Cambridge
International
AS \& A Level

CHEMISTRY
9701/42
Paper 4 A Level Structured Questions
October/November 2016
MARK SCHEME
Maximum Mark: 100

## Published

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| Question |  |  | Answer | Marks |
| :---: | :---: | :---: | :---: | :---: |
| 1(a) | (an element) forming (one or more stable) ions with incomplete d subshell [1] |  |  | 1 |
| 1 (b)(i) |  | co-ordination number | oxidation number |  |
|  | $\left[\mathrm{Ni}(\mathrm{CN})_{2}\left(\mathrm{NH}_{3}\right)_{2}\right]$ | 4 | +2 |  |
|  | $\left[\mathrm{CrCl}_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]^{+}$ | 6 | +3 |  |
|  |  |  |  | 2 |
| 1 (b)(ii) | dative (covalent)/co-ordinate |  |  | 1 |
| 1(b)(iii) |  <br> or <br> or |  |  |  |
| 1(c)(i) | (concentrated) hydrochloric acid / soluble chloride ion |  |  |  |
| 1(c)(ii) | ligand exchange/substitution |  |  | 1 |
| 1(d)(i) | cis-trans (isomerism) / geometric(al) |  |  | 1 |


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| Question | Answer |  | Marks |
| :---: | :---: | :---: | :---: |
| 1 (d)(ii) | one 3D isomer one correct isomer other isomer correct in 3D allow |  | $\begin{aligned} & 1 \\ & 1 \\ & 1 \end{aligned}$ |
|  |  | Total: | 12 |


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| Question | Answer | Marks |
| :---: | :---: | :---: |
| 2(a) | $\mathrm{NaN}_{3} \rightarrow \mathrm{Na}+1.5 \mathrm{~N}_{2}$ | 1 |
| 2(b) | all atoms must have 8 outer electrons <br> coding for electrons correct $=16(10 \times 5 \cdot 1$ 口) central N must have 8 bonding electrons (inc. $5 \cdot$ and no non-bonded electrons) allow | 1 1 |
| 2(c)(i) | (energy change) when 1 mole of an (ionic) compound is formed or (energy change) when $\mathbf{1}$ mole of an ionic solid/lattice/crystal is formed (from) <br> gas (phase) ions/gaseous ions (under standard conditions) | $1$ |
| 2(c)(ii) | forming an (ionic) bond | 1 |

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| Question | Answer |  | Marks |
| :---: | :---: | :---: | :---: |
| 2(c)(iii) | $\begin{aligned} & \text { use of } \Delta H_{i 1} 494\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right) \\ & \Delta H_{\mathrm{f}}^{\mathrm{o}}=+107+494+142-732 \\ & \Delta H_{\mathrm{f}}=+11\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right) \end{aligned}$ |  | $\begin{array}{ll} 1 & \\ 1 & \\ 1 & 3 \end{array}$ |
| 2(c)(iv) | (ionic) radius /size of $\mathrm{Na}^{+}$is smaller (so stronger attraction to azide ion) OR ionic radius increases down the group |  |  |
|  |  | Total: | 11 |


| Question | Answer | Mark |
| :---: | :---: | :---: |
| 3(a) | $\begin{array}{ll} \mathrm{Fe} & {[\mathrm{Ar}] 3 \mathrm{~d}^{6} 4 \mathrm{~s}^{2}} \\ \mathrm{Fe}^{3+} & {[\mathrm{Ar}] 3 d^{5}} \end{array}$ | $\begin{aligned} & 1 \\ & 1 \end{aligned}$ |
| 3(b)(i) | (catalyst is in) the same phase/state as the reactants | 1 |
| 3 (b)(ii) | $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}+2 \mathrm{I}^{-} \rightarrow 2 \mathrm{SO}_{4}{ }^{2-}+\mathrm{I}_{2}$ | 1 |
| 3 (b)(iii) | (two) negatively-charged species repel each other | 1 |
| 3(b)(iv) | Equation 1: $2 \mathrm{Fe}^{3+}+2 \mathrm{I}^{-} \rightarrow 2 \mathrm{Fe}^{2+}+\mathrm{I}_{2}$ <br> Equation 2: $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}+2 \mathrm{Fe}^{2+} \rightarrow 2 \mathrm{SO}_{4}{ }^{2-}+2 \mathrm{Fe}^{3+}$ | 1 1 |


