

Chemistry A

Advanced GCE

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

Mark Scheme for June 2011

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Mark schemes should be read in conjunction with the published question papers and the Report on the Examination.

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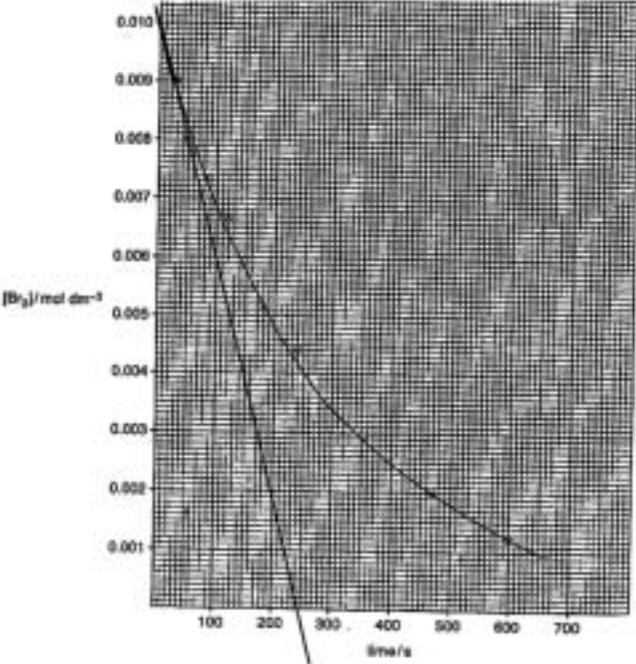
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| Question | Answer | Mark | Guidance |
|----------|---|------|--|
| 1 (a) | (The enthalpy change that accompanies) the formation of one mole of a(n ionic) compound ✓ from its gaseous ions ✓ (under standard conditions) | 2 | <p>IGNORE 'Energy needed' OR 'energy required'</p> <p>ALLOW as alternative for compound: lattice, crystal, substance, solid</p> <p>Note: 1st mark requires 1 mole 2nd mark requires gaseous ions</p> <p>IF candidate response has '1 mole of gaseous ions', award 2nd mark but NOT 1st mark</p> <p>IGNORE: $\text{Mg}^{2+}(\text{g}) + 2\text{Cl}^{-}(\text{g}) \longrightarrow \text{MgCl}_2(\text{s})$ (question asks for words)</p> |
| (b) | (i) Hydration involves bond forming OR bonds are made ✓ | 1 | <p>ALLOW statement of any type of bond being formed ALLOW (chloride) ions attract water (molecules)</p> <p>ALLOW a response in terms of hydrogen bonds breaking AND bond making</p> <p>DO NOT ALLOW response stating that energy is required DO NOT ALLOW response that refers to ions in H_2O, eg H^+</p> |
| | (ii) | 2 | <p>Correct species AND state symbols required for both marks Mark each marking point independently</p> <p>ALLOW response on upper line: $\text{Mg}^{2+}(\text{g}) + 2\text{Cl}^{-}(\text{aq})$ (ie Cl^{-} hydrated before Mg^{2+})</p> <p>ALLOW $\text{MgCl}_2(\text{aq})$</p> |

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

| Question | Answer | Mark | Guidance |
|----------|---|------|--|
| 2 (a) | <p>Temperature: (Forward) reaction is exothermic OR gives out heat OR reverse reaction is endothermic OR takes in heat ✓</p> <p>Pressure: Right-hand side has fewer number of (gaseous) moles ✓ ORA</p> <p>Equilibrium Lower temperature/cooling AND increasing pressure shifts (equilibrium position) to the right ✓</p> | 3 | <p>ANNOTATE WITH TICKS AND CROSSES, etc</p> <p>ALLOW K_c increases at lower temperatures</p> <p>3rd mark is for stating that BOTH low temperature and high pressure shift equilibrium to the right (Could be separate statements)</p> <p>Note: ALLOW suitable alternatives for 'to right', e.g.: towards NO_2 OR towards products OR in forward direction OR increases yield of NO_2/products</p> <p>ALLOW 'favours the right', as alternative for 'shifts equilibrium to right'</p> <p>IGNORE responses in terms of rate</p> |
| (b) | <p>$4\text{NH}_3 + 5\text{O}_2 \longrightarrow 4\text{NO} + 6\text{H}_2\text{O}$ ✓</p> <p>$2\text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{HNO}_2$ ✓</p> | 2 | <p>ALLOW multiples, e.g. $2\text{NH}_3 + 2\frac{1}{2}\text{O}_2 \longrightarrow 2\text{NO} + 3\text{H}_2\text{O}$</p> <p>ALLOW \rightleftharpoons OR \rightarrow in equations</p> |
| (c) (i) | <p>$(K_c =) \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]}$ ✓</p> | 1 | <p>Square brackets are essential</p> |

