

Chemistry A

Advanced GCE

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

Mark Scheme for January 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 |

12. 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(a); Question 2(c), 2d(ii); Question 3e(i); Question 4d(i), 4d(ii); Question 6d; Question 7(a); Question 8(c)

All the Additional Pages in the examination script must be checked to see if any candidates include any answers.

- When you open question **1(a)** you will see a view of page 22, one of the Additional Pages.
- If the page is blank then, using the marking mode, annotate the page with an omission mark, ^.
- Scroll down to page 23 and annotate with a ^ if the page is blank.
- Scroll down to page 24 and annotate with a ^ if the page is blank.

- If pages 22, 23 or 24 are not blank then use the paper clip icon to link the pages to the correct questions.
- You may need to contact your Team Leader if you do not know how to do this.

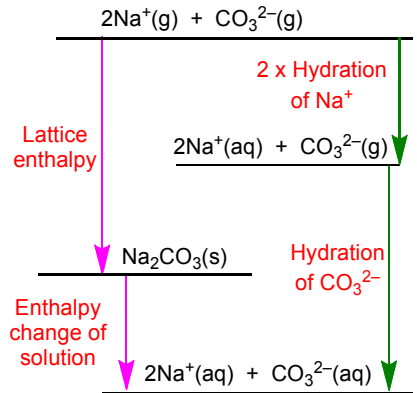
| Question | Expected answers | Marks | Additional guidance |
|----------|--|-------|---|
| 1 a | <p>graph: Rate does not change with concentration AND zero-order with respect to I₂ ✓</p> <p>initial rates data: Mark independently</p> <p>When [(CH₃)₂CO] × 2, rate × 2 (2¹) ✓ 1st order with respect to (CH₃)₂CO ✓</p> <p>When [HCl] × 2.5, rate × 2.5 ✓ 1st order with respect to HCl ✓</p> | | <p>ANNOTATIONS MUST BE USED</p> <p>ALLOW (straight) line with zero gradient AND zero-order ALLOW horizontal line AND zero-order IGNORE just 'constant line' OR just 'straight line' <i>also fits 1st order</i></p> <p>CARE with comparisons in opposite direction ALLOW [(CH₃)₂CO] × 0.5, rate × 0.5 (0.5¹)</p> <p>ALLOW [HCl] × 0.4, rate × 0.4 (0.4¹) ALLOW H⁺ for HCl</p> <p>CARE: Comparison of Experiments 1 and 3 may be valid despite BOTH concentrations changing</p> |
| | <p>Rate equation and rate constant:</p> <p>rate = k[(CH₃)₂CO(aq)] [HCl(aq)] ✓</p> $k = \frac{\text{rate}}{[(\text{CH}_3)_2\text{CO}(\text{aq})] [\text{HCl}(\text{aq})]} \text{ OR}$ $\frac{2.10 \times 10^{-9}}{(1.50 \times 10^{-3}) \times (2.00 \times 10^{-2})} \checkmark$ <p>= 7(.00) × 10⁻⁵ OR 0.00007(00) ✓</p> <p>units: dm³ mol⁻¹ s⁻¹ ✓</p> | 9 | <p>ALLOW ECF from incorrect orders In rate equation, square brackets are required</p> <p>rate = k[(CH₃)₂CO(aq)][HCl(aq)][I₂(aq)]⁰ ALLOW H⁺ for HCl IGNORE state symbols, even if wrong</p> <p>ALLOW ECF for units 'correct' for incorrect expression used to calculate k, e.g. <i>upside down or wrong orders</i> $\frac{[(\text{CH}_3)_2\text{CO}(\text{aq})] [\text{H}^+(\text{aq})]}{\text{rate}} \times \text{units: mol s dm}^{-3} \checkmark$</p> |

| Question | | Expected answers | Marks | Additional guidance |
|--------------|---|--|-----------|---|
| 1 | b | <p>step 1: $\text{H}_2(\text{g}) + \text{ICl}(\text{g}) \longrightarrow$ LHS of step 1 ✓</p> <p style="text-align: center;">$\longrightarrow \text{HCl}(\text{g}) + \text{HI}(\text{g})$</p> <p>step 2: $\text{HI}(\text{g}) + \text{ICl}(\text{g}) \longrightarrow \text{HCl}(\text{g}) + \text{I}_2(\text{g})$ products of step 1 AND step 2 ✓</p> | 2 | <p>State symbols NOT required</p> <p>2nd mark can ONLY be awarded provided that</p> <ul style="list-style-type: none"> • 1st mark has been awarded • step 1 AND step 2 add up to the overall equation. <p>e.g. ALLOW $\longrightarrow \text{H}_2\text{ICl}(\text{g})$</p> <p>step 2: $\text{H}_2\text{ICl}(\text{g}) + \text{ICl}(\text{g}) \longrightarrow 2\text{HCl}(\text{g}) + \text{I}_2(\text{g})$</p> <p>In step 2, ALLOW inclusion of extra species on both sides of the equation only if they cancel, e.g. $\text{HI}(\text{g}) + \text{HCl}(\text{g}) + \text{ICl}(\text{g}) \longrightarrow 2\text{HCl}(\text{g}) + \text{I}_2(\text{g})$</p> |
| Total | | | 11 | |