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| Question | Answer | Marks |
| :---: | :---: | :---: |
| 4(a) | d orbitals split into lower and upper orbitals <br> light/photon absorbed <br> electron(s) promoted/excited/jumps up to (higher) (d-) orbital or electron(s) moves/jumps (from lower ( $\mathrm{d}-$ )) to higher ( $\mathrm{d}-$ ) orbital | $1$ |
| 4(b)(i) | $\begin{aligned} & \mathrm{Cu}+4 \mathrm{HNO}_{3} \rightarrow \mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}+2 \mathrm{NO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \\ & \text { or ionic } \mathrm{Cu}+4 \mathrm{H}^{+}+2 \mathrm{NO}_{3}^{-} \rightarrow \mathrm{Cu}^{2+}+2 \mathrm{NO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \\ & \text { correct species } \\ & \text { correct balancing } \end{aligned}$ | $\begin{aligned} & 1 \\ & 1 \end{aligned}$ |
| 4(b)(ii) | $\begin{aligned} & \text { moles } \mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}=0.1 \times 22.4 / 1000=\mathbf{2 . 2 4} \times \mathbf{1 0}^{-3} \\ & \text { moles of } \mathrm{Cu}^{2+} \text { in } 25 \mathrm{~cm}^{3}=\mathbf{2 . 2 4} \times \mathbf{1 0}^{-3} \\ & \text { moles of } \mathrm{Cu}^{2+} \text { in } 250 \mathrm{~cm}^{3}==2.24 \times 10^{-2} \\ & \text { mass of } \mathrm{Cu}=2.24 \times 10^{-2} \times 63.5=1.4224 \mathrm{~g} \\ & \% \mathrm{Cu}=1.42 / 1.75 \times 100=\mathbf{8 1 . 1} \text { or } \mathbf{8 1 . 3} \% \end{aligned}$ |  |
|  |  | 9 |


| Question | Answer | Marks |
| :---: | :---: | :---: |
| 5(a) | $K_{\mathrm{a}}=\frac{\left[\mathrm{HPO}_{4}{ }^{2-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]}$ | 1 |
| 5(b)(i) | a solution that resists changes in pH when small amounts of acid and base/alkali are added | $1$ |
| 5(b)(ii) | ```addition of acid: }\mp@subsup{\textrm{H}}{}{+}+\mp@subsup{\textrm{HPO}}{4}{2-}->\mp@subsup{\textrm{H}}{2}{}\mp@subsup{\textrm{PO}}{4}{-}\mathbf{OR H addition of base: }\mp@subsup{\textrm{HO}}{}{-}+\mp@subsup{\textrm{H}}{2}{}\mp@subsup{\textrm{PO}}{4}{-}->\mp@subsup{\textrm{HPO}}{4}{2-}+\mp@subsup{\textrm{H}}{2}{}\textrm{O OROH}+\mp@subsup{HPOO4}{2-}{2-}\mp@subsup{\textrm{H}}{2}{}\textrm{O}+\mp@subsup{\textrm{PO}}{4}{3-``` | 1 |
| 5(c) | $\begin{aligned} & {\left[\mathrm{H}^{+}\right]=10^{-7.4}=3.98 \times 10^{-8}} \\ & {\left[\mathrm{HPO}_{4}{ }^{2-}\right] /\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]=K_{\mathrm{a}} /\left[\mathrm{H}^{+}\right]} \\ & \left(\left[\mathrm{HPO}_{4}{ }^{2-}\right] /\left[\mathrm{H}_{2} \mathrm{PO}_{4}\right]\right)=6.31 \times 10^{-8} / 3.98 \times 10^{-8}=1.58-1.6 \end{aligned}$ |  |
| 5(d)(i) | $\begin{aligned} & \mathrm{HCl}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightarrow \mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{C} t \text { OR } \mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightarrow \mathrm{H}_{3} \mathrm{PO}_{4} \\ & \mathrm{OR} \mathrm{H}_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightarrow \mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{OH}^{-} \end{aligned}$ | 1 |


| Question | Answer | Marks |  |
| :---: | :--- | ---: | ---: |
| $5(\mathrm{~d})(\mathrm{ii})$ | $\mathrm{NaOH}+\mathrm{HPO}_{4}{ }^{2-} \rightarrow \mathrm{PO}_{4}{ }^{3-}+\mathrm{H}_{2} \mathrm{O}+\mathrm{Na}^{+} \mathrm{OR} \mathrm{OH}^{-}+\mathrm{HPO}_{4}{ }^{2-} \rightarrow \mathrm{PO}_{4}{ }^{3-}+\mathrm{H}_{2} \mathrm{O}$ <br> $\mathrm{OR} \mathrm{H}_{2} \mathrm{O}+\mathrm{HPO}_{4}{ }^{2-} \rightarrow \mathrm{PO}_{4}{ }^{3-}+\mathrm{H}_{3} \mathrm{O}^{+}$ | 1 |  |
|  |  | Total: | 10 |