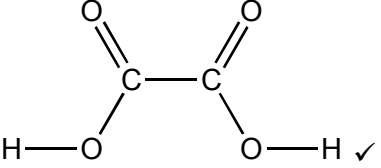
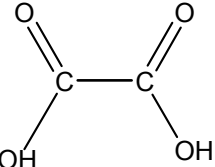
| Question | Answer | Mark | Guidance |
|------------|---|-----------|--|
| 2 (c) (ii) | <p>FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 45 dm³ mol⁻¹, award 5 marks IF answer = 45 with incorrect units, award 4 marks</p> <p>-----</p> <p>Equilibrium moles 0.60 mol NO₂ ✓</p> <p>0.20 mol NO AND 0.40 mol O₂ ✓</p> <p>Equilibrium concentrations (equilibrium moles ÷ 2) [NO₂] = 0.30 mol dm⁻³ AND [NO] = 0.10 mol dm⁻³ AND [O₂] = 0.20 mol dm⁻³ ✓</p> <p>Calculation of K_c and units $K_c = \frac{0.30^2}{0.10^2 \times 0.20} = 45 \text{ ✓ dm}^3 \text{ mol}^{-1} \text{ ✓}$</p> | 5 | <p>IF there is an alternative answer, check to see if there is any ECF credit possible using working below</p> <p>-----</p> <p>ANNOTATE WITH TICKS AND CROSSES, etc ALLOW ECF throughout</p> <p><i>Alternative route if concs NO and O₂ calculated at start:</i></p> <p>initial concentrations: 0.40 mol dm⁻³ NO AND 0.35 mol dm⁻³ O₂ ✓</p> <p>Equilibrium concentrations: [NO₂] = 0.30 mol dm⁻³ ✓ [NO] = 0.10 mol dm⁻³ AND [O₂] = 0.20 mol dm⁻³ ✓</p> <p>For units, ALLOW mol⁻¹ dm³</p> <p>ALLOW ECF using any incorrect values for concentrations OR moles of NO, O₂ AND NO₂ For ECF, ALLOW 2 significant figures up to calculator value correctly rounded ALLOW ECF from incorrect K_c expression for both calculation and units</p> <p>Common ECFs worth less than 5 marks: 22.5 not ÷2 3 marks + unit mark 1.61 0.6 for NO₂ but 0.8 for NO and 0.7 for O₂ No mark for moles NO and O₂ 3 marks + unit mark 0.804 As above but also no ÷2 No mark for moles NO and O₂ AND ÷2 2 marks + unit mark</p> |
| | Total | 11 | |

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

| Question | Answer | Mark | Guidance |
|----------|---|----------|---|
| 3 | $\text{rate} = \frac{0.010}{250} = 0.000040 \text{ OR } 4.0 \times 10^{-5} \checkmark$ <p>units: mol dm⁻³ s⁻¹ ✓</p> | 2 | <p>ALLOW values from 1 SF (0.00004 OR 4 x 10⁻⁵) up to calculator value, correctly rounded</p> <p>ALLOW range ~ $\frac{0.010}{160}$ to $\frac{0.010}{300}$:</p> <p>i.e. ALLOW a calculated gradient in the range 6 x 10⁻⁵ – 3 x 10⁻⁵ from a tangent drawn at t = 0</p> <p>IF tangent is drawn on graph at a different time or incorrectly (e.g. crossing curve), then mark rate calculation by ECF using the gradient of the tangent drawn by the candidate (<i>ie</i> not the range above).</p> <p>IF no tangent is drawn ALLOW a value in the range above ONLY</p> <p>Credit only attempts at tangents, not just a random straight line</p> <p>IGNORE a ‘– sign’</p> |
| | $\text{rate} = k[\text{Br}_2] \text{ OR } k = \frac{\text{rate}}{[\text{Br}_2]} \checkmark$ <p>$k = \text{calculated result from } \frac{\text{calculated value for rate}}{0.010} \checkmark$</p> <p>units: s⁻¹ ✓</p> | 3 | <p>DO NOT ALLOW rate = k[Br], <i>ie</i> Br instead of Br₂</p> <p>DO NOT ALLOW just k[Br₂], <i>ie</i> ‘rate =’ OR ‘r =’ must be present</p> <p>Calculation of k is from candidate’s calculated initial rate</p> <p>From 0.00004, $k = \frac{0.000040}{0.010} = 4 \times 10^{-3} \text{ s}^{-1}$</p> <p>Note:</p> <p>IF order with respect to Br₂ has been shown as 2nd order, then mark this part by ECF, e.g. if Br₂ shown to be 2nd order, rate = k[Br₂]²</p> <p>$k = \text{calculated result from } \frac{\text{calculated value for rate}}{0.010^2}$</p> <p>units: dm³ mol⁻¹ s⁻¹ OR mol⁻¹ dm³ s⁻¹</p> <p>Note: Units mark must correspond to the candidate’s stated rate equation, NOT an incorrectly rearranged k expression</p> |
| | Total | 9 | |

