
CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

March 2017

MARK SCHEME

Maximum Mark: 100

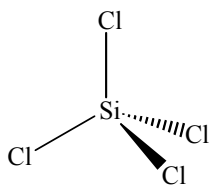
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This mark scheme is published as an aid to teachers and candidates, to indicate the requirements of the examination. It shows the basis on which Examiners were instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began, which would have considered the acceptability of alternative answers.

Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

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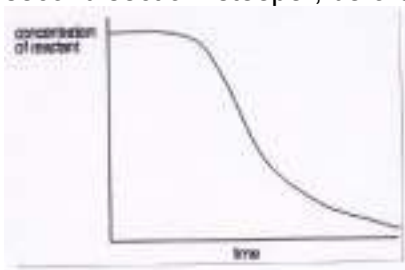
| Question | Answer | Marks |
|-----------|---|-------------|
| 1(a)(i) | $(28 \times 0.922) + (29 \times 0.047) + (30 \times 0.031) = 28.11$ | 1 |
| 1(a)(ii) | $\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_4 + 4\text{HCl}$ | 1 |
| 1(a)(iii) |  <p>diagram</p> | 1 |
| | bond angle = 109.5 | 1 |
| 1(a)(iv) | SiO_2 | 1 |
| | SiO_2 is giant covalent / molecular but SiCl_4 is simple molecular / covalent | 1 |
| 1(b)(i) | $2\text{A}(\text{NO}_3)_2 \rightarrow 2\text{AO} + 4\text{NO}_2 + \text{O}_2$ correct formula balanced equation | 2 1 1 |
| 1(b)(ii) | giant ionic | 1 |

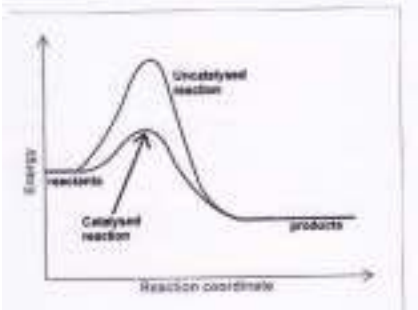
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| Question | Answer | Marks | | | | | | | | | | | | | | | | | | | | |
|--------------------------------|---|-----------------|-----------------------------|----------|-----------------------------|-------------------|--|--|---|--------------------------------|---|--|--|-------------------------------|---|--|--|------------------|--|---|--|----------|
| 2(a) | <table border="1"> <tr> <td data-bbox="542 217 1052 316">enthalpy change</td> <td data-bbox="1052 217 1279 316">positive</td> <td data-bbox="1279 217 1505 316">negative</td> <td data-bbox="1505 217 1731 316">either positive or negative</td> </tr> <tr> <td data-bbox="542 316 1052 383">electron affinity</td> <td data-bbox="1052 316 1279 383"></td> <td data-bbox="1279 316 1505 383"></td> <td data-bbox="1505 316 1731 383">✓</td> </tr> <tr> <td data-bbox="542 383 1052 450">enthalpy change of atomisation</td> <td data-bbox="1052 383 1279 450">✓</td> <td data-bbox="1279 383 1505 450"></td> <td data-bbox="1505 383 1731 450"></td> </tr> <tr> <td data-bbox="542 450 1052 517">enthalpy change of ionisation</td> <td data-bbox="1052 450 1279 517">✓</td> <td data-bbox="1279 450 1505 517"></td> <td data-bbox="1505 450 1731 517"></td> </tr> <tr> <td data-bbox="542 517 1052 584">lattice enthalpy</td> <td data-bbox="1052 517 1279 584"></td> <td data-bbox="1279 517 1505 584">✓</td> <td data-bbox="1505 517 1731 584"></td> </tr> </table> | enthalpy change | positive | negative | either positive or negative | electron affinity | | | ✓ | enthalpy change of atomisation | ✓ | | | enthalpy change of ionisation | ✓ | | | lattice enthalpy | | ✓ | | 2 |
| enthalpy change | positive | negative | either positive or negative | | | | | | | | | | | | | | | | | | | |
| electron affinity | | | ✓ | | | | | | | | | | | | | | | | | | | |
| enthalpy change of atomisation | ✓ | | | | | | | | | | | | | | | | | | | | | |
| enthalpy change of ionisation | ✓ | | | | | | | | | | | | | | | | | | | | | |
| lattice enthalpy | | ✓ | | | | | | | | | | | | | | | | | | | | |
| 2(b)(i) | the second electron is removed from a (more) positively charged ion | 1 | | | | | | | | | | | | | | | | | | | | |
| 2(b)(ii) | ΔH_6 is lattice (energy/enthalpy) AND ΔH_7 is (energy/enthalpy of) formation | 1 | | | | | | | | | | | | | | | | | | | | |
| 2(c) | the electron affinity becomes less exothermic/negative down the Group 17 | 1 | | | | | | | | | | | | | | | | | | | | |
| | electron affinity depends (mainly) on the electron-nucleus distance which increases down Group 17 | 1 | | | | | | | | | | | | | | | | | | | | |
| 2(d) | M1 correct use of $\Delta G = \Delta H - T\Delta S$ | 1 | | | | | | | | | | | | | | | | | | | | |
| | M2 $\Delta S = 26.9 - (32.7 + 102.5) = -108.3 \text{ JK}^{-1} \text{ mol}^{-1}$ OR $-0.1083 \text{ kJK}^{-1} \text{ mol}^{-1}$ | 1 | | | | | | | | | | | | | | | | | | | | |
| | M3 $\Delta G = -602 - (298 \times (-0.1083)) = -570$ | 1 | | | | | | | | | | | | | | | | | | | | |
| | M4 units: kJ mol^{-1} | 1 | | | | | | | | | | | | | | | | | | | | |

