51 \times 10^{-5} \times 0.250)$ No ✓</p> <p>pH = 2.11 2 marks $-\log\left(\sqrt{\frac{1.51 \times 10^{-5}}{0.250}}\right)$</p> <p>pH = 4.22 1 mark $-\log\left(\frac{1.51 \times 10^{-5}}{0.250}\right)$ No ✓</p> <p>DO NOT ALLOW just $-\log(1.51 \times 10^{-5}) = 4.82$ NO MARKS</p> |

| Question | | | Answer | Marks | Guidance |
|----------|-----|------|--|-------|--|
| 3 | (b) | (i) | $\text{Mg} + 2\text{H}^+ \longrightarrow \text{Mg}^{2+} + \text{H}_2 \checkmark$ | 1 | IGNORE state symbols ALLOW $\text{Mg} + 2 \text{CH}_3(\text{CH}_2)_2\text{COOH} \longrightarrow$ $2\text{CH}_3(\text{CH}_2)_2\text{COO}^- + \text{Mg}^{2+} + \text{H}_2$ DO NOT ALLOW on RHS: $(\text{CH}_3(\text{CH}_2)_2\text{COO}^-)_2\text{Mg}^{2+}$ <i>ions must be shown separately</i> |
| | | (ii) | $\text{CO}_3^{2-} + 2\text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{CO}_2 \checkmark$ | 1 | IGNORE state symbols ALLOW $\text{CO}_3^{2-} + 2 \text{CH}_3(\text{CH}_2)_2\text{COOH} \longrightarrow$ $2 \text{CH}_3(\text{CH}_2)_2\text{COO}^- + \text{H}_2\text{O} + \text{CO}_2$ ALLOW as product H_2CO_3 |
| | (c) | (i) | $\text{CH}_3(\text{CH}_2)_2\text{COONa}$ OR $\text{CH}_3(\text{CH}_2)_2\text{COO}^-$ forms OR $\text{CH}_3(\text{CH}_2)_2\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3(\text{CH}_2)_2\text{COO}^- + \text{H}_2\text{O} \checkmark$ $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ is in excess OR acid is in excess OR some acid remains \checkmark | 2 | ALLOW names throughout ALLOW 'sodium salt of butanoic acid' ALLOW $\text{CH}_3(\text{CH}_2)_2\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3(\text{CH}_2)_2\text{COONa} + \text{H}_2\text{O}$ DO NOT ALLOW just 'forms a salt/conjugate base' i.e. identity of product is required |

| Question | Answer | Marks | Guidance |
|----------|----------|---|---|
| 3 | (c) (ii) | <p>Moles (2 marks) amount CH₃(CH₂)₂COOH = 0.0100 (mol) ✓ amount CH₃(CH₂)₂COO⁻ = 0.0025 (mol) ✓</p> <p>Concentration (1 mark) [CH₃(CH₂)₂COOH] = 0.100 mol dm⁻³ AND [CH₃(CH₂)₂COO⁻] = 0.025 mol dm⁻³ ✓</p> <p>[H⁺] and pH (2 marks) $[H^+] = 1.51 \times 10^{-5} \times \frac{0.100}{0.025} = 6.04 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$ ✓ pH = -log 6.04 × 10⁻⁵ = 4.22 ✓ pH to 2 DP</p> | <p>ANNOTATIONS MUST BE USED</p> <p>-----</p> <p>ALLOW HA and A⁻ throughout</p> <p>Mark by ECF throughout</p> <p>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)</p> |
| | | <p>ALLOW alternative approach based on Henderson–Hasselbalch equation for final 2 marks</p> <p>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 –logK_a for pK_a</p> | |
| | | <p>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.</p> <p>Common errors pH = 5.42 As above for 4.22 but with acid/base ratio inverted. Award 4 OR 3 marks</p> <p>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)</p> | <p>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 ✓ $1.51 \times 10^{-5} \times \frac{0.125}{0.025} = 7.55 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$ ✓ pH = -log[H⁺] = 4.12 ✓</p> <p>Award last 2 marks for: $1.51 \times 10^{-5} \times \frac{0.250}{0.050} = 7.55 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$ ✓ pH = -log[H⁺] = 4.12 ✓</p> <p>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</p> |

