**Cambridge International Examinations**
Cambridge International Advanced Subsidiary and Advanced Level

**CHEMISTRY** **9701/42**

Paper 4 A Level Structured Questions **May/June 2017**

MARK SCHEME

Maximum Mark: 100

**Published**

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

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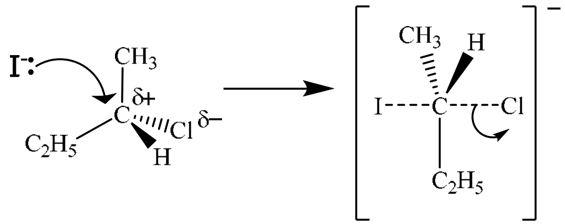
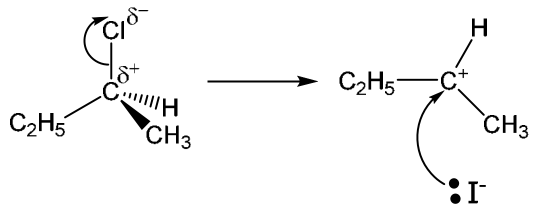
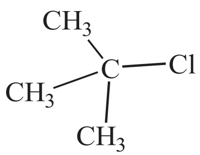
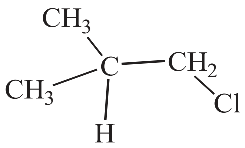
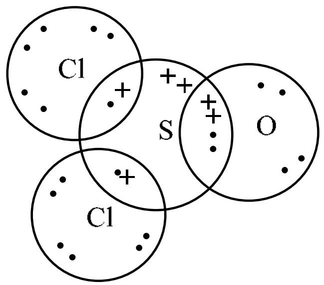
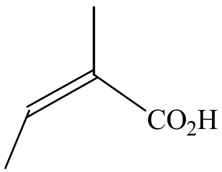
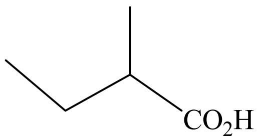
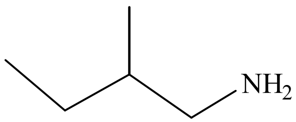
| Question | Answer | Marks |
|---|---|---|
| 1(a)(i) | increases down the group | **1** |
| | radius / size of (cat)ion/$M^{2+}$ increases | **1** |
| | less polarisation / distortion of anion / carbonate **ion** / $CO_3^{2-}$ | **1** |
| 1(a)(ii) | $Na^+$ has smaller ionic charge **and** larger ionic radii<br><br>OR the **charge density** of the **$Na^+$** is **lower** | **1** |
| 1(b)(i) | $2KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O$ | **1** |
| 1(b)(ii) | $NaHCO_3$ because $Na^+$ is **smaller** OR charge density $Na^+$ is **larger** | **1** |
| 1(c)(i) | LE $= \Delta H_f - 2(\Delta H_{at} + IE) - ½(O{=}O) - (EA_1 + EA_2)$ **1**<br>$= -361 - 2(89) - 2(418) - 496/2 - (-141+798)$ **1**<br>$=$ **$-2280$** (kJ $mol^{-1}$) correct answer scores [3] **1** | **3** |
| 1(c)(ii) | LE of $Na_2O$ will be **more negative** AND as $Na^{(+)}$ is smaller / larger charge density / smaller radii AND so greater attraction (between the ions) OR (ionic) bonds will be stronger | **1** |
| | **Total:** | **10** |

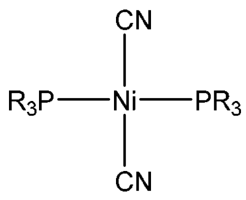
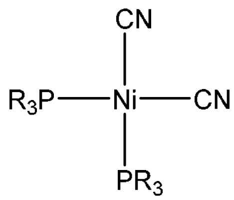
| Question | Answer | Marks |
|---|---|---|
| 2(a) | Add $AgNO_3$ $Cl^-$ gives a white ppt **and** $I^-$ gives a yellow ppt. | **1** |
| | Add $NH_3$(aq); ppt dissolves **and** ppt is insoluble | **1** |
| 2(b)(i) | conductivity **decreases** during the reaction,<br>AND number of $Na^+$ / $I^-$ / **ions** are **decreased** / used up (from solution) | **1** |
| 2(b)(ii) | (Equilibrate) solutions at 40 °C / with a water bath (cannot be after mixing)<br><br>mix **known volumes and** start the clock / timing clearly mentioned/implied<br><br>measure conductance / conductivity at regular intervals / every measured time [method A]<br>OR measure the time for conductance to go to zero / a specific value / to be constant [method B]<br><br>prepare a curve of conductance vs. time [related to method A]<br>OR prepare a curve of conductance vs. concentration [related to method A]<br>OR repeating the experiment at different concentrations [related to method A and B]<br>any 3 points | **3** |
| 2(c)(i) | [R-C$l$]: rate increases by 5 / 3 when concentration increases by 10 / 6 (5 / 3),<br>so order = 1 | **1** |
| | [$I^-$]: rate increases by 5 / 3 when concentration increases by 5 / 3,<br>so order = 1 | **1** |
| 2(c)(ii) | rate = $k[I^-][CH_3CH_2CHClCH_3]$ AND units of $k$ = $dm^3\ mol^{-1}\ s^{-1}$ | **1** |
| 2(c)(iii) | relative rate = 5 / 5.3 | **1** |