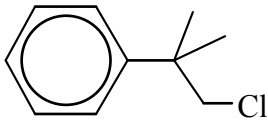
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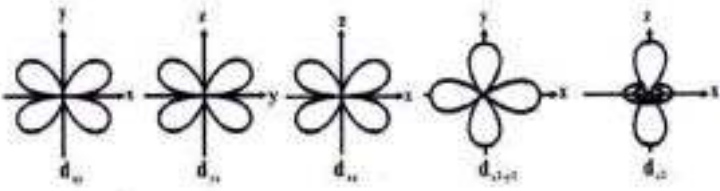
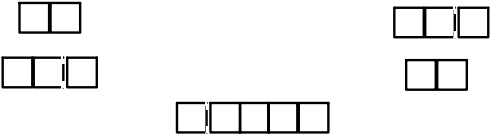
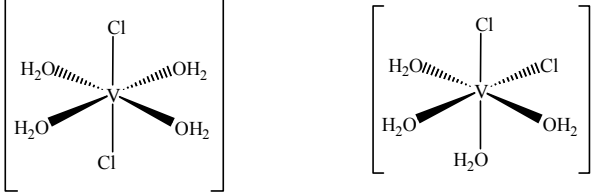
| Question | Answer | Marks |
|----------|--|----------|
| 3(a)(i) | A – H ₂ , 1 atm B – platinum C – 1 mol dm ⁻³ H ⁺ /HCl etc. D – salt bridge / KNO ₃ etc. E – platinum F – 1 mol dm ⁻³ Fe ²⁺ AND 1 mol dm ⁻³ Fe ³⁺ | 3 |
| 3(a)(ii) | positive electrode is (Pt) on RHS AND electrons flow clockwise | 1 |
| 3(b) | cell potential is 0.77 – 0.34 = (+) 0.43 (V) | 1 |
| 3(c)(i) | electrode potential would become more negative as equilibrium shifts to left / explanation in terms of the Nernst equation | 1 |
| 3(c)(ii) | $E = -0.41 + (0.059/1)\log[\text{Cr}^{3+}]/[\text{Cr}^{2+}]$ $= -0.41 + 0.059 \log 4.0$ | 1 |
| | $= -0.37 \text{ (V)}$ | 1 |