| Question | | Answer | Marks | Guidance |
|--------------|-----|---|-----------|---|
| 3 | (d) | $\text{HCOOH} + \text{CH}_3(\text{CH}_2)_2\text{COOH} \rightleftharpoons \text{HCOO}^- + \text{CH}_3(\text{CH}_2)_2\text{COOH}_2^+$ <p>✓</p> <p style="text-align: center;">acid 1 base 2 base 1 acid 2 ✓</p> <p>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</p> | 2 | <p>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</p> <p>For 1st mark, DO NOT ALLOW COOH^- (i.e. H at end rather than start) but within 2nd mark ALLOW COOH^- by ECF</p> <p>IF proton transfer is wrong way around then ALLOW 2nd mark for idea of acid–base pairs, i.e.</p> $\text{HCOOH} + \text{CH}_3(\text{CH}_2)_2\text{COOH} \rightleftharpoons \text{HCOOH}_2^+ + \text{CH}_3(\text{CH}_2)_2\text{COO}^- *$ <p style="text-align: center;">base 2 acid 1 acid 2 base 1 ✓</p> <p>For H_2COOH^+ shown with wrong proton transfer, DO NOT ALLOW an ECF mark for acid–base pairs</p> |
| Total | | | 16 | |

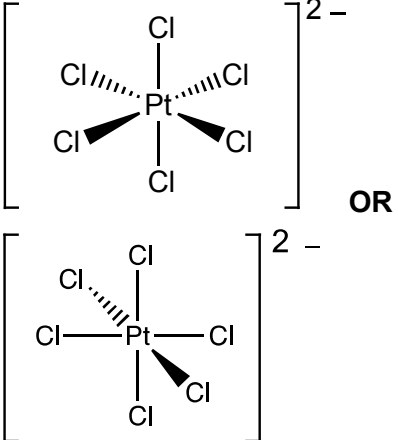
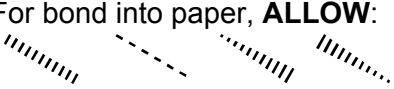
| Question | Answer | Marks | Guidance |
|----------|---------|-------|--|
| 4 | (a) (i) | | <p>ANNOTATIONS MUST BE USED</p> <p>Quality of Written Communication:</p> <hr/> <p>Changes MUST be linked to Experiment numbers in writing (<i>Could be described unambiguously</i>)</p> <p>IGNORE annotations in the table</p> <hr/> <p>For 2nd condition, ALLOW 'when [NO₂] increases by half, rate increases by half'</p> <p>NOTE: Orders may be identified within a rate equation</p> <p>ALLOW: working from any of the Experiments : All give the same calculated answer 0.0128 subsumes previous rearrangement mark</p> <p>ALLOW: mol⁻¹ dm³ s⁻¹ ✓ DO NOT ALLOW 0.013 <i>over-rounding</i></p> <hr/> <p>ALLOW ECF from inverted k expression: $k = \frac{[\text{NO}_2][\text{O}_3]}{\text{rate}}$ $k = 78.125$ ✓ ALLOW 3 SF or more NOTE units must be from rate equation ✓</p> |

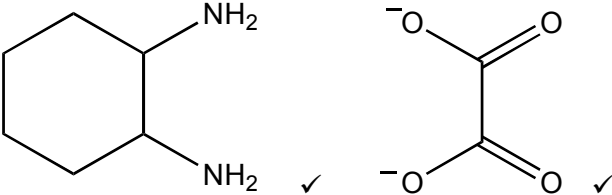
| Question | Answer | Marks | Guidance |
|----------|----------|---|--|
| 4 | (a) (ii) | <p>step 1: $\text{NO}_2 + \text{O}_3$ LHS of step one ✓</p> $\longrightarrow \text{NO}_3 + \text{O}_2$ <p>step 2: $\text{NO}_2 + \text{NO}_3 \longrightarrow \text{N}_2\text{O}_5$ rest of equations for step 1 AND step 2 ✓</p> <p>CHECK that each equation is balanced</p> <p>CARE: Step 1 AND Step 2 must add up to give overall equation</p> <p>In Step 2, IGNORE extra species shown on both sides, e.g. $\text{NO}_2 + \text{NO}_3 + \text{O}_2 \longrightarrow \text{N}_2\text{O}_5 + \text{O}_2$</p> <p>Step 2 can only gain a mark when Step 1 is correct</p> | <p>2</p> <p>State symbols NOT required</p> <p>For 'rest of equations', ALLOW other combinations that together give the overall equation, e.g.: $\text{NO}_2 + \text{NO}_5 \longrightarrow \text{N}_2\text{O}_5 + \text{O}_2$ e.g.: $\text{NO} + \text{NO}_2 + \text{O}_2 \longrightarrow \text{N}_2\text{O}_5$</p> <p>DO NOT ALLOW use of algebraic species, e.g. X</p> |
| | (b) (i) | <p>3 gaseous moles \longrightarrow 2 gaseous moles ✓</p> <p>Less randomness OR becomes more ordered ✓</p> | <p>2</p> <p>ALLOW products have fewer gaseous moles ORA ALLOW 'molecules' instead of 'moles'</p> <p>ALLOW fewer ways of distributing energy OR fewer degrees of freedom OR fewer ways to arrange</p> |
| | (ii) | <p>FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = -148 award 3 marks</p> <p>-----</p> $\Delta G = \Delta H - T\Delta S \checkmark$ $= -198 - (298 \times -168/1000) \checkmark$ $= -148 \text{ (kJ mol}^{-1}\text{)} \checkmark$ | <p>3</p> <p>IF there is an alternative answer, check calculator value and working for intermediate marks by ECF</p> <p>-----</p> <p>2nd mark subsumes 1st mark for $\Delta G = \Delta H - T\Delta S$</p> <p>ALLOW -148 to calculator value of -147.936 ALLOW for 2 marks: 49866 (kJ mol⁻¹): <i>not converting ΔS from J to kJ (no ÷ 1000)</i> -193.8 (kJ mol⁻¹) <i>use of 25 instead of 298</i></p> |