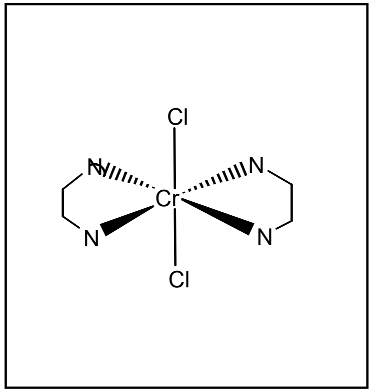
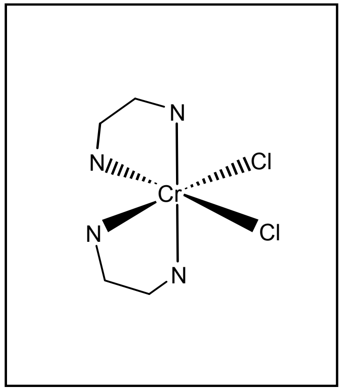
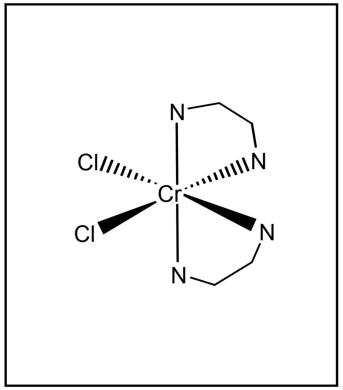
| Question | Answer | Marks |
|---|---|---|
| 2(d)(i) | either $S_N1$ or $S_N2$ mechanism<br>$S_N2$ <br>$S_N1$  | |
| | C-C*l* dipole AND C-C*l* curly arrow | **1** |
| | intermediate cation OR 5-valent transition state (charge essential) | **1** |
| | $I^-$ with lone pair AND other curly arrow | **1** |
| 2(d)(ii) | If $S_N1$ in 2(d)(i) **mixture of / two** optical isomers will be formed,<br>AND the intermediate can be formed by the $I^-$ approaching from top or bottom plane<br><br>If $S_N2$ in 2(d)(i) **one optical isomer** AND attack always from fixed direction / opposite side | **1** |

| Question | Answer | | Marks |
|---|---|---|---|
| 2(e)(i) | **4** peaks | | 1 |
| 2(e)(ii) |  |  | 1 + 1 |
| | number of peaks = 2 | number of peaks = 3 | 1 |
| | | **Total:** | **18** |

| Question | Answer | Marks |
|---|---|---|
| 3(a) |  | |
| | four shared pairs: S=O and 2 × S-C*l* | 1 |
| | all (9) lone pairs | 1 |
| 3(b)(i) | $NaOH + HCl \longrightarrow NaCl + H_2O$ | 1 |
| | $2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$ | 1 |

| Question | Answer | Marks |
|---|---|---|
| 3(b)(ii) | moles (at start) = $0.5 \times 60 / 1000 = 3 \times 10^{-2}$ AND<br>moles (at end) = $0.5 \times 10.8 / 1000 = 5.4 \times 10^{-3}$ | 1 |
| | moles reacted (= $(30–5.4) \times 10^{-3}$ =) **$2.5 \times 10^{-2}$** correct ans. scores [2] | 1 |
| 3(b)(iii) | moles of $RCO_2H$ = $2.46 \times 10^{-2}/3 = 8.2–8.3 \times 10^{-3}$ mole | 1 |
| 3(b)(iv) | $M_r = 1.00 / (8.2 \times 10^{-3}) = 121.95$ (=122) | 1 |
| 3(b)(v) | $C_7H_6O_2$ OR $C_6H_5CO_2H$ | 1 |
| 3(c)(i) | $LiAlH_4$ | 1 |
| 3(c)(ii) |  angelic acid  **T**  **U** | 3 |
| 3(c)(iii) | angelic acid: geometrical OR cis-trans<br>compound **T**: optical | 1 |
| | **Total:** | **14** |