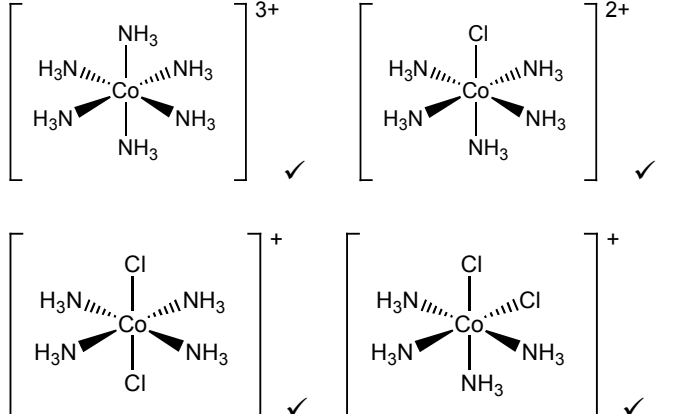
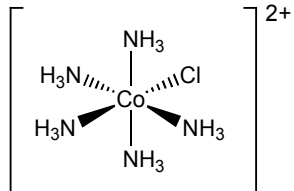
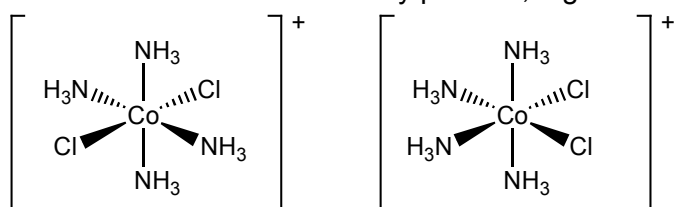
| Question | Expected answers | Marks | Additional guidance |
|----------|---|-------|---|
| 2 a | (The enthalpy change that accompanies) the formation of one mole of a(n ionic) compound ✓ from its gaseous ions ✓ (under standard conditions) | 2 | IGNORE 'Energy needed' OR 'energy required' ALLOW as alternative 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: $2\text{Na}^+(\text{g}) + \text{O}^{2-}(\text{g}) \longrightarrow \text{Na}_2\text{O}(\text{s})$ <i>Question asks for a definition, not an equation</i> |
| b i | C (or 2C) A B D G E (or 2E) F All seven correct ✓✓✓ Five OR six correct ✓✓ Three OR four correct ✓ | 3 | ALLOW 496 (OR 992) -141 790 249 G OR Lattice enthalpy/LE [OR answer to (ii)] 108 (OR 216) -414 |
| | ii FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = -2520 (kJ mol⁻¹) award 2 marks ----- $-414 = (2 \times 108) + 249 + (2 \times 496) + (-141) + 790 + \Delta H_{\text{LE}}$ OR $\Delta H_{\text{LE}} = -414 - [(2 \times 108) + 249 + (2 \times 496) + (-141) + 790] \checkmark$ $= -414 - 2106 = \mathbf{-2520 \text{ (kJ mol}^{-1}\text{)}} \checkmark$ | 2 | IF there is an alternative answer, check the list below for marking of answers from common errors ----- ALLOW for 1 mark: -1692 wrong sign for 414 -1916 2×108 and 2×496 not used for Na^+ -2412 2×108 not used for Na^+ -2024 2×496 not used for Na^+ +2520 wrong sign for final answer -2802 sign changed for 1st electron affinity of oxygen -2395.5 atomisation of oxygen halved |

| Question | Expected answers | Marks | Additional guidance |
|----------|--|-------|--|
| | | | Any other number: CHECK for ECF from 1st marking point for expressions with ONE error only ANNOTATIONS MUST BE USED |
| 2 | c ALLOW reverse argument throughout (ORA) Comparison of size AND charge of cations Mg^{2+} is smaller AND Mg^{2+} has a greater charge OR Mg^{2+} has a greater charge density ✓ Comparison of size of anions S^{2-} is larger OR S^{2-} has a smaller charge density ✓ Comparison of attraction of a cation and an anion Mg^{2+} has stronger attraction OR Na^+ has weaker attraction AND S^{2-} has weaker attraction OR O^{2-} has stronger attraction ✓ | 3 | NOTE: For ALL marking points, assume that the following refer to 'ions', Mg^{2+} , etc. For 'ions', ALLOW 'atoms' For Mg^{2+} , Na^+ , O^{2-} and S^{2-} , ALLOW symbols: Mg, Na, O and S ALLOW names: magnesium, sodium, oxygen, oxide, sulfur, sulfide BUT DO NOT ALLOW molecules <i>i.e. ALLOW</i> Mg has a smaller (atomic) radius IGNORE idea of close packing of ions ----- ORA: Na^+ is larger AND Na^+ has a smaller charge OR Na^+ has a smaller charge density ✓ IGNORE just Mg^{2+} is small <i>comparison required</i> ORA O^{2-} is smaller OR O^{2-} has a larger charge density ✓ IGNORE just S^{2-} is large <i>comparison required</i> ALLOW pull for attraction ALLOW 'attracts with more force' for greater attraction BUT ... IGNORE just 'greater force' (<i>could be repulsion</i>) OR comparison of bond strength/energy to break bonds IGNORE comparisons of numbers of ions |

| Question | Expected answers | Marks | Additional guidance |
|----------|---|-------|---|
| d i | Cycle needs formation of CO_3^{2-} ions (from C and O) ✓ i.e. NOT breaking up of CO_3^{2-} ion | 1 | ALLOW carbonate ion contains C and O ALLOW carbonate ion contains 2 elements IGNORE sodium carbonate contains 3 elements IGNORE carbonate ion has covalent bonds |
| 2 d ii | See also Appendix 1 at end of mark scheme Mark allocation 1 – $2\text{Na}^+(\text{g}) + \text{CO}_3^{2-}(\text{g})$ on a top line AND $\text{Na}_2\text{CO}_3(\text{s})$ on a lower line AND 'Lattice enthalpy' label (as below) links the lines ✓ 2 – $2\text{Na}^+(\text{g}) + \text{CO}_3^{2-}(\text{g})$ on a top line AND $2\text{Na}^+(\text{aq}) + \text{CO}_3^{2-}(\text{g})$ on a middle line AND $2\text{Na}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ on a lower line AND ' ΔH hydration' labels (as below) link the lines ✓ NOTE: For hydration labels, see diagram below 2 x hydration of Na^+ OR hydration of 2 x Na^+ is required 3 – ' ΔH solution' label BELOW $\text{Na}_2\text{CO}_3(\text{s})$ AND ALL arrows in correct directions ✓ | 3 | ANNOTATIONS MUST BE USED MARK AS FOLLOWS 1. Mark the cycle 2. IF there is no cycle , mark the equation below ----- State symbols are required for ALL species IGNORE direction of any arrows until MARK 3 ALLOW $\text{Na}_2\text{CO}_3(\text{aq})$ on a lower line as an alternative for $2\text{Na}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ ALLOW CO_3^{2-} hydrated first: i.e. $2\text{Na}^+(\text{g}) + \text{CO}_3^{2-}(\text{aq})$ on middle line ALLOW two hydration stages combined i.e. $2\text{Na}^+(\text{g}) + \text{CO}_3^{2-}(\text{g})$ on a top line AND $2\text{Na}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ on a lower line AND BOTH 'Hydration' labels link the lines ✓ IF cycle shown using NaCO_3 , Na^+ and CO_3^- ALLOW ECF for third marking point only NOTE: DO NOT ALLOW ECF from any other species For simple energy cycles a maximum of 2 marks only can be awarded – See APPENDIX 1 ----- For an equation , only 1 mark can be awarded Lattice enthalpy = $-\Delta H(\text{solution}) \text{Na}_2\text{CO}_3$ + $[2 \times \Delta H(\text{hydration}) \text{Na}^+] + \Delta H(\text{hydration}) \text{CO}_3^{2-}$ |