| Question | | | Answer | Mark | Guidance |
|----------|-----|-------|--|------|---|
| 4 | (a) | (i) | proton donor ✓ | 1 | ALLOW H ⁺ donor |
| | | (ii) | (the proportion of) dissociation ✓ Correct equation for any of the four acids: C ₆ H ₅ COOH ⇌ H ⁺ + C ₆ H ₅ COO ⁻ OR CH ₃ COOH ⇌ H ⁺ + CH ₃ COO ⁻ OR CH ₃ COCOOH ⇌ H ⁺ + CH ₃ COCOO ⁻ OR CH ₃ CHOHCOOH ⇌ H ⁺ + CH ₃ CHOHCOO ⁻ ✓ | 2 | ALLOW a weak acid partly dissociates ALLOW a strong acid totally dissociates ALLOW ionisation for dissociation ALLOW the ability to donate a proton Equilibrium sign required ALLOW equilibria involving H ₂ O and H ₃ O ⁺ e.g. C ₆ H ₅ COOH + H ₂ O ⇌ H ₃ O ⁺ + C ₆ H ₅ COO ⁻ , etc DO NOT ALLOW HA ⇌ H ⁺ + A ⁻ |
| | | (iii) | weakest: CH ₃ COOH acetic acid C ₆ H ₅ COOH benzoic acid CH ₃ CHOHCOOH lactic acid strongest: CH ₃ COCOOH ✓ pyruvic acid | 1 | ALLOW correct order using any identifier from the table, <i>ie</i> , common name, systematic name, structural formula OR pK _a value |
| | | (iv) | C ₆ H ₅ COOH ₂ ⁺ + CH ₃ CHOHCOO ⁻ ✓ | 1 | BOTH products AND correct charges required for mark Mark ECF from incorrect order in (iii) See response from (iii) below response to (iv) |

| Question | Answer | Mark | Guidance |
|-----------|---|------|--|
| 4 (b) (i) | $2\text{CH}_3\text{COCOOH} + \text{Ca}(\text{OH})_2 \rightarrow (\text{CH}_3\text{COCOO})_2\text{Ca} + 2\text{H}_2\text{O} \checkmark$ <p>Note: pyruvic acid must have been used here and formula of pyruvic acid and pyruvate must be correct</p> | 1 | All species AND balancing required for the mark ALLOW $(\text{CH}_3\text{COCOO}^-)_2\text{Ca}^{2+}$ ALLOW equation showing $2\text{CH}_3\text{COCOO}^- + \text{Ca}^{2+}$ IF charges shown, charges must balance, e.g. DO NOT ALLOW $(\text{CH}_3\text{COCOO}^-)_2\text{Ca}$ IGNORE state symbols if shown ALLOW multiples ALLOW equilibrium sign |
| | (ii) $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$ | 1 | ALLOW multiples but not same species on both sides ALLOW equilibrium sign IGNORE state symbols if shown ALLOW $\text{H}_3\text{O}^+ + \text{OH}^- \longrightarrow 2\text{H}_2\text{O}$ ALLOW $\text{CH}_3\text{COCOOH} + \text{OH}^- \longrightarrow \text{CH}_3\text{COCOO}^- + \text{H}_2\text{O}$ |
| (c) | <p>FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 2.11, award 4 marks</p> <p>-----</p> $K_a = 10^{-\text{p}K_a}$ $= 10^{-2.39} \text{ OR } 0.00407 \checkmark$ $K_a = \frac{[\text{H}^+][\text{CH}_3\text{COCOO}^-]}{[\text{CH}_3\text{COCOOH}]} \text{ (ALLOW use of HA, H}^+ \text{ and A}^-)$ <p>OR $[\text{H}^+] = \sqrt{K_a \times [\text{HA}]}$</p> <p>OR $[\text{H}^+] = \sqrt{0.00407 \times 0.0150} \checkmark$ (subsumes 1st marking point) $[\text{H}^+] = 0.00782 \text{ (mol dm}^{-3}) \checkmark$</p> <p>$\text{pH} = -\log 0.00782 = 2.11 \checkmark$</p> | 4 | <p>IF there is an alternative answer, check to see if there is any ECF credit possible using working below</p> <p>-----</p> <p>IF ECF, ANNOTATE WITH TICKS AND CROSSES, etc</p> <p>ALLOW 0.0041 to calculator value: 0.004073802</p> <p>IF the $\text{p}K_a$ of a different weak acid has been used use ECF from 2nd marking point</p> <p>ALLOW 0.0078 to calculator value (depending on previous rounding) ALLOW ONLY 2.11 (This is to take into account poor previous rounding)</p> <p>IF candidate has used $0.0150 \text{ mol dm}^{-3}$ (<i>ie</i> assumes strong acid) ALLOW final mark ONLY by ECF for a pH of 1.82</p> <p>IF no square root used, pH = 4.21 3 marks</p> |