| Question | Answer | Marks | | | | | | | | | | | | |
|---|---|--------------------|---------------|-------------|---|---|--|--|---|--|---|--|---|---|
| 4(a)(i) | experiments 1 and 2: doubling $[\text{ClO}_2]$ quadruples the rate, so second order | 1 | | | | | | | | | | | | |
| | experiments 2 and 3: doubling $[\text{OH}^-]$ doubles the rate, so first order | 1 | | | | | | | | | | | | |
| | rate equation = $k[\text{ClO}_2]^2[\text{OH}^-]$ | 1 | | | | | | | | | | | | |
| 4(a)(ii) | from experiment t 2: $9.34 \times 10^{-4} = k(2.50 \times 10^{-2})^2 \times 1.30 \times 10^{-3}$ $k = 1.15 \times 10^3$ | 1 | | | | | | | | | | | | |
| | units: $\text{mol}^{-2}\text{dm}^6 \text{ s}^{-1}$ | 1 | | | | | | | | | | | | |
| 4(b)(i) | heterogeneous catalysts are in different physical state from the reactants AND homogeneous catalysts are in the same physical state as the reactants | 1 | | | | | | | | | | | | |
| 4(b)(ii) | <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>catalysed reaction</th> <th>heterogeneous</th> <th>homogeneous</th> </tr> </thead> <tbody> <tr> <td>manufacture of ammonia in the Haber process</td> <td style="text-align: center;">✓</td> <td></td> </tr> <tr> <td>removal of nitrogen oxides from car exhausts</td> <td style="text-align: center;">✓</td> <td></td> </tr> <tr> <td>oxidation of sulfur dioxide in the atmosphere</td> <td></td> <td style="text-align: center;">✓</td> </tr> </tbody> </table> | catalysed reaction | heterogeneous | homogeneous | manufacture of ammonia in the Haber process | ✓ | | removal of nitrogen oxides from car exhausts | ✓ | | oxidation of sulfur dioxide in the atmosphere | | ✓ | 2 |
| catalysed reaction | heterogeneous | homogeneous | | | | | | | | | | | | |
| manufacture of ammonia in the Haber process | ✓ | | | | | | | | | | | | | |
| removal of nitrogen oxides from car exhausts | ✓ | | | | | | | | | | | | | |
| oxidation of sulfur dioxide in the atmosphere | | ✓ | | | | | | | | | | | | |
| 4(c)(i) | $2\text{MnO}_4^- + 6\text{H}^+ + 5(\text{CO}_2\text{H})_2 \rightarrow 2\text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O}$ correct Mn : $(\text{CO}_2\text{H})_2$ ratio rest of equation | 2 1 1 | | | | | | | | | | | | |
| 4(c)(ii) | <p>first section: flatter second section: steeper, before flattening</p>  | 2 1 1 | | | | | | | | | | | | |

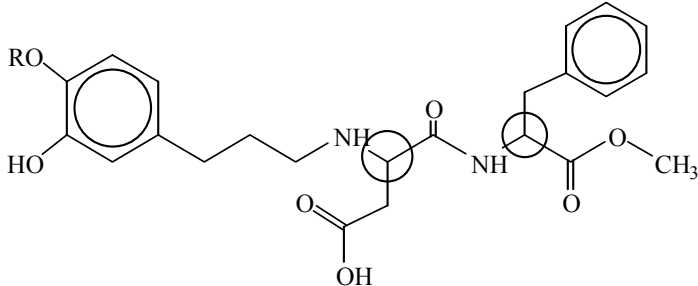
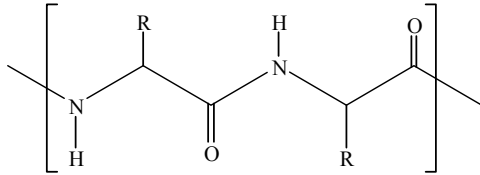
| Question | Answer | Marks |
|----------|---|--------------------------------------|
| ,4(d)(i) |  <p>diagram catalyst lowers E_a for both the forward and reverse reactions so the process requires less energy / can occur at a lower temperature</p> | <p>3</p> <p>1 1 1</p> |
| 4(d)(ii) | $K_p = \frac{(\rho\text{NH}_3)^2}{(\rho\text{N}_2)(\rho\text{H}_2)^3}$ $1.45 \times 10^{-5} = \frac{(\rho\text{NH}_3)^2}{20 \times 60 \times 60 \times 60}$ | 1 |
| | $\rho\text{NH}_3 = 7.91$ | 1 |