| Question | Expected answers | Marks | Additional guidance |
|----------|---|-----------|---|
| |  | | <p>OR</p> <p>Lattice enthalpy + $\Delta H(\text{solution}) \text{Na}_2\text{CO}_3$ $= 2 \times \Delta H(\text{hydration}) \text{Na}^+ + \Delta H(\text{hydration}) \text{CO}_3^{2-}$ ✓</p> <p>IGNORE state symbols for equation approach</p> |
| | Total | 14 | |

| Question | Expected answers | Marks | Additional guidance | | |
|----------|------------------|-------|---|---|--|
| 3 | a | | <p>Co: $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^7 4s^2$ ✓</p> <p>Co³⁺: $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^6$ ✓</p> | 2 | <p>ALLOW $(1s^2 2s^2 2p^6) 3s^2 3p^6 4s^2 3d^7$ (i.e. 4s before 3d)</p> <p>ALLOW upper case D, etc. and subscripts, e.g. [Ar]4S₂3D₇</p> <p>If included, ALLOW 4s⁰</p> |
| | b | | catalyst OR coloured ✓ | 1 | IGNORE forms different oxidation states |
| | c | | Donates an electron/lone pair to a metal ion OR forms a coordinate bond to a metal ion ✓ | 1 | <p>ALLOW donates an electron pair/lone pair to a metal/transition element</p> <p>ALLOW dative (covalent) bond for coordinate bond</p> |
| | d | i | Co(OH) ₂ ✓ precipitation ✓ | 2 | <p>Mark independently</p> <p>ALLOW Co(OH)₂(H₂O)₄</p> <p>ALLOW precipitate (reaction)</p> |
| | | ii | CoCl ₄ ²⁻ ✓ ligand substitution ✓ | 2 | <p>Mark independently</p> <p>ALLOW ligand exchange</p> <p>DO NOT ALLOW just substitution</p> |

| Question | Expected answers | Marks | Additional guidance |
|-------------|--|-------|---|
| 3 e i |  | 4 | <p>ANNOTATIONS MUST BE USED CARE: Cl can be on any position, e.g. for B</p>  <p>complex ions in C and D can be other way around In one complex ion, the 2 Cls must be opposite one another In the other complex ion, the 2 Cls must be next to one another CARE: Cl atoms can be on any position, e.g. for C and D</p>  |
| | <p>Marking sequence See also Appendix 2 for examples</p> <ol style="list-style-type: none"> 1. Mark any correct complex ions first Do not look at these complex ions again 2. Mark with crosses any complex ions with incorrect ligands. This could include Cl in complex A, and NH_3Cl and NH_3^+Cl^-, but NOT $\text{NH}_3\text{-----}$ connectivity on the LEFT only and NOT Cl^- and NOT just NH_3^+ Do not look at these complex ions again 3. In the remaining complex ions, identify errors in ligands (See Appendix 2): e.g. <ul style="list-style-type: none"> • NH_3 ligands bonded to an H on the LEFT only: $\text{NH}_3\text{-----}$ (<i>connectivity error</i>) • Cl^- • NH_3^+ Mark these complex ions to maximise errors but treat any incorrectly bonded NH_3, Cl^- and NH_3^+ as ECF | | |

| Question | | | Expected answers | Marks | Additional guidance |
|------------------------------------|---|----|--|-----------|--|
| SEE APPENDIX 2 FOR EXAMPLES | | | | | |
| 3 | e | ii | <p>143.4 OR 107.9 + 35.5 (g mol⁻¹) used <i>i.e. molar mass AgCl</i> OR amount of AgCl = 0.02(000) mol ✓</p> <p>Ratio ratio complex : Cl⁻ = 1 : 2 OR 0.01 : 0.02 ✓</p> <p>Identification – available from 1 : 2 ratio OR 2Cl⁻ Therefore the complex is B ✓</p> | 3 | <p>DO NOT ALLOW AgCl₂</p> <p>DO NOT ALLOW $\frac{2.868}{0.01}$ 0.01 linked to AgCl, not complex ALLOW this mark ONLY for evidence of Cl⁻</p> <p>Quality of Written Communication Identification as B is dependent on correct 1 : 2 ratio OR 2Cl⁻ for this mark</p> |
| | | | Total | 15 | |

| Question | Expected answers | Marks | Additional guidance |
|-------------|--|-------|--|
| 4 a i | A strong acid completely dissociates AND a weak acid partially dissociates ✓ | 1 | ALLOW ionises for dissociates |
| | ii $(K_a =) \frac{[H^+][NO_2^-]}{[HNO_2]}$ ✓ | 1 | DO NOT ALLOW $\frac{[H^+]^2}{[HNO_2]}$ Square brackets are required |
| | iii FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 1.89 award 2 marks IF answer = 1.9 award 1 mark ----- pH = $-\log 0.0129 = 1.89$ ✓✓ OR pH = $-\log 0.0129 = 1.9$ ✓ <i>not two decimal places</i> | 2 | IF there is an alternative answer to more decimal places, check calculator value ----- Working to get to 0.0129 (mol dm⁻³) Not required and no credit $[H^+] = \sqrt{K_a \times [HNO_2]} = \sqrt{4.43 \times 10^{-4} \times 0.375}$ ALLOW 1 mark for an answer with more than 2 decimal places that rounds back to 1.89 |
| | iv $HNO_3 + HNO_2 \rightleftharpoons NO_3^- + H_2NO_2^+$ ✓ Acid 1 Base 2 Base 1 Acid 2 ✓ | 2 | State symbols NOT required ALLOW 1 AND 2 labels the other way around. ALLOW 'just acid' and 'base' labels if linked by lines so that it is clear what the acid–base pairs are IF proton transfer is wrong way around ALLOW 2nd mark for idea of acid–base pairs, <i>i.e.</i> $HNO_3 + HNO_2 \rightleftharpoons H_2NO_3^+ + NO_2^-$ * Base 2 Acid 1 Acid 2 Base 1 ✓ NOTE For the 2nd marking point (acid–base pairs), this is the ONLY acceptable ECF |