| 4 | Question | Answer | Mark | Guidance |
|---|----------|--|------|--|
| | (d) (i) |  | 1 | <p>ALLOW correct structural OR displayed OR skeletal formula OR recognisable mixture of formulae</p> <p>DO NOT ALLOW molecular formula but ALLOW (COOH)₂ OR (CO₂H)₂</p>  <p>ALLOW OH BUT not O-H-C</p> |
| | (ii) | $\text{C}_2\text{H}_2\text{O}_4 \rightleftharpoons \text{H}^+ + \text{C}_2\text{HO}_4^- \checkmark$ $\text{C}_2\text{HO}_4^- \rightleftharpoons \text{H}^+ + \text{C}_2\text{O}_4^{2-} \checkmark$ | 2 | <p>ALLOW in either order</p> <p>ALLOW arrow instead of equilibrium sign</p> <p>ALLOW molecular formulae for this part</p> <p>ALLOW equilibria involving H₂O and H₃O⁺</p> <p>ALLOW equations using structures</p> |

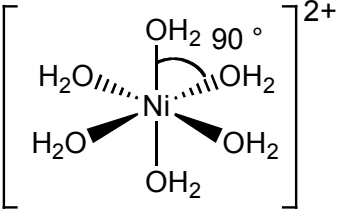
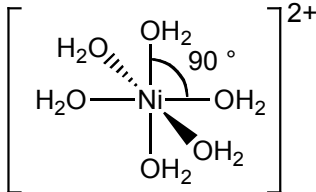
| Question | Answer | Mark | Guidance |
|----------|---|------|--|
| 4 (e) | <p>Chemicals (1 mark) lactic acid / CH₃CHOHCOOH AND (sodium) lactate / CH₃CHOHCOO⁻ (Na⁺) ✓</p> <p>Concentrations (4 marks)</p> <p>EITHER [H⁺(aq)] = 10^{-3.55} OR 2.8 x 10⁻⁴ OR 2.82 x 10⁻⁴ (mol dm⁻³) ✓ <i>separate marking point</i></p> <p>$K_a = 10^{-3.86}$ OR 1.4 x 10⁻⁴ OR 1.38 x 10⁻⁴ (mol dm⁻³) ✓ <i>separate marking point</i></p> <p>$\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_a}$ OR $\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$ ✓</p> <p>$\frac{[HA]}{[A^-]} = \frac{2.8 \times 10^{-4}}{1.4 \times 10^{-4}}$ OR $\frac{2}{1}$ OR 2 OR $\frac{[A^-]}{[HA]} = \frac{0.5}{1}$ OR 0.5 ✓</p> <p>This marking point subsumes previous marking point ONLY</p> <p>Comment (1 mark) Magic tang/taste could come from other chemicals/substances in the sweet OR The buffer would have the same taste/tang as the magic tang ✓</p> | 6 | <p>ANNOTATE WITH TICKS AND CROSSES, etc</p> <p>ALLOW any lactate salt ALLOW lactic acid AND NaOH OR lactic acid AND OH⁻</p> <p>-----</p> <p>FOR ALTERNATIVE using Henderson–Hasselbalch equation, SEE PAGE 11</p> <p>-----</p> <p>If another weak acid has been selected and salt has been selected, allow ECF for remainder of question SEE PAGE 12</p> <p>-----</p> <p>ALLOW 2.8 x 10⁻⁴ up to calculator value of 2.81838 x 10⁻⁴ ALLOW 0.00028, etc</p> <p>ALLOW 1.4 x 10⁻⁴ up to calculator value of 1.38038 x 10⁻⁴ ALLOW 0.00014, etc</p> <p>ALLOW use of CH₃CHOHCOOH AND CH₃CHOHCOO⁻(Na⁺) ALLOW use of acid AND salt</p> <p>ALLOW value from $\frac{\text{calculated value of } [H^+]}{\text{calculated value of } K_a}$</p> <p>ALLOW 2SF up to calculator value of 2.041742129 correctly rounded but ALLOW 2 if 2.8 x 10⁻⁴ and 1.4 x 10⁻⁴ used ALLOW 2 mol dm⁻³ HA AND 1 mol dm⁻³ A⁻ OR any concentration ratio of 2(acid) : 1(salt)</p> <p>ALLOW 2SF up to calculator value of 0.489778819 correctly rounded but ALLOW 0.5 if 2.8 x 10⁻⁴ and 1.4 x 10⁻⁴ used</p> |