| Question | Answer | Marks |
| :---: | :---: | :---: |
| 6(a) |  | 1 |
| 6(b)(i) | ratio of the concentration of a solute in the (two immiscible) solvents/liquids at equilibrium |  |
| 6(b)(ii) | $\begin{array}{ll} K_{\text {partition }}=(0.06 / 40) /(0.25-0.06 / 10) & \text { or reversed ratio: } K_{\text {partition }}=(0.25-0.06 / 10) /(0.06 / 40) \\ K_{\text {partition }}=0.079(0.0789) & K_{\text {partition }}=12.7 / 13.0 \end{array}$ | $1$ |


| Question | Answer |  |  | Marks |
| :---: | :---: | :---: | :---: | :---: |
| 6(c) | reagent | structure of product(s) | type of reaction |  |
|  | $\begin{aligned} & \text { excess } \\ & \mathrm{Br}_{2}(\mathrm{aq}) \end{aligned}$ |  <br> addition of bromine to alkene <br> $2 \times \mathrm{Br}$ substituted in phenol at positions $\mathbf{2}$ and 6 | (electrophilic) substitution <br> or <br> (electrophilic) addition | $\begin{aligned} & 1 \\ & 1 \end{aligned}$ |
|  | $\mathrm{NaBH}_{4}$ |  | reduction <br> (allow nucleophilic addition) | 1 |


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| Question | Answer |  |  |  |  | Marks |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | excess hot $\mathrm{NaOH}(\mathrm{aq})$ <br> all three reac |  <br> on types |  | hydrolysis |  | $1+1$ <br> 1 |
| 6(d) | mixture of (two) optical/stereo isomers formed |  |  |  |  | 1 |
|  | Total: |  |  |  |  | 12 |


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| Question | Answer | Marks |
| :---: | :---: | :---: |
| 7(a)(i) | electrophilic substitution | 1 |
| 7(a)(ii) | $\left(\mathrm{Br}_{2}+\mathrm{AlBr}_{3}\right) \rightarrow \mathrm{Br}^{+}+\mathrm{AlBr}_{4}^{-}$ <br> curly arrow from ring system to $\mathrm{Br}^{+}$ correct intermediate curly arrow from C-H bond into ring and loss of $\mathrm{H}^{+}$ | 1 $\begin{aligned} & 1 \\ & 1 \\ & 1 \end{aligned}$ |
| 7(b) | both amide | 1 |
| 7(c)(i) | step 1, $\mathrm{AlBr}_{3}$ and $\mathrm{CH}_{3} \mathrm{Br} \quad$ OR other suitable halogen instead of Br step 2, $\mathrm{KMnO}_{4}$ or potassium manganate(VII) <br> step 3, conc. $\mathrm{H}_{2} \mathrm{SO}_{4}$ and conc. $\mathrm{HNO}_{3}$ <br> step 4. Sn and (conc.) HCl (heat) |  |


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| Question | Answer |  | Marks |
| :---: | :---: | :---: | :---: |
| 7(c)(ii) |   <br> R <br> S <br> T | 1 mark for each correct structure | 3 |
| 7(d) (i) |   | 1 mark for each correct structure | 2 |
| 7(d)(ii) | reduction |  | 1 |


| Question | Answer | Marks |
| :---: | :---: | :---: |
| 7(e)(i) | 1 mark for each correct structure | 2 |
| 7(e)(ii) |  | 1 |
| 7(e)(iii) | (precipitate) compound is less polar/more non-polar/non-ionic resulting in less hydrogen bonding to water | 1 |
|  | Total: | 20 |


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| Question | Answer |  |  |  |  | Marks |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 8(d)(i) | 8/ppm | type of proton | number of protons | splitting |  | 4 |
|  | 0.9 | alkane $/ \mathrm{CH} / \mathrm{CH}_{3}$ | 6 | doublet |  |  |
|  | 1.6 | alkane/CH | 1 | [multiplet] |  |  |
|  | 2.4 | alkyl next to $\mathrm{C}=\mathrm{O} / \mathrm{CH}_{(2)} \mathrm{CO} / \mathrm{CH}$ | 2 | doublet |  |  |
|  | 11.5 | $\mathrm{OH} / \mathrm{CO}_{2} \mathrm{H} /$ carboxylic acid | 1 | singlet |  |  |
| 8(d)(ii) |  |  |  |  |  | 1 |
| 8(e) | $\mathrm{CDCl}_{3}$ OR D2 $\mathrm{O}, \mathrm{DMSO}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \mathrm{CC} l_{4}$ |  |  |  |  | 1 |
|  | Total |  |  |  |  | 13 |