| Question | | | Expected answers | Marks | Additional guidance |
|----------|---|----|---|-------|--|
| | | | | | <i>i.e., NO ECF from impossible chemistry</i> |
| 4 | b | i | Proton acceptor ✓ | 1 | ALLOW H ⁺ acceptor |
| | | ii | <p>Marks are for correctly calculated values. Working shows how values have been derived.</p> <p>$[\text{OH}^-] = 2 \times 0.04(00) = 0.08(00) \text{ (mol dm}^{-3}\text{)} \checkmark$</p> <p>$[\text{H}^+] = \frac{1.00 \times 10^{-14}}{0.08(00)} \text{ OR } 1.25 \times 10^{-13} \text{ (mol dm}^{-3}\text{)} \checkmark$</p> <p>$\text{pH} = -\log 1.25 \times 10^{-13} = \mathbf{12.90} \checkmark$</p> <p>-----</p> <p>pOH variation (also worth 3 marks)</p> <p>$[\text{OH}^-] = 2 \times 0.04(00) = 0.08(00) \text{ (mol dm}^{-3}\text{)} \checkmark$</p> <p>$\text{pOH} -\log 0.08(00) = 1.10 \checkmark$</p> <p>$\text{pH} = 14.00 - 1.10 = 12.90 \checkmark$</p> | 3 | <p>ALLOW by ECF $\frac{1.00 \times 10^{-14}}{\text{calculated value of } [\text{OH}^-]}$</p> <p>DO NOT ALLOW 12.9 <i>not two decimal places</i></p> <p>-----</p> <p>COMMON ERRORS</p> <p>12.60 ✓✓ <i>no × 2 for [OH⁻]</i></p> <p>12.6 ✓ <i>no × 2 for [OH⁻] AND 1 DP only</i></p> <p>12.30 ✓✓ <i>÷ 2 [OH⁻]</i></p> <p>12.3 ✓ <i>÷ 2 [OH⁻] AND 1 DP only</i></p> <p>1.40 NO marks</p> |
| | c | | <p>$\text{Ca(OH)}_2 + 2\text{HNO}_2 \rightarrow \text{Ca(NO}_2)_2 + 2\text{H}_2\text{O} \checkmark$</p> <p>$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \checkmark$</p> | 2 | ALLOW: $2\text{H}^+ + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O}$ |

| Question | Expected answers | Marks | Additional guidance |
|-------------|---|-------|---|
| 4 d i | <p>Equilibrium $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \checkmark$</p> | | <p><i>ANNOTATIONS MUST BE USED</i> Equilibrium sign is required IGNORE $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ DO NOT ALLOW $\text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$ DO NOT ALLOW $\text{NaHCO}_3 \rightleftharpoons \text{Na}^+ + \text{HCO}_3^-$ IGNORE $\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$</p> |
| | <p>Action of buffer</p> <p>Added alkali H_2CO_3 reacts with added alkali OR $\text{H}_2\text{CO}_3 + \text{OH}^- \rightarrow$ OR added alkali reacts with H^+ OR $\text{H}^+ + \text{OH}^- \rightarrow \checkmark$</p> <p>Equilibrium \rightarrow right OR equilibrium shifts forming H^+ OR $\text{HCO}_3^- \checkmark$</p> | | <p>IF $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ OR $\text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$ have been used above: ALLOW all marks that meet marking alternatives as written NOTE The 1st 'added acid' mark cannot then be accessed</p> <p>Equilibrium responses must refer back to a written equilibrium BUT IF $\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-$ shown above, assume that any equilibrium comments apply to the correct equilibrium</p> <p>IF more than one equilibrium shown, it must be clear which equilibrium is being referred to</p> <p>ALLOW added alkali reacts with weak acid</p> <p>Quality of Written Communication Mark is for linking the action of the buffer in controlling added alkali and hence pH</p> |

| Question | Expected answers | Marks | Additional guidance |
|----------|---|----------|--|
| | <p>Added acid HCO_3^- reacts with added acid ✓</p> <p>Equilibrium → left OR equilibrium shifts forming H_2CO_3 ✓</p> | 5 | <p>HCO_3^- is required for this mark BUT ... ALLOW added acid reacts with conjugate base ONLY if HCO_3^- is present in equilibrium with H_2CO_3 DO NOT ALLOW salt reacts with added acid</p> |
| 4 | <p>d ii FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 6.6 : 1 OR 1 : 0.15 CHECK ratio is $\text{HCO}_3^- : \text{H}_2\text{CO}_3$ and award 5 marks. IF answer = 0.15 : 1 , CHECK ratio is $\text{H}_2\text{CO}_3 : \text{HCO}_3^-$ and award 4 marks</p> <p>-----</p> <p>In blood at pH 7.40, $[\text{H}^+] = 10^{-\text{pH}} = 10^{-7.40} = 3.98 \times 10^{-8} \text{ (mol dm}^{-3}\text{)} \checkmark$ $K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{3.98 \times 10^{-8} \times 10.5}{1}$ OR $K_a = 4.18 \times 10^{-7} \text{ (mol dm}^{-3}\text{)} \checkmark$</p> <p>In blood at pH 7.20, $[\text{H}^+] = 10^{-\text{pH}} = 10^{-7.20} = 6.31 \times 10^{-8} \text{ (mol dm}^{-3}\text{)} \checkmark$ $\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{K_a}{[\text{H}^+]} \text{ OR } \frac{4.18 \times 10^{-7}}{6.31 \times 10^{-8}} \checkmark$ $= \frac{6.6}{1} \text{ OR } 6.6 : 1 \checkmark \text{ (up to calc. value, see below)}$ ALLOW any answer with > 1 decimal place that rounds back to 6.62 OR 6.63</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>ANNOTATIONS MUST BE USED FOR ALTERNATIVE using Henderson–Hasselbalch equation below</p> <p>-----</p> <p>ALLOW 3.98×10^{-8} up to calculator value of $3.981071706 \times 10^{-8}$ correctly rounded</p> <p>ALLOW 6.31×10^{-8} up to calculator value of $6.309573445 \times 10^{-8}$ correctly rounded</p> <p>-----</p> <p>Common errors 0.15 : 1 ✓✓✓✓ <i>Inverse ratio of $\text{H}_2\text{CO}_3 : \text{HCO}_3^-$</i> 16.6 : 1 OR 0.06 : 1 ✓✓✓✓ <i>10.5/1 swapped over in 2nd mark giving K_a value of 3.79×10^{-9}</i></p> <p>ALLOW answer with > 1 decimal place that rounds back to 16.64 OR 16.65</p> |
| | <p>ALTERNATIVE approach for concentrations using Henderson–Hasselbalch equation (5 marks)</p> <p>$\text{pH} = \text{p}K_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \text{ OR } -\log K_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \checkmark$</p> <p>$\text{p}K_a = \text{pH} - \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 7.40 - \log \frac{10.5}{1} = 6.38 \checkmark \text{ (subsumes previous mark) Calculator: } 6.378810701$</p> | | |