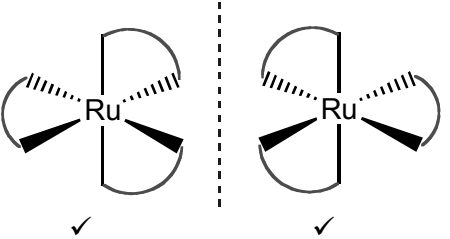
| Question | Answer | Mark | Guidance |
|----------|---|------|---|
| | <p>ALTERNATIVE approach for concentrations using Henderson–Hasselbalch equation (4 marks)</p> $\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{A}^{-}]}{[\text{HA}]} \quad \text{OR} \quad -\log K_{\text{a}} + \log \frac{[\text{A}^{-}]}{[\text{HA}]} \quad \checkmark$ $\log \frac{[\text{A}^{-}]}{[\text{HA}]} = 3.55 - 3.86 \quad \checkmark \quad (\text{subsumes previous mark})$ $\log \frac{[\text{A}^{-}]}{[\text{HA}]} = -0.31 \quad \checkmark \quad (\text{subsumes previous mark})$ $\frac{[\text{A}^{-}]}{[\text{HA}]} = 10^{-0.31} = \frac{0.490}{1} \quad \text{OR} \quad 0.490 \quad \checkmark$ | | <p>ALLOW use of $\text{CH}_3\text{CHOHCOOH}$ AND $\text{CH}_3\text{CHOHCOO}^{-}(\text{Na}^{+})$ ALLOW use of acid AND salt ALLOW $\text{pH} = \text{p}K_{\text{a}} - \log \frac{[\text{HA}]}{[\text{A}^{-}]}$ OR $-\log K_{\text{a}} - \log \frac{[\text{HA}]}{[\text{A}^{-}]}$</p> <p>ALLOW $\log \frac{[\text{HA}]}{[\text{A}^{-}]} = 3.86 - 3.55$ (subsumes previous mark)</p> <p>ALLOW $\log \frac{[\text{HA}]}{[\text{A}^{-}]} = 0.31$ (subsumes previous mark)</p> <p>ALLOW $\frac{[\text{HA}]}{[\text{A}^{-}]} = 10^{0.31} = \frac{2.04}{1}$ OR $\frac{2}{1}$ OR 2</p> <p>For $\frac{[\text{A}^{-}]}{[\text{HA}]}$, ALLOW 2 SF up to calculator value of 0.48978819</p> <p>For $\frac{[\text{HA}]}{[\text{A}^{-}]}$, ALLOW 2 SF up to calculator value of 2.041737945 but ALLOW 2 if $10^{-0.31}$ used</p> |

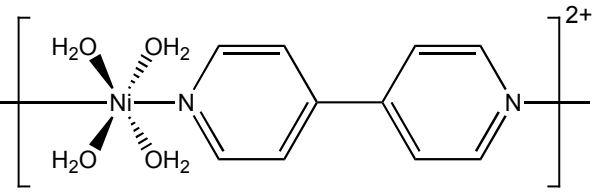
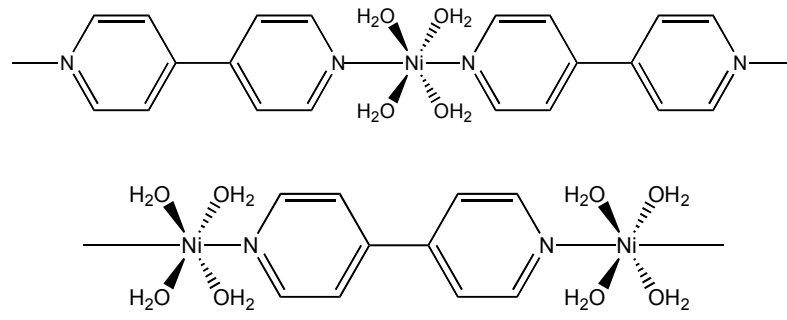
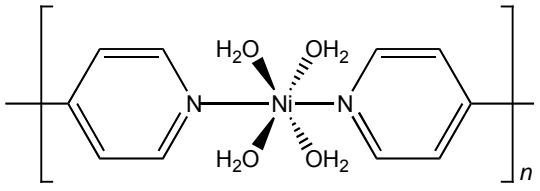
| Question | Answer | Mark | Guidance |
|--|--|---|---|
| 4 (e) | <p>SUMMARY OF 4(e) MARKING POINTS FOR EACH POSSIBLE ACID CHOSEN FIRST, CHECK THE ANSWER ON ANSWER LINE: IF answer is correct for weak acid chosen, award MP2–MP5 IF there is an alternative answer, check to see if there is any ECF credit possible using working below</p> | | |
| | lactic | pyruvic | acetic |
| pK_a | 3.86 | 2.39 | 4.76 |
| MP1 | lactic AND lactate OR lactic acid AND OH ⁻ | No mark | No mark |
| MP2: [H ⁺] | $10^{-3.55}$ OR 2.82×10^{-4} (calc : 2.81838×10^{-4}) | | |
| MP3: K_a | $10^{-3.86}$ OR 1.38×10^{-4} calc : $1.380384265 \times 10^{-4}$ | $10^{-2.39}$ OR 4.07×10^{-3} calc : $4.073802778 \times 10^{-3}$ | $10^{-4.76}$ OR 1.74×10^{-5} calc : $1.737800829 \times 10^{-5}$ |
| MP4: ratio expression | $\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_a}$ OR $\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$ | | |
| MP5: $\frac{[HA]}{[A^-]}$ | $\frac{2.82 \times 10^{-4}}{1.38 \times 10^{-4}}$ OR 2.04 calc : 2.041737945 | $\frac{2.82 \times 10^{-4}}{4.07 \times 10^{-3}}$ OR 0.0693 calc : 0.069183097 | $\frac{2.82 \times 10^{-4}}{1.74 \times 10^{-5}}$ OR 16.2 calc : 16.21810097 |
| OR $\frac{[A^-]}{[HA]}$ | $\frac{1.38 \times 10^{-4}}{2.82 \times 10^{-4}}$ OR 0.489 calc : 0.489778819 | $\frac{4.07 \times 10^{-3}}{2.82 \times 10^{-4}}$ OR 14.4 calc : 14.45439771 | $\frac{1.74 \times 10^{-5}}{2.82 \times 10^{-4}}$ OR 0.0617 calc : 0.0616595 |
| <p>TAKE CARE: Calc values are completely unrounded and may differ between brands of calculator Use actual candidate values at each stage using rounding to 2 or more SF. MP5: calculated using 3 SF from MP2 and MP3 calc values for MP5 are completely unrounded (using calculator values from MP2 and MP3) Be slightly flexible as candidates may have written down rounded values but carried on with calculator values – This approach is ACCEPTABLE</p> | | | |
| Total | | 20 | |