| Question | Answer | Marks |
|---|---|---|
| 4(a)(i) | $M_r = 52 + 6 \times 18 + 3 \times 35.5 = 266.5$ | 1 |
| 4(a)(ii) | 1.00g = 1 / 266.5 **OR** $3.75 \times 10^{-3}$ moles (of complex in 1g)<br><br>for **A**, n=2 **AND** $[Cr(H_2O)_4Cl_2]Cl.2H_2O$<br>for **B**, n=1 **AND** $[Cr(H_2O)_5Cl]Cl_2.H_2O$<br>for **C**, n=0; **AND** $[Cr(H_2O)_6]Cl_3$ | 2 |
| 4(b)(i) | Geometric(al) / cis-trans | 1 |
| 4(b)(ii) | <br>isomer 1<br><br>isomer 2 | 1 |
| 4(b)(iii) | isomer 2 AND<br>dipoles do not cancel OR $CN^-$ are on the same side of the molecule | 1 |
| | **Total:** | 6 |

| Question | Answer | Marks |
|---|---|---|
| 5(a)(i) | *bidentate*: (a species that) forms **<u>two</u>** dative bonds / donates **<u>two</u>** lone pairs | **1** |
| | *ligand:* a species that uses a **lone pair** to form a **dative** bond to **a metal atom / metal ion** | **1** |
| 5(a)(ii) |    each structure [1] x 3 | **3** |
| 5(b)(i) | $K_{stab1} = [Cu(NH_3)_4{}^{2+}]/[Cu^{2+}][NH_3]^4$ | **1** |
| | $K_{stab2} = [Cu(en)_2{}^{2+}]/[Cu^{2+}][en]^2$ | **1** |
| | $mol^{-4}\ dm^{12}$ AND $mol^{-2}\ dm^{6}$ | **1** |
| 5(b)(ii) | $K_{eq3} = K_{stab2} / K_{stab1}$ | **1** |
| 5(b)(iii) | $K_{eq3} = K_{stab2} / K_{stab1} = 4.4(2) \times 10^6$ | **1** |
| | $mol^2\ dm^{-6}$ | **1** |
| 5(c)(i) | ($\Delta S_{eq1}$ is negative as) **more / 5** moles of reactants are forming (one mole of) the complex<br>OR ($\Delta S_{eq2}$ is positive as) **fewer / 3** moles of reactants are forming (one mole of) the complex | **1** |
| 5(c)(ii) | $\Delta G_{eq2}$ = –100 – 298 × 40 / 1000 OR $\Delta G = \Delta H - T\Delta S$<br>= –112 or –111.9 (kJ $mol^{-1}$) correct answer [2] | **2**<br>**1**<br>**1** |

| Question | Answer | Marks |
|---|---|---|
| 5(c)(iii) | Since ($\Delta G_{eq2}$) is **more** negative (than $\Delta G_{eq1}$) AND<br>equilibrium 2 is more feasible | 1 |
| 5(c)(iv) | $\Delta H_{(3)}$ = –8 (kJ $mol^{-1}$) | 1 |
| 5(c)(v) | **<u>ligand</u>** exchange / replacement / substitution / displacement | 1 |
| | **Total:** | **17** |

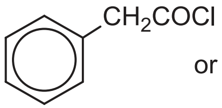
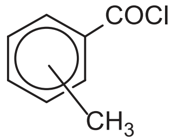
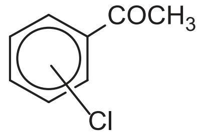
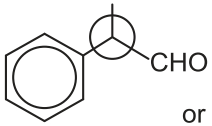
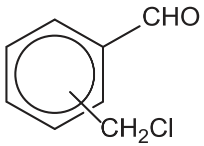
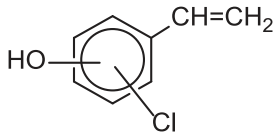
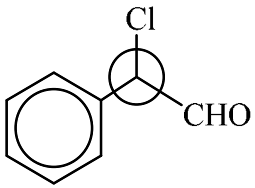
| Question | Answer | Marks |
|---|---|---|
| 6(a)(i) | the lower / smaller the $pK_a$, the stronger the acid | 1 |
| 6(a)(ii) | $pK_a = -\log(K_a)$ or $pK_a = -\lg(K_a)$ or $K_a = 10^{-pka}$ | 1 |
| 6(a)(iii) | (stronger than ethanoic acid because) C*l* is electron-withdrawing | 1 |
| | and so stabilises the $RCO_2^-$ anion / conjugate base<br>**or** weakens O-H bond (so $H^+$ is more easily released) | 1 |
| 6(b)(i) | $NH_3^+CH_2CO_2^- \longrightarrow NH_2CH_2CO_2^- + H^+$<br>OR $NH_3^+CH_2CO_2^- + H_2O \longrightarrow NH_2CH_2CO_2^- + H_3O^+$ | 1 |
| 6(b)(ii) | $K_a = 10^{-9.87} = 1.35 \times 10^{-10}$<br>$[H^+] = \sqrt{(K_a.c)} = 3.67 \times 10^{-6}$ | 1 |
| | pH = **5.4** (5.43–5.44) min 2sf | 1 |