| Question | Expected answers | Marks | Additional guidance |
|----------|---|-----------|---------------------|
| | <p>At pH = 7.20, $\log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \text{pH} - \text{p}K_a = 7.20 - 6.38 = 0.82 \checkmark$ (subsumes previous mark)</p> <p>$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{0.82} \checkmark = \frac{6.6}{1} \text{ OR } 6.6 : 1 \checkmark$</p> | | |
| | Total | 22 | |

| Question | Expected answers | Marks | Additional guidance |
|-------------|--|-----------|---|
| 5 a i | Complete circuit with electrodes to voltmeter AND salt bridge between solutions ✓ Fe ³⁺ /Fe ²⁺ half-cell with Pt electrode AND 1 mol dm ⁻³ / 1 M Fe ²⁺ and 1 mol dm ⁻³ / 1 M Fe ³⁺ ✓ Ni electrode in (1 mol dm ⁻³) Ni ²⁺ half-cell ✓ | 3 | circuit shown must be complete, <i>i.e. must be capable of working</i> salt bridge must be labelled. electrodes AND salt bridge must dip into/touch both solutions ALLOW cells drawn either way around ALLOW Fe ³⁺ /Fe ²⁺ 1 mol dm ⁻³ / 1 M / 1 molar ALLOW BOTH solutions same concentration/equimolar DO NOT ALLOW 1 mol OR 1 dm ⁻³ IGNORE any temperature or pressure, even if wrong |
| | ii 1.02 V AND – sign ✓ 0.49 V AND + sign ✓ | 2 | IGNORE any sign BEFORE cell potential ALLOW 1 mark for correct values AND signs BOTH the wrong way round: <i>i.e.</i> 1.02 V AND + sign AND 0.49 V AND – sign |
| b | Cell A (based on 1 and 2) Ni + 2Fe ³⁺ → Ni ²⁺ + 2Fe ²⁺ ✓ Cell B (based on 1 and 3) 2Cr + 3Ni ²⁺ → 2Cr ³⁺ + 3Ni ✓ concentrations (of the ions in each cell) change OR concentrations are not standard ✓ | 3 | In equations, ALLOW equilibrium sign, ⇌ instead of → Equations are required for the first two marking points ALLOW Ni → Ni ²⁺ + 2e ⁻ ALLOW Ni ²⁺ + 2e ⁻ → Ni ALLOW any statement that a concentration is changing IGNORE 'non-standard conditions' |
| c i | MH + OH ⁻ → M + H ₂ O + e ⁻ ✓ | 1 | ALLOW MH → M + H ⁺ + e ⁻ |
| | ii adsorbed (on a solid) OR on the surface (of a solid) OR as a liquid under pressure ✓ | 1 | DO NOT ALLOW adsorbed into the solid CON DO NOT ALLOW just 'as a liquid' |
| | Total | 10 | |

| Question | Expected answers | Marks | Additional guidance |
|----------|------------------|-------|---------------------|
| 6 | a | 1 | |
| | b | 2 | |
| | c | 2 | |
| | d | 2 | |

Expected answers for Question 6:

a $\Delta G = \Delta H - T\Delta S$ ✓

b process sign

$2\text{CO(g)} + \text{O}_2\text{(g)} \longrightarrow 2\text{CO}_2\text{(g)}$ —

$\text{NaCl(s)} + \text{(aq)} \longrightarrow \text{NaCl(aq)}$ +

$\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{O(s)}$ —

$\text{Mg(s)} + \text{H}_2\text{SO}_4\text{(aq)} \longrightarrow \text{MgSO}_4\text{(aq)} + \text{H}_2\text{(g)}$ +

$\text{CuSO}_4\text{(s)} + 5\text{H}_2\text{O(l)} \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O(s)}$ —

All 5 correct → 2 marks ✓✓
4 correct → 1 mark ✓

c $\Delta S = (4 \times 211 + 6 \times 189) - (4 \times 192 + 5 \times 205)$ ✓
 $\Delta S = (+)185 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$ ✓

d With increasing temperature
 $T\Delta S$ is more negative **OR** $T\Delta S$ decreases
OR $-T\Delta S$ increases **OR** $|T\Delta S|$ increases
OR magnitude of $T\Delta S$ increases ✓

At high temperature $T\Delta S$ is more negative than ΔH
OR
at high T , $T\Delta S$ outweighs/is more significant than ΔH
OR
At low temperature $\Delta H - T\Delta S < 0$
OR
At high temperature $\Delta H - T\Delta S > 0$ ✓

Additional guidance for Question 6c:

ALLOW ECF from working line above from a single error

COMMON ERRORS

(+)3 (J K⁻¹ mol⁻¹) ✓ (211 + 189) – (192 + 205)
– 185 (J K⁻¹ mol⁻¹) ✓ *incorrect sign*

Additional guidance for Question 6d:

ANNOTATIONS MUST BE USED

DO NOT ALLOW just $T\Delta S$ increases

DO NOT ALLOW At high T , ' $-T\Delta S$ is greater (than ΔH)'

APPROACH BASED ON TOTAL ENTROPY:

With increasing temperature
 $\Delta H/T$ is less negative **OR** $\Delta H/T$ increases
OR $-\Delta H/T$ decreases **OR** $|\Delta H/T|$ decreases
OR magnitude of $\Delta H/T$ decreases ✓

ALLOW at high temperatures
 $\Delta S - \Delta H/T < 0$

| Question | | Expected answers | Marks | Additional guidance |
|--------------|---|--|-----------|--|
| | | | | OR ΔS is more negative than $\Delta H/T$ OR ΔS outweighs/ is more significant than $\Delta H/T$ |
| 6 | e | (For feasibility,) $\Delta G < 0$ OR $\Delta G = 0$ OR $0 < \Delta H - T\Delta S$ OR $0 = \Delta H - T\Delta S$ OR $0 = 493 - T \times 543/1000 \checkmark$ $T = \frac{\Delta H}{\Delta S} = 493 \times 1000/543 \checkmark$ $= 908 \text{ K} \checkmark$ Units of temperature are required | 3 | ALLOW total entropy statement: $\Delta S(\text{total}) = 0$ OR $\Delta S(\text{total}) > 0$ ALLOW $0 = 493 - T \times 543 \checkmark$ <i>i.e. This mark focuses on ΔG OR $\Delta H - T\Delta S$ being = 0 and NOT on conversion of ΔS value into $\text{kJ K}^{-1} \text{mol}^{-1}$</i> Mark temperature given on answer line ALLOW 3 SF up to calculator value 907.9189687 correctly rounded, e.g. 907.9, 907.92 ALLOW temperature in $^{\circ}\text{C}$: i.e. ALLOW by subtraction of 273: 635, 634.9, 634.91 $^{\circ}\text{C}$ ALLOW by subtraction of 273.15: 635, 634.8, 634.77 $^{\circ}\text{C}$ up to calculator value correctly rounded ALLOW C for $^{\circ}\text{C}$; $^{\circ}\text{K}$ for K IF ΔS has not been converted to kJ, DO NOT ALLOW 2nd mark BUT ... ALLOW calculated answer = $493/543 = 0.91 \text{ K}$ (calculator: 0.907918968) ALLOW 2 marks only for absence of one of the statements required for 1st marking point |
| Total | | | 10 | |