| Question | Answer | Mark | Guidance |
|----------|--|------|---|
| 5 (a) | <p>process increase decrease</p> <p>$C_2H_5OH(l) \rightarrow C_2H_5OH(g)$ ✓</p> <p>$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$ ✓</p> <p>$NH_4Cl(s) + aq \rightarrow NH_4Cl(aq)$ ✓</p> <p>$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$ ✓</p> <p>$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$ ✓</p> <p>All 5 correct → 2 marks</p> <p>4 correct → 1 mark</p> | 2 | |
| (b) | <p>ΔH: + AND bonds broken ✓</p> <p>ΔS: + AND more random/more disorder/more ways of arranging energy ✓</p> | 2 | <p>Sign and reason required for each mark</p> <p>ALLOW forces of attraction/hydrogen bonds are overcome</p> <p>DO NOT ALLOW response in terms of bonds breaking AND bond making (for melting bonds are just broken)</p> <p>DO NOT ALLOW responses implying that bonds within H₂O molecules are broken</p> <p>IGNORE comments related to ΔG</p> <p>IGNORE comments related to ΔG</p> |
| (c) (i) | <p>$\Delta S = (3 \times 131 + 198) - (186 + 189)$ ✓</p> <p>$\Delta S = (+)216 \text{ (J K}^{-1} \text{ mol}^{-1})$ ✓</p> | 2 | <p>ALLOW 1 mark for -216 (wrong sign)</p> <p>ALLOW 1 mark for -46 (131 instead of 3 x 131)</p> <p>ALLOW 1 mark for 594 (sign of 189)</p> |

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

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

| Question | | | Answer | Mark | Guidance |
|----------|-----|-------|--|------|--|
| 6 | (b) | (ii) | A: NiCl_4^{2-} ✓ B: $\text{Ni}(\text{OH})_2$ ✓ | 2 | ALLOW $[\text{NiCl}_4]^{2-}$ DO NOT ALLOW $\text{Ni}(\text{Cl}^-)_4^{2-}$ ALLOW $\text{Ni}(\text{OH})_2(\text{H}_2\text{O})_4$ OR $[\text{Ni}(\text{OH})_2(\text{H}_2\text{O})_4]$ |
| | | (iii) | C: $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ✓ | 1 | Square brackets essential 2+ charge must be outside square brackets ALLOW $[\text{Ni}(\text{OH})_6]^{4-}$ |
| | | (iv) | $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \longrightarrow [\text{Ni}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O}$ ✓ ✓ | 2 | 1 mark for each side of equation ALLOW equilibrium sign ALLOW ECF from (iii) for the following: $[\text{Ni}(\text{NH}_3)_4]^{2+}$ (wrong number of NH_3) Any 6 coordinate Ni^{2+} complex with NH_3 and H_2O ligands, e.g. $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, $[\text{Ni}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$, etc ALLOW from $[\text{Ni}(\text{OH})_6]^{4-}$, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 6\text{OH}^- \longrightarrow [\text{Ni}(\text{OH})_6]^{4-} + 6\text{H}_2\text{O}$ OR $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \longrightarrow [\text{Ni}(\text{OH})_6]^{4-} + 6\text{NH}_4^+$ |
| | (c) | (i) | $\text{C}_{10}\text{H}_8\text{N}_2$ ✓ | 1 | ALLOW atoms in any order |
| | | (ii) | 4 ✓ | 1 | |
| | | (iii) |  One mark for each structure 2nd structure must be correct mirror image of 1st structure | 2 | Charge and N atom labels NOT needed ALLOW any attempt to show bipy. Bottom line is the diagram on the left. 1 mark for 3D diagram with ligands attached for ONE stereoisomer. Must contain 2 out wedges, 2 in wedges and 2 lines in plane of paper: ALLOW structures with Ni in centre |