| Question | Answer | Marks | Guidance |
|----------|-----------|---|---|
| 4 | (b) (iii) | <p>CARE: responses involve changes of negative values</p> <hr/> <p>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 ✓</p> <p>***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</p> <hr/> <p>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 ✓</p> <hr/> | <p>ANNOTATIONS MUST BE USED</p> <hr/> <p>As alternative for 'not feasible' ALLOW 'not spontaneous' OR a comment that implies 'reaction does not take place'</p> <p>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</p> <hr/> <p>DO NOT ALLOW $T\Delta S$ increases</p> <hr/> <p>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 $\Delta H/T$ ✓</p> <p>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 ✓</p> |
| | | Total | 17 |

| Question | Answer | Marks | Guidance |
|----------|--|-------|--|
| 5 (a) | <p>(A transition element) has (at least) one ion with a partially filled d sub-shell/ d orbital ✓</p> <p>Fe AND $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ ✓</p> <p>Fe(II) / Fe^{2+} AND $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ ✓</p> <p>Fe(III) / Fe^{3+} AND $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ ✓</p> | 4 | <p>ALLOW incomplete for partially filled DO NOT ALLOW d shell</p> <p>ALLOW 4s before 3d, i.e. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$</p> <p>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]4s²3d⁶</p> <p>For Fe^{2+} and Fe^{3+}, ALLOW 4s⁰ in electron configuration</p> <p>IGNORE electron configurations of elements other than Fe</p> |
| (b) | <p>EXAMPLES MUST REFER TO Cu^{2+} FOR ALL MARKS</p> <hr/> <p>PRECIPITATION Reagent NaOH(aq) OR KOH(aq) ✓ States not required</p> <p>Transition metal product AND observation $Cu(OH)_2$ AND blue precipitate/solid ✓</p> <p>Correct balanced equation $Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$ ✓ state symbols not required</p> <p>IF more than one example shown, mark example giving lower mark</p> | 3 | <p>ANNOTATIONS MUST BE USED</p> <hr/> <p>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^-</p> <p>ALLOW $Cu(OH)_2(H_2O)_4$ ALLOW any shade of blue ALLOW (s) as state symbol for ppt (may be in equation)</p> <p>ALLOW $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2(H_2O)_4 + 2H_2O$ For NH_3, also ALLOW: $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow Cu(OH)_2(H_2O)_4 + 2NH_4^+$</p> <p>ALLOW full equation, e.g. $CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$ $CuCl_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaCl$</p> |