| Question | Expected answers | Marks | Additional guidance | | | | | | | | | | | | | | | | | | |
|--|---|--|--|--|------------|--|---------|-------------|---|---------|-------------|---|--------|-------------|---|------|-----------------------------------|---|-------|--------------------------|--|
| 7 a | <p>FIRST, CHECK THE ANSWER ON ANSWER LINE IF numerical value = 7.81×10^{-2} OR 0.0781 AND $[N_2O_4] = 0.2(00 \text{ mol dm}^{-3}$ AND $[NO_2] = 1.6(0)$, award 4 calculation marks and check for the mark for correct units</p> <hr/> <p>Equilibrium amount of N₂O₄ 0.400 mol N₂O₄ ✓</p> <p>Equilibrium concentrations $[N_2O_4] = 0.200 \text{ mol dm}^{-3}$ AND $[NO_2] = 1.60 \text{ mol dm}^{-3}$ ✓</p> <p>K_c expression $K_c = \frac{[N_2O_4]}{[NO_2]^2}$ (Square brackets essential) OR $\frac{0.200}{1.60^2}$ ✓</p> <p>Calculation = 7.81×10^{-2} ✓</p> <p>Units dm³ mol⁻¹ ✓</p> | 5 | <p>IF there is an alternative answer, check to see if there is any ECF credit possible using working below</p> <hr/> <p>ANNOTATIONS MUST BE USED</p> <hr/> <p>ALLOW ECF for equilibrium amounts ÷ 2</p> <p>ALLOW 3 SF up to calculator value of 0.078125 correctly rounded ALLOW ECF using calculated equilibrium concentrations</p> <p>For units, ALLOW mol⁻¹ dm³ ALLOW ECF from incorrect K_c expression</p> | | | | | | | | | | | | | | | | | | |
| | <p>Common errors for 4 calculation marks – Remember there is another mark for units</p> <table border="0" style="width: 100%;"> <tr> <td style="width: 30%;">7.81 x 10⁻² from wrong concs</td> <td style="width: 30%;">✓✓ + units</td> <td style="width: 40%;"><i>look for $[N_2O_4] = 0.8$ AND $[NO_2] = 3.2$</i></td> </tr> <tr> <td>0.03906</td> <td>✓✓✓ + units</td> <td><i>no conversion of both moles to concentration</i></td> </tr> <tr> <td>0.01953</td> <td>✓✓✓ + units</td> <td><i>no conversion of NO₂ moles to concentration</i></td> </tr> <tr> <td>0.3125</td> <td>✓✓✓ + units</td> <td><i>moles of N₂O₄ taken as 3.2/2</i></td> </tr> <tr> <td>12.8</td> <td>✓✓✓ + units: mol dm⁻³</td> <td><i>K_c expression upside down</i></td> </tr> <tr> <td>0.125</td> <td>✓✓✓ + units; none</td> <td><i>$[NO_2]$ instead of $[NO_2]^2$ ‘No units’ MUST be stated</i></td> </tr> </table> <p>0.15625 MARK BY ECF as there are many different routes to this answer</p> | | | 7.81 x 10 ⁻² from wrong concs | ✓✓ + units | <i>look for $[N_2O_4] = 0.8$ AND $[NO_2] = 3.2$</i> | 0.03906 | ✓✓✓ + units | <i>no conversion of both moles to concentration</i> | 0.01953 | ✓✓✓ + units | <i>no conversion of NO₂ moles to concentration</i> | 0.3125 | ✓✓✓ + units | <i>moles of N₂O₄ taken as 3.2/2</i> | 12.8 | ✓✓✓ + units: mol dm ⁻³ | <i>K_c expression upside down</i> | 0.125 | ✓✓✓ + units; none | <i>$[NO_2]$ instead of $[NO_2]^2$ ‘No units’ MUST be stated</i> |
| 7.81 x 10 ⁻² from wrong concs | ✓✓ + units | <i>look for $[N_2O_4] = 0.8$ AND $[NO_2] = 3.2$</i> | | | | | | | | | | | | | | | | | | | |
| 0.03906 | ✓✓✓ + units | <i>no conversion of both moles to concentration</i> | | | | | | | | | | | | | | | | | | | |
| 0.01953 | ✓✓✓ + units | <i>no conversion of NO₂ moles to concentration</i> | | | | | | | | | | | | | | | | | | | |
| 0.3125 | ✓✓✓ + units | <i>moles of N₂O₄ taken as 3.2/2</i> | | | | | | | | | | | | | | | | | | | |
| 12.8 | ✓✓✓ + units: mol dm ⁻³ | <i>K_c expression upside down</i> | | | | | | | | | | | | | | | | | | | |
| 0.125 | ✓✓✓ + units; none | <i>$[NO_2]$ instead of $[NO_2]^2$ ‘No units’ MUST be stated</i> | | | | | | | | | | | | | | | | | | | |

| Question | Expected answers | Marks | Additional guidance |
|----------|--|----------|--|
| 7 b | <p><i>Each marking point is independent</i></p> <p>Effect on K_c K_c does not change (with pressure) ✓</p> <p>Comparison of conc terms after increase in pressure $[\text{NO}_2]^2$ increases more than $[\text{N}_2\text{O}_4]$ OR concentration (term) on bottom (of K_c) increases more than concentration (term) on top (of K_c) ✓</p> <p>Changes in concentrations linked to K_c (amount /concentration of) N_2O_4 increases AND (amount /concentration of) NO_2 decreases AND to maintain/restore K_c ✓</p> | 3 | <p>ALLOW K_c only changes with temperature IGNORE K_c changes with temperature</p> <p>ALLOW $\frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} < K_c$ OR $\frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$ decreases</p> <p>IGNORE K_c decreases</p> <p>ALLOW top of K_c expression increases and bottom decreases until K_c is reached ALLOW equilibrium shifts to right to maintain/restore K_c</p> <p>IGNORE just 'restores equilibrium' K_c IS REQUIRED IGNORE just 'equilibrium shifts to right' IGNORE le Chatelier response: 'equilibrium shifts to right' because there are fewer moles of gas on right-hand side</p> |
| | Total | 8 | |