| Question | Answer | Mark | Guidance |
|------------|---|---|----------|
| 6 (c) (iv) | <p>3 marks available</p> <p>1st mark Correct 4,4'-bipy structure shown separately or within attempted structure with Ni²⁺ ✓</p> <p>2 marks The remaining 2 marks are available for a section of the polymer with repeat unit identified as follows:</p> <p>IF Ni is bonded to 4 H₂O (bond to O) with a bond to N end of two 4,4'-bipy structure</p> <p>OR</p> <p>IF each N of 4,4'-bipy is bonded to a Ni bonded to 4 H₂O (bond to O), award 1 mark ✓</p> <p>IF correct repeat unit is shown, award 2 marks ✓✓</p>  | <p>3</p>  <p>Charge NOT needed. Square brackets NOT needed</p> <p>Bonds around Ni do NOT need to be shown 3D Accept bonds to H₂O (does NOT need to go to 'O')</p> <p>ALLOW the following structure for repeat unit for all 2nd and 3rd marks:</p>  | |
| | Total | 21 | |

| Question | | Answer | Mark | Guidance |
|----------|-----|---|------|---|
| 7 | (a) | <p>Definition The e.m.f. (of a half-cell) compared with a standard hydrogen half-cell/standard hydrogen electrode ✓</p> <p>Standard conditions Temperature of 298 K / 25°C AND (solution) concentrations of 1 mol dm⁻³ AND pressure of 101 kPa OR 100 kPa ✓</p> | 2 | <p>ALLOW voltage OR potential difference OR p.d. OR electrode potential OR reduction potential OR redox potential as alternative for e.m.f. IGNORE S.H.E. (as abbreviation for standard hydrogen electrode)</p> <p>ALLOW 1 atmosphere/1 atm OR 10⁵ Pa OR 1 bar</p> |
| | (b) | 1.25 (V) ✓ | 1 | IGNORE any sign |
| | (c) | (i) | 2 | <p>2 marks for correct equation ALLOW NiOOH OR NiO₂H</p> <p>ALLOW ⇌ sign for equation (ie assume reaction goes from left to right) ALLOW 1 mark for correctly balanced equation with e⁻ and/or OH⁻ shown e.g.: Cd + 2NiO(OH) + 2H₂O + 2OH⁻ + 2e⁻ → Cd(OH)₂ + 2Ni(OH)₂ + 2OH⁻ + 2e⁻</p> <p>ALLOW 1 mark for balanced correct reverse equation with OH⁻ AND e⁻ cancelled: Cd(OH)₂ + 2Ni(OH)₂ → Cd + 2NiO(OH) + 2H₂O</p> |
| | | (ii) | 2 | <p>oxidation: Cd from 0 to +2 ✓ '+' sign not required reduction: Ni from +3 to +2 ✓ '+' sign not required</p> <p>ALLOW Cd⁰ → Cd²⁺ (shows 0 and 2+) ALLOW Ni³⁺ → Ni²⁺ (shows 3+ and 2+) ALLOW ECF from (c)(i) equation written 'wrong way around'.</p> |
| | (d) | (i) | 1 | <p>reverse reactions to charging OR Cd(OH)₂ + 2e⁻ → Cd + 2OH⁻ Ni(OH)₂ + OH⁻ → NiO(OH) + H₂O + e⁻ OR reaction that is reverse to reaction given in c(i): Cd(OH)₂ + 2Ni(OH)₂ → Cd + 2NiO(OH) + 2H₂O ✓</p> <p>If half-equations are given, then BOTH equations required</p> <p>ALLOW ⇌ sign for equation (ie assume reaction goes from left to right)</p> |