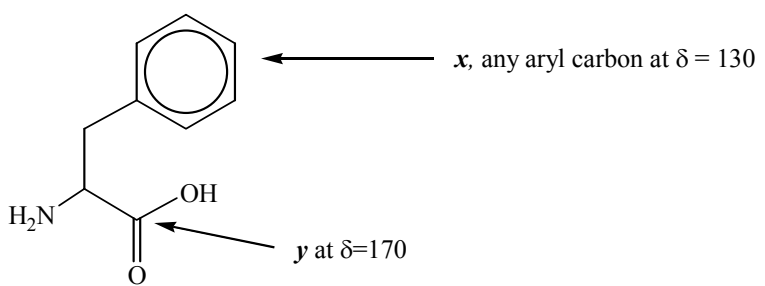
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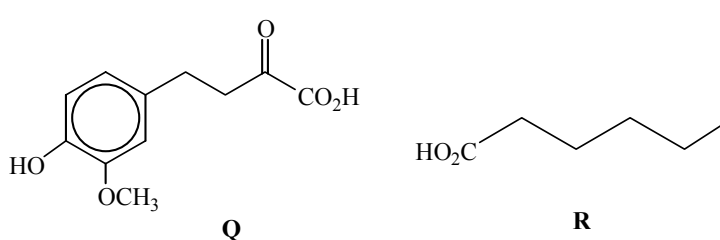
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|-----------|--|-------|
| 5(a)(i) | $(\text{CH}_3)_3\text{C-Cl} / (\text{CH}_3)_2\text{C} = \text{CH}_2$ | 1 |
| | $\text{AlCl}_3 + \text{heat}$ | 1 |
| 5(a)(ii) | (UV) light | 1 |
| 5(a)(iii) |  | 1 |
| 5(a)(iv) | ammonia / NH_3 | 1 |
| | heat in sealed tube / heat under pressure | 1 |
| 5(b) | $\text{C}_{10}\text{H}_{13}\text{NH}_2 + \text{H}_3\text{O}^+ \rightleftharpoons \text{C}_{10}\text{H}_{13}\text{NH}_3^+ + \text{H}_2\text{O}$ | 1 |
| 5(c) | in compound H , the alkyl groups are electron donating / have a positive inductive effect, so it is more basic than NH_3 | 1 |
| | in phenylamine, the lone pair (of N) is delocalised over the aryl group / benzene ring, so phenylamine is less basic than NH_3 | 1 |

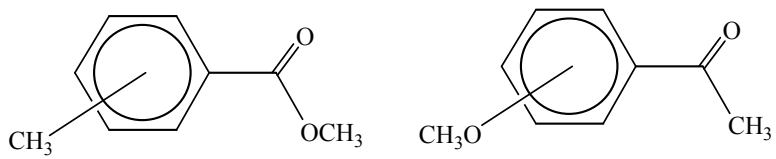
| Question | Answer | Marks |
|-----------|--|-------|
| 6(a)(i) |  | 1 |
| 6(a)(ii) | Ni : $[1s^2 2s^2 2p^6 3s^2 3p^6] 3d^8 4s^2$ Ni ³⁺ : $[1s^2 2s^2 2p^6 3s^2 3p^6] 3d^7$ | 1 |
| 6(b)(i) |  <p>octahedral complex isolated ion tetrahedral complex</p> | 1 |
| 6(b)(ii) | energy / photon is absorbed in the visible region / light | 1 |
| | electron jumps from the lower to the upper energy level / is excited | 1 |
| 6(b)(iii) | different frequency / wavelength of light are absorbed by the two complexes OR different size of energy gap | 1 |
| 6(c) | colour of solution: green | 1 |
| | explanation: because the solution absorbs most strongly in the blue AND red regions | 1 |
| 6(d)(i) |  | 2 |