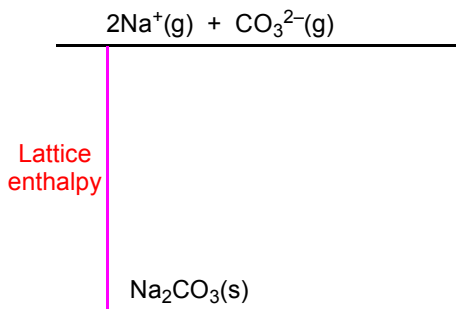
| Question | Expected answers | Marks | Additional guidance |
|----------|---|-------|--|
| 8 a | $\text{Fe}_2\text{O}_3 + 6\text{H}^+ \longrightarrow 2\text{Fe}^{3+} + 3\text{H}_2\text{O} \checkmark$ | 1 | <p>ALLOW $\text{Fe}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O}$ OR $\text{Fe}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{Fe}^{3+} + 6\text{Cl}^- + 3\text{H}_2\text{O}$</p> <p>ALLOW correct multiples</p> <p>IGNORE state symbols</p> <p>DO NOT ALLOW Fe_2Cl_6 as a product</p> |
| b | $\text{Sn}^{2+} + 2\text{Fe}^{3+} \longrightarrow \text{Sn}^{4+} + 2\text{Fe}^{2+} \checkmark$ $6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \longrightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \checkmark$ | 2 | <p>IGNORE state symbols</p> <p>ALLOW overall equations: $\text{SnCl}_2 + 2\text{FeCl}_3 \longrightarrow \text{SnCl}_4 + 2\text{FeCl}_2$</p> <p>$6\text{FeCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} \longrightarrow 6\text{FeCl}_3 + 2\text{CrCl}_3 + 2\text{KCl} + 7\text{H}_2\text{O}$</p> <p>ALLOW correct multiples</p> |

| Question | Expected answers | Marks | Additional guidance |
|----------|---|-------|--|
| 8 c | <p>FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 54.6%, award 5 marks</p> <hr/> <p>Amount Fe²⁺ in 250 cm³ solution – 3 marks amount Cr₂O₇²⁻ used = $0.0200 \times \frac{26.5}{1000}$ = 5.30×10^{-4} (mol) ✓</p> <p>amount Fe²⁺ = $6 \times 5.30 \times 10^{-4}$ = 3.18×10^{-3} mol ✓</p> <p>amount Fe²⁺ in original 250 cm³ = $10 \times 3.18 \times 10^{-3}$ = 3.18×10^{-2} (mol) ✓</p> | | <p>ANNOTATIONS MUST BE USED IF there is an alternative answer, 1st check common errors below. Then see if there is any ECF credit possible using working below</p> <hr/> <p>Working must be to at least 3 SF throughout BUT ignore trailing zeroes, <i>i.e.</i> for 0.490 allow 0.49</p> <p>ALLOW ECF from different Fe²⁺ ratio in equation from 8(b) BUT still ALLOW 6 : 1 even from different ratio in equation If no equation use actual 6 : 1 ratio DO NOT AWARD 'ratio mark' at all for use of 1 : 1 ratio – <i>makes problem easier</i></p> <p>ECF 10 × answer above</p> |
| | <p>% Fe in ore – 2 marks mass of Fe in ore = $55.8 \times 3.18 \times 10^{-2}$ g = 1.77444 g ✓</p> | | <p>ECF 55.8 × answer above</p> <p>IF answer above has not been used AND × 55.8, DO NOT ALLOW this mark but do ALLOW final %</p> <p>IF answer above AND 55.8 are BOTH not used, then DO NOT ALLOW ANY further marks</p> |
| | <p>percentage Fe in ore = $\frac{1.77444}{3.25} \times 100$ = 54.6% ✓</p> | 5 | <p>ECF $\frac{\text{answer above}}{3.25} \times 100$</p> <p>ALLOW 54.5% (from 1.77 g) AND any answer with > 1 decimal place that rounds back to 54.5 OR 54.6</p> |
| | | | <p>COMMON ERRORS</p> <p>5.46 ✓✓✓✓ × 10 omitted 51.5 ✓✓✓✓ titre taken as 25.0 156.2 ✓✓✓✓ × 159.6 instead of 55.8 15.62 ✓✓✓ × 159.6 and × 10 omitted 45.5 ✓✓✓✓ 5 : 1 ratio 1.52 ✓✓✓✓ ÷ 6 instead of × 6</p> |

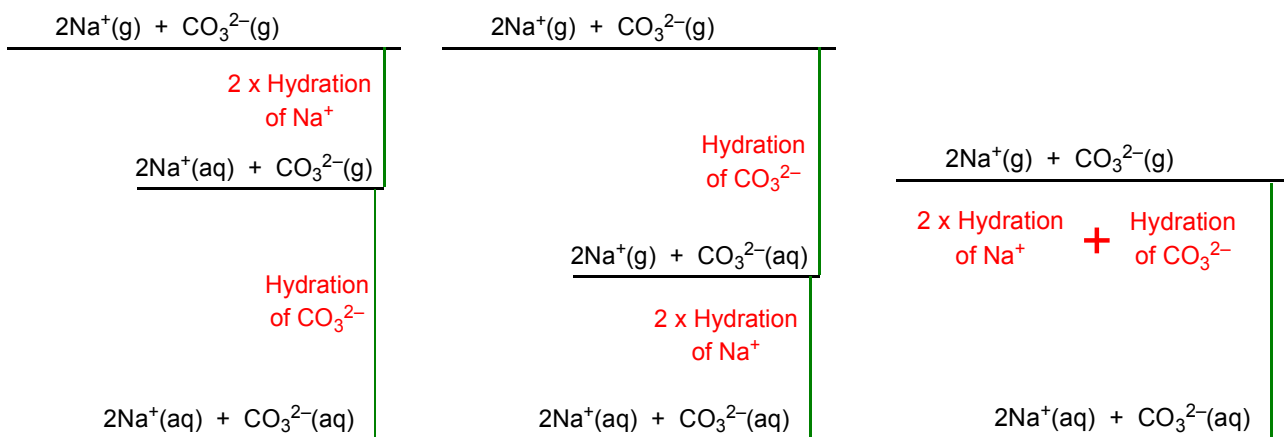
| Question | | Expected answers | Marks | Additional guidance |
|--------------|---|---|-----------|--|
| 8 | d | E^\ominus for MnO_4^- is more positive/greater than Cl_2 OR E^\ominus for $\text{Cr}_2\text{O}_7^{2-}$ is less positive/smaller than Cl_2 ✓ MnO_4^- reacts with Cl^- OR HCl (forming Cl_2 gas) OR $\text{Cr}_2\text{O}_7^{2-}$ does not react with Cl^- ions ✓ | 2 | ORA: E^\ominus for Cl_2 is less positive/smaller than MnO_4^- OR E^\ominus for Cl_2 is more positive/greater than $\text{Cr}_2\text{O}_7^{2-}$ |
| Total | | | 10 | |