| Question | | | Answer | Mark | Guidance |
|--------------|-----|------|--|-----------|--|
| 7 | (d) | (ii) | $4\text{OH}^- \longrightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \checkmark$ $2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^- \checkmark$ | 2 | ALLOW multiples; ALLOW \rightleftharpoons sign for each equation Note: These are the only correct responses |
| Total | | | | 10 | |

| Question | Answer | Mark | Guidance |
|----------|--|------|--|
| 8 | <p>step 1 $\text{Cu} + 4\text{HNO}_3 \longrightarrow \text{Cu}^{2+} + 2\text{NO}_3^- + 2\text{NO}_2 + 2\text{H}_2\text{O}$ OR $\text{Cu} + 2\text{H}^+ + 2\text{HNO}_3 \longrightarrow \text{Cu}^{2+} + 2\text{NO}_2 + 2\text{H}_2\text{O}$ OR $\text{Cu} + 4\text{H}^+ + 2\text{NO}_3^- \longrightarrow \text{Cu}^{2+} + 2\text{NO}_2 + 2\text{H}_2\text{O} \checkmark$</p> <p>step 2 2 equations with 1 mark for each $\text{Cu}^{2+} + \text{CO}_3^{2-} \longrightarrow \text{CuCO}_3 \checkmark$ $2\text{H}^+ + \text{CO}_3^{2-} \longrightarrow \text{H}_2\text{O} + \text{CO}_2 \checkmark$</p> <p>step 4 $2\text{Cu}^{2+} + 4\text{I}^- \longrightarrow 2\text{CuI} + \text{I}_2 \checkmark$</p> | 4 | <p>ANNOTATE ALL Q8 WITH TICKS AND CROSSES, etc</p> <p>ALLOW multiples throughout IGNORE state symbols throughout</p> <p>ALLOW $\text{Cu}(\text{NO}_3)_2$ for $\text{Cu}^{2+} + 2\text{NO}_3^-$</p> <p>AWARD 2 MARKS for a combined equation: $\text{Cu}^{2+} + 2\text{H}^+ + 2\text{CO}_3^{2-} \longrightarrow \text{CuCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \checkmark\checkmark$</p> <p>DO NOT ALLOW $2\text{H}^+ + \text{CO}_3^{2-} \longrightarrow \text{H}_2\text{CO}_3$</p> <p>ALLOW $2\text{Cu}^{2+} + 4\text{KI} \longrightarrow 2\text{CuI} + \text{I}_2 + 4\text{K}^+$ ALLOW $\text{Cu}^{2+} + \text{I}^- \longrightarrow \text{Cu}^+ + \frac{1}{2}\text{I}_2$</p> |

| Question | Answer | Mark | Guidance |
|----------|---|----------|---|
| 8 | <p>FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 67.6%, award 5 marks. Ignore any attempted equation in step 4</p> <p>IF answer = 33.8% AND IF Cu²⁺/I₂ in step 4 equation shown with 1:1 molar ratio, award 5 marks for ECF</p> <p>-----</p> <p>amount S₂O₃²⁻ used = $0.100 \times \frac{29.8}{1000} = 2.98 \times 10^{-3} \text{ mol } \checkmark$</p> <p>amount I₂ = $1.49 \times 10^{-3} \text{ mol}$ OR amount Cu²⁺ = $2.98 \times 10^{-3} \text{ mol } \checkmark$</p> <p>amount Cu²⁺ in original 250 cm³ = 10 x 2.98×10^{-3} = $2.98 \times 10^{-2} \text{ mol } \checkmark$</p> <p>Mass of Cu/Cu²⁺ in brass = $63.5 \times 2.98 \times 10^{-2} \text{ g}$ = $1.8923 \text{ g } \checkmark$</p> <p>percentage Cu in brass = $\frac{1.8923}{2.80} \times 100$ = $67.6\% \checkmark$</p> <p>MUST be to one decimal place (in the question)</p> | 5 | <p>IF there is an alternative answer, check to see if there is any ECF credit possible using working below</p> <p>-----</p> <p>Working must be to 3 SF throughout until final % mark BUT ignore trailing zeroes, ie for 0.490 allow 0.49</p> <p>ECF answer above</p> <p>ECF 10 x answer above</p> <p>ECF 63.5 x answer above ALLOW 1.88 g</p> <p>ECF $\frac{\text{answer above}}{2.80} \times 100$ Answer must be to one decimal place</p> <p>ALLOW % Cu = 67.5 % IF mass of Cu has been rounded to 1.89 g in previous step</p> <p>Common ECFs: 6.76% x10 missing 3/5 marks for calculation 2 d.p. MS states 1 d.p.</p> <p>33.8% IF Cu²⁺/I₂ in step 4 equation with 2:1 ratio OR not attempted, response, 4/5 marks for calculation (moles Cu²⁺ incorrect)</p> |
| | Total | 9 | |

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