| Question | Answer | Marks |
|-----------|---|-------|
| 6(d)(ii) | cis-trans / geometrical | 1 |
| 6(e)(i) |  | 2 |
| 6(e)(ii) | optical | 1 |
| 6(f)(i) | $K_{\text{stab}} = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}]}{[\text{Ni}(\text{H}_2\text{O})_6^{2+}][\text{NH}_3]^6}$ | 1 |
| 6(f)(ii) | $[\text{Ni}(\text{en})_3]^{2+}$ would be formed because it is much more stable / K_{stab} is much greater OR in the presence of both ligands the overall equilibrium $[\text{Ni}(\text{NH}_3)_6]^{2+} \rightleftharpoons [\text{Ni}(\text{H}_2\text{O})_6]^{2+} \rightleftharpoons [\text{Ni}(\text{en})_3]^{2+}$ would shift right | 1 |
| 6(f)(iii) | cis-trans isomers identified | 1 |
| | two cis isomers identified | 1 |

| Question | Answer | Marks |
|-----------|--|-----------------|
| 7(a) |  | 1 |
| 7(b)(i) | $\text{H}^+(\text{aq}) + \text{heat}$ | 1 |
| 7(b)(ii) | hydrolysis | 1 |
| 7(b)(iii) | CH_3OH | 1 |
| 7(c)(i) | white precipitate | 1 |
| 7(c)(ii) | $\text{C}_{14}\text{H}_{19}\text{O}_6\text{N} + 3\text{NaOH} \rightarrow \text{C}_{14}\text{H}_{16}\text{O}_6\text{NNa}_3 + 3\text{H}_2\text{O}$ | 2 |
| 7(d)(i) | no change / colour remains orange | 1 |
| 7(d)(ii) |  amide bond displayed two repeat units | 2 1 1 |
| 7(e)(i) | seven | 1 |

| Question | Answer | Marks |
|----------|--|-------|
| 7(e)(ii) |  | 1 |

| Question | Answer | Marks |
|-----------|---|-------|
| 8(a) | oxidation of -OH / alcohol to C=O / ketone / carbonyl | 1 |
| 8(b)(i) | dehydration / elimination | 1 |
| 8(b)(ii) | heat with Al_2O_3 OR heat with $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$ | 1 |
| 8(b)(iii) |  | 2 |
| 8(c) | phenol | 1 |
| | ketone | 1 |

| Question | Answer | Marks |
|-----------|--|-------|
| 9(a)(i) | $n = 100 \times (M+1)/(1.1 \times M) = 100 \times 3.4/(1.1 \times 33.9) = 9.1$ | 1 |
| | hence <u>9</u> carbons atoms | 1 |
| 9(a)(ii) | $C_9H_{10}O_2$ | 1 |
| 9(a)(iii) | $(150 - 119 = 31)$, hence fragment is CH_3O | 1 |
| 9(b) | V is $C=O$ AND W is $C-O$ | 1 |
| 9(c)(i) | δ 3.9 is CH or alkyl/ CH_3 next to oxygen AND δ 7.2–7.9 is CH/aryl hydrogens | 1 |
| 9(c)(ii) | alkyl H next to $C=O$ AND alkyl H next to aryl ring | 1 |
| 9(c)(iii) | none of the functional groups in T contains a labile proton/ T does not contain $-OH$ or $-NH$ groups. | 1 |
| 9(d) |  | 2 |