APPENDIX 1

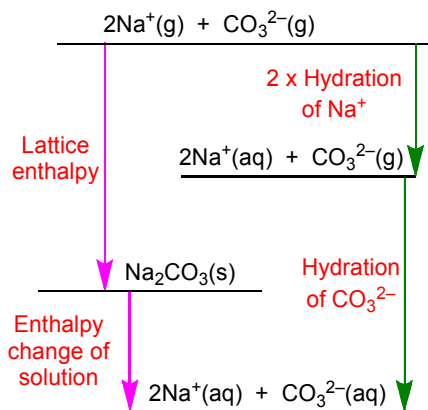
MARK 1



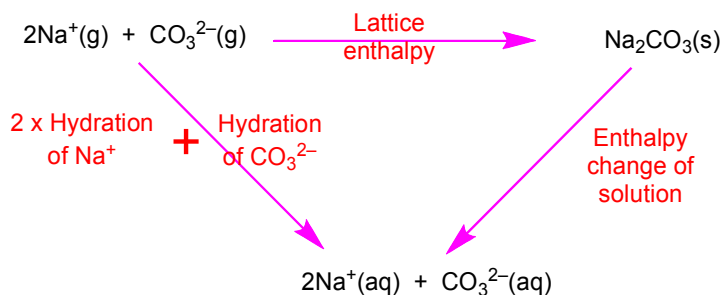
MARK 2



MARK 3



A simple energy cycle can be awarded 2 marks only



Mark 1

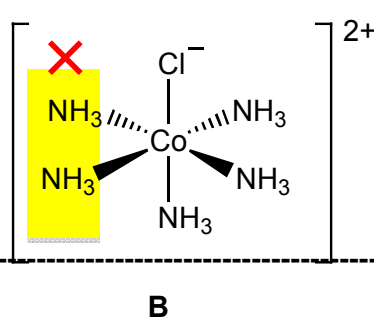
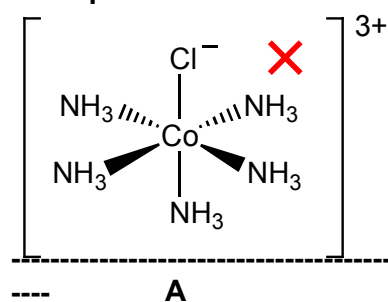
All species, state symbols and labels

Mark 2

Arrows added in correct directions

APPENDIX 2

Example 1



No complex ions are correct

A is wrong because a wrong ligand has been attached. This would have been wrong even if Cl had been attached so the Cl⁻ charge is ignored at this stage

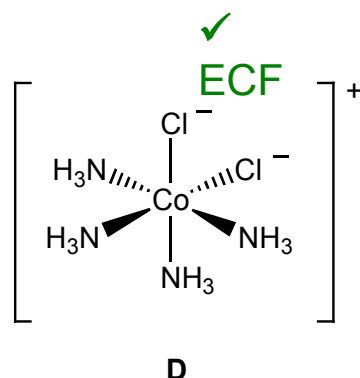
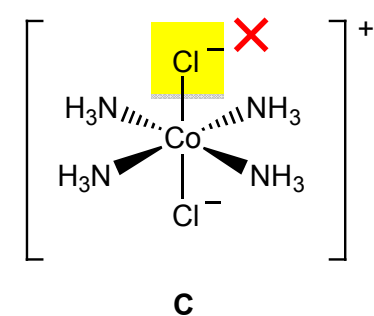
B has connectivity **and** Cl⁻ errors

C and **D** have Cl⁻ errors

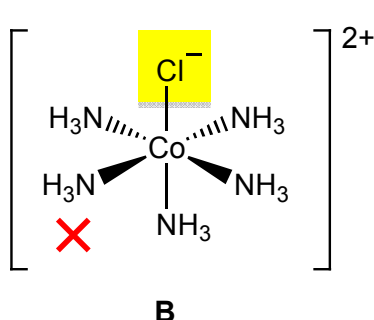
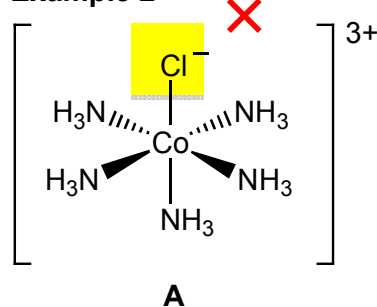
In **B**, either connectivity **OR** Cl⁻ could have been penalised. Choose which to penalise based on maximising identification of errors

If Cl⁻ had been penalised in **B**, then **C** would have been marked correctly by **ECF**.

But the candidate has clearly made 2 mistakes across **B** and **C** so NH₃ connectivity had been penalised in **B**



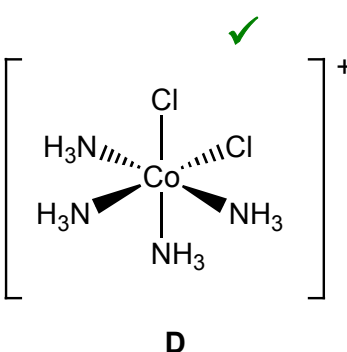
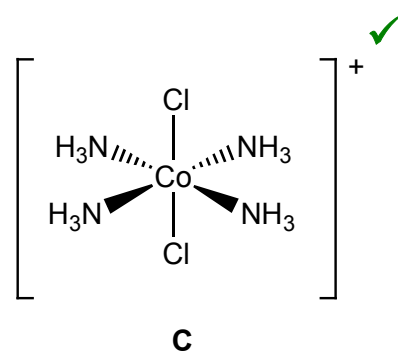
Example 2



C and **D** are correct and they have been marked correct

A is wrong because a wrong ligand has been attached. This would have been wrong even if Cl had been attached so the Cl⁻ charge is ignored at this stage

In **B**, the only error is Cl⁻. **A** also had Cl⁻ but the charge had been ignored as Cl was incorrect anyway. **B** is therefore marked wrong



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