## MARK SCHEME for the October/November 2014 series

## 9701 CHEMISTRY

9701/41
Paper 4 (A2 Structured Questions), maximum raw mark 100

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| Question | Marking point | Marks | Marks total |
| :---: | :---: | :---: | :---: |
| 1 (a) (i) | [NO] $2^{\text {nd }}$ order and the concentration is $\times 2$, rate $\times 4$ <br> $\left[\mathrm{O}_{2}\right] \quad 1^{\text {st }}$ order and evidence of using expt $1 \& 2$ when the concentration is $\times 2$, rate doubles | $\begin{aligned} & 1 \\ & 1 \end{aligned}$ |  |
| (ii) | $\begin{aligned} & (0.00408 \times 27) \\ & \text { rate }=\underline{\mathbf{0 . 1 1}}\left(\mathrm{mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}\right) \text { to } \mathbf{2 s f} \end{aligned}$ | 1 |  |
| (iii) | $($ Rate $=) k\left[\mathrm{O}_{2}\right][\mathrm{NO}]^{2}$ | 1 |  |
| (iv) | $\begin{aligned} & \mathrm{k}=332(.03125) \\ & \mathrm{mol}^{-2} \mathrm{dm}^{6} \mathrm{~s}^{-1} \end{aligned}$ | $\begin{aligned} & 1 \\ & 1 \end{aligned}$ | [6] |
| (b) (i) | labelled axes $x$-axis: energy (KE) and $y$-axis: molecules or particles two curves: starts origin; not touching $x$-axis again; no levelling out; curves only intersecting once curves labelled and T2 is to the right and lower max than T1 | $\begin{aligned} & 1 \\ & 1 \\ & 1 \end{aligned}$ |  |
| (ii) | rate increases and energy of the particles increases more particles have $E_{a}$ | $1$ <br> 1 | [5] |
| (c) | 1 mole of $\mathrm{F}_{2}$ and 1 mole NO reacting in the slow step <br> a balanced mechanism consistent with overall equation <br> e.g. $\quad \mathrm{F}_{2}+\mathrm{NO} \rightarrow \mathrm{NOF}+\mathrm{F} \quad \mathrm{OR}$ <br> $\mathrm{F}_{2}+\mathrm{NO} \rightarrow \mathrm{NOF}_{2}$ $\mathrm{NO}+\mathrm{F} \rightarrow \mathrm{NOF}$ <br> $\mathrm{NO}+\mathrm{NOF}_{2} \rightarrow 2 \mathrm{NOF}$ | $\begin{aligned} & 1 \\ & 1 \end{aligned}$ | [2] |
| Total |  |  | [13] |


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| 2 (a) | 3d |  |  |  |  |  | 4s ${ }^{\text {4s }}$ | $1$ | [2] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | (Ni) | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow$ | $\uparrow$ |  |  |  |
|  | $\left(\mathrm{Ni}^{2+}\right)$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow \downarrow$ | $\uparrow$ | $\uparrow$ |  |  |  |
| (b) (i) | degenerate |  |  |  |  |  |  | 1 |  |
| (ii) | 2 upper orbitals and 3 lower orbitals |  |  |  |  |  |  | 1 |  |
| (iii) | correct lower orbital diagram |  |  |  |  |  |  | 1 | [4] |
| (c) | electron(s) move from lower to upper level absorb (red/blue) light/photon complementary colour (green) is seen OR green light is transmitted |  |  |  |  |  |  | 1 1 1 | [3] |


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| (d) | A $\mathrm{Ni}(\mathrm{OH})_{2} \quad$ OR $\quad \mathrm{Ni}(\mathrm{OH})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}$ <br> B $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$ OR $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{n}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6-n}\right]^{2+} \quad$ OR $\quad\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{n}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4-n}\right]^{2+}$ $\begin{aligned} & \mathrm{Ni}^{2+}+2 \mathrm{OH}^{-} \rightarrow \mathrm{Ni}\left(\mathrm{OH}_{2}\right. \\ & \mathrm{OR}\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+2 \mathrm{OH}^{-} \rightarrow \mathrm{Ni}(\mathrm{OH})_{2}+6 \mathrm{H}_{2} \mathrm{O} \\ & \mathrm{OR}\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6} \mathrm{l}^{\mathrm{l}^{++}}+2 \mathrm{NH}_{3} \rightarrow \mathrm{Ni}(\mathrm{OH})_{2}+4 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{NH}_{4}^{+}\right. \\ & \mathrm{OR}\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{++}+2 \mathrm{OH}^{-} \rightarrow \mathrm{Ni}(\mathrm{OH})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}+2 \mathrm{H}_{2} \mathrm{O} \end{aligned}$ $\begin{aligned} & \mathrm{Ni}(\mathrm{OH})_{2}+6 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+-}+2 \mathrm{OH}^{-} \\ & \left.\mathrm{OR} \mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+6 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+-}+6 \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | $\begin{aligned} & 1 \\ & 1 \\ & 1 \\ & 1 \end{aligned}$ | [4] |
| :---: | :---: | :---: | :---: |
| Total |  |  | [13] |


| 3 (a) (i) | $\begin{aligned} & 101=\mathrm{P}^{35} \mathrm{C} l^{35} \mathrm{C} l \\ & 103=\mathrm{P}^{35} \mathrm{C} l^{37} \mathrm{C} \\ & 105=