| Question | Answer | Marks | Guidance |
|----------|--|-------|--|
| 5 (b) | <p>LIGAND SUBSTITUTION – 2 likely</p> <p>Reagent $\text{NH}_3(\text{aq})$/ammonia ✓ State not required</p> <p>Transition metal product AND observation $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ AND deeper/darker blue (solution) ✓</p> <p>Correct balanced equation $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 4\text{H}_2\text{O}$ ✓</p> <p>OR -----</p> <p>Reagent Concentrated HCl OR (dilute) HCl(aq) OR NaCl(aq) ✓ State not required</p> <p>Transition metal product AND observation $[\text{CuCl}_4]^{2-}$ AND yellow (solution) ✓</p> <p>Correct balanced equation $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \longrightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$ ✓</p> | 3 | <p>IF more than one example shown, mark example giving lower mark</p> <p>ALLOW NH_3 in equation if 'reagent' not given in description</p> <p>DO NOT ALLOW precipitate ALLOW royal blue, ultramarine blue or any blue colour that is clearly darker than for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ✓</p> <hr/> <p>ALLOW CuCl_4^{2-} i.e. no brackets ALLOW any shades of yellow, e.g. yellow–green DO NOT ALLOW precipitate</p> <p>ALLOW other correct ligand substitutions using same principles for marking as in two examples given</p> |
| (c) | (i) Pt oxidised from 0 to +4 ✓ N reduced from +5 to +4 ✓ | 2 | <p>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</p> <p>DO NOT ALLOW Pt is oxidised and N reduced with no evidence</p> <p>DO NOT ALLOW responses using other incorrect oxidation numbers (CON)</p> |

| Question | Answer | Marks | Guidance |
|----------|----------|--|--|
| 5 | (c) (ii) | $\text{Pt} + 6\text{HCl} + 4\text{HNO}_3 \longrightarrow \text{H}_2\text{PtCl}_6 + 4\text{NO}_2 + 4\text{H}_2\text{O} \checkmark\checkmark$ | <p>2</p> <p>1st mark for ALL species correct and no extras: i.e: $\text{Pt} + \text{HCl} + \text{HNO}_3 \longrightarrow \text{H}_2\text{PtCl}_6 + \text{NO}_2 + \text{H}_2\text{O}$ DO NOT ALLOW charge on Pt, e.g. Pt^{2+}</p> <p>2nd mark for correct balancing ALLOW correct multiples</p> |
| | (d) |  <p>3-D Shape 1 mark Correct 3-D diagram of Pt surrounded by 6Cl ONLY ✓</p> <p>Bond angle 1 mark bond angle of 90° on diagram or stated ✓</p> <p>Charge 1 mark $2-$ charge shown outside of brackets ✓</p> | <p>3</p> <p>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'</p> <p>For bond into paper, ALLOW:</p>  <p>IGNORE charges on Pt and Cl for this mark</p> <p>The 2 marks for charge AND bond angle are ONLY available from a diagram showing Pt bonded to 6Cl ONLY</p> <p>ALLOW ONLY if diagram has Pt surrounded by 6Cl ONLY BUT 3-D shape may not be correct</p> <p>DO NOT ALLOW if ANY charges shown on Pt or Cl within brackets</p> |

| 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 ₂ N |
| 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⁺ → Cr ³⁺ + 3Fe ²⁺ ✓ | | 1 | ALLOW ⇌ sign DO NOT ALLOW if e ⁻ shown uncanceled on both sides, e.g. Cr + 3Fe ³⁺ + 3e ⁻ → Cr ³⁺ + 3Fe ²⁺ + 3e ⁻ |
| | | (iii) | 1.51 V ✓ | | 1 | IGNORE sign |
| | (b) | | Cr ₂ O ₇ ²⁻ AND H ⁺ ✓ | 1 | ALLOW acidified dichromate | |
| | (c) | | Cr ₂ O ₇ ²⁻ (aq) + 8H ⁺ (aq) + 3HCOOH(aq) → 2Cr ³⁺ (aq) + 7H ₂ O(l) + 3CO ₂ (l) ✓✓ State symbols not required | 2 | 1st mark for ALL species correct and no extras: Cr ₂ O ₇ ²⁻ , H ⁺ , HCOOH, Cr ³⁺ , H ₂ O AND CO ₂ NOTE: H ⁺ may be shown on both sides ALLOW ⇌ sign 2nd mark for correct balancing with H ⁺ cancelled down | |
| | (d) | (i) | E ^o for chromium (redox system) is more negative/lower/less (than copper redox system) ORA ✓ chromium system shifts to the left / Cr(s) → Cr ³⁺ (aq) + 3e ⁻ AND copper system shifts to the right / Cu ²⁺ (aq) + 2e ⁻ → 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: $2\text{Cr} + 6\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{H}_2$ (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) | <p>2 marks, ✓ ✓, for two points from the following list:</p> <ol style="list-style-type: none"> 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 Hydrogen is explosive/more flammable HCOOH gives a greater cell potential/voltage HCOOH has more public/political acceptance than hydrogen as a fuel | 2 | <p>ASSUME 'it' refers to HCOOH</p> <p>DO NOT ALLOW 'produces no CO₂'</p> <p>IGNORE comments about biomass and renewable <i>HCOOH and H₂ are both manufactured from natural gas</i></p> |
| | | | Total | 14 | |