| Question | Answer | Marks |
|---|---|---|
| 6(b)(iii) | curve starts at 5.4 and continuous | **1** |
| | vertical portion (end point) at vol added = 10.0 $cm^3$ | **1** |
| | finishes at pH = 12.5 **at 20 $cm^3$**<br>(and does not increase in pH) | **1** |
| | **Total:** | **10** |

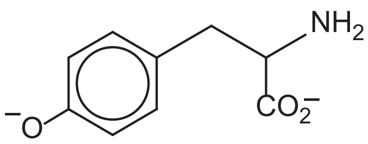
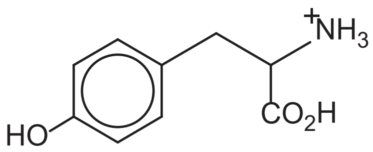
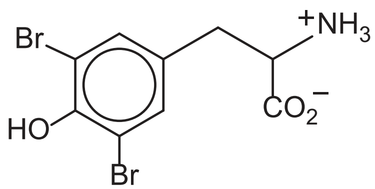
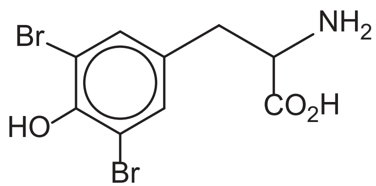
| Question | Answer | Marks |
|---|---|---|
| 7(a) | | **5** |

| W | X | Y | Z |
|---|---|---|---|
| acyl chloride / COC*l* | methyl ketone / CH3CO group<br><br>aryl chloride | aldehyde / CHO<br><br>chloro(alkane) / RC*l* | Alkene / C=C<br><br>phenol / $C_6H_5OH$<br><br>aryl chloride |

0–1 [0]; 2 [1]; 3 [2]; 4 [3]; 5 [4]; 6–8 [5]

| Question | Answer | Marks |
|---|---|---|
| 7(b)(i) | **W**   or   **X**  <br>Cl | **1 + 1** |
| | **Y**   or   **Z**   | **1 + 1** |
| 7(b)(ii) | **Y**  <br>OR any chiral atom correctly labelled | **1** |
| | **Total:** | **10** |

| Question | Answer | Marks |
|---|---|---|
| 8(a)(i) | step 1 electrophilic substitution **ignore** acylation | **1** |
| | step 2 nucleophilic addition | **1** |
| 8(a)(ii) | hydrolysis | **1** |

| Question | Answer | Marks |
|---|---|---|
| 8(a)(iii) | step 1 $ClCH_2CHO$ (**allow** Br, I for Cl) | 1 |
| | $AlCl_3$ | 1 |
| | step 2 HCN + NaCN | 1 |
| | step 3 heat in $H_3O^+$ / heat $H^+(aq)$ | 1 |
| | step 5 $NH_3$ under pressure (+ heat) **or** heat $NH_3$ in a sealed tube | 1 |
| 8(a)(iv) | with NaOH(aq)   [2] | **1 + 1** |
| | with HCl(aq)   [1] | 1 |
| | with $Br_2(aq)$   or   [1] | 1 |
| 8(b)(i) | **P** is tyr | 1 |
| | tyr is 2– AND it is small / has a small *M*r | 1 |

| Question | Answer | Marks |
|---|---|---|
| 8(b)(ii) | *(dipeptide / phe-tyr)* 2– is about double the $M_r$ / mass of (*phe*) *1*<br><br>OR mass / charge ratios are about the same for each (for dipeptide / phe-tyr and phe) | **1** |
| | **Total:** | **15** |