| Question | Answer | Marks | Guidance |
|----------|---|-------|---|
| 7 (a) | $\text{MnO}_2 + 4\text{OH}^- \longrightarrow \text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \checkmark$ $3\text{H}_2\text{O} + \text{ClO}_3^- + 6\text{e}^- \checkmark \longrightarrow 6\text{OH}^- + \text{Cl}^-$ | 2 | ALLOW 'e': i.e. – sign not required |
| (b) | <p>Role of CO₂ CO₂ reacts with H₂O forming an acid OR carbonic acid/H₂CO₃ forms OR CO₂ is acidic ✓</p> <p>Equation involving OH⁻ $\text{H}_2\text{CO}_3 + \text{OH}^- \longrightarrow \text{H}_2\text{O} + \text{HCO}_3^-$ OR $\text{H}_2\text{CO}_3 + 2\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + \text{CO}_3^{2-}$ OR $\text{CO}_2 + \text{OH}^- \longrightarrow \text{CO}_3^{2-} + \text{H}^+$ OR $\text{CO}_2 + \text{OH}^- \longrightarrow \text{HCO}_3^-$ OR $\text{CO}_2 + 2\text{OH}^- \longrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$ OR $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} \checkmark$</p> <p>Effect on equilibrium with reason equilibrium shifts to right AND to restore OH⁻ ✓</p> | 3 | <p>ANNOTATIONS MUST BE USED</p> <p>-----</p> <p>ALLOW equation: $\text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CO}_3$ OR $\text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}^+ + \text{HCO}_3^-$ OR $\text{CO}_2 + \text{H}_2\text{O} \longrightarrow 2\text{H}^+ + \text{CO}_3^{2-}$</p> <p>ALLOW for 'restores OH⁻' the following: 'makes more OH⁻', 'OH⁻ has been used up' DO NOT ALLOW just 'equilibrium shifts to right'</p> |

| Question | Answer | Marks | Guidance |
|----------|---|-----------|---|
| 7 (c) | <p>FOLLOW through stages to mark</p> <p>-----</p> <p>Moles in titration</p> $n(\text{KMnO}_4) = 0.0200 \times \frac{26.2}{1000} = 5.24 \times 10^{-4} \text{ mol } \checkmark$ $n(\text{SO}_3^{2-}) = 1.31 \times 10^{-3} \text{ mol } \checkmark$ <p>Scaling</p> $n(\text{SO}_3^{2-}) \text{ in original } 100 \text{ cm}^3$ $= 4 \times 1.31 \times 10^{-3} = 5.24 \times 10^{-3} \text{ mol } \checkmark$ <p>Mass</p> $\text{Mass of Na}_2\text{SO}_3 \text{ in sample}$ $= 126.1 \times 5.24 \times 10^{-3} \text{ g} = 0.660764 \text{ g } \checkmark$ <p>Percentage</p> $\% \text{ Na}_2\text{SO}_3 = \frac{0.660764}{0.720} \times 100 = 91.8\% \checkmark$ | 5 | <p>ANNOTATIONS MUST BE USED AT LEAST 3 SF for each step</p> <p>-----</p> <p>ECF 2.5 x answer above</p> <p>ECF 4 x answer above</p> <p>ECF 126.1 x answer above ALLOW 0.661 g up to calculator value</p> <p>ECF $\frac{\text{calculated mass above}}{0.720} \times 100$</p> <p>ALLOW 91.8% (1 DP) up to calculator value of 91.77277778 i.e. DO NOT ALLOW 92%</p> |
| | <p>ALLOW alternative approach based on theoretical content of Na_2SO_3 for last 2 marks</p> <p>Theoretical amount, in moles, of Na_2SO_3 in sample</p> $n(\text{Na}_2\text{SO}_3) = \frac{0.720}{126.1} = 5.71 \times 10^{-3} \text{ mol } \checkmark$ <p>Percentage</p> $\% \text{ Na}_2\text{SO}_3 = \frac{5.24 \times 10^{-3}}{5.71 \times 10^{-3}} \times 100 = 91.8\% \checkmark$ | | <p>COMMON ERRORS:</p> <p>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</p> <p>Watch for random ECF %s for % from incorrect $M(\text{Na}_2\text{SO}_3)$, e.g. use of $M(\text{SO}_3^{2-}) = 80.1$ giving 58.3%</p> |
| | Total | 10 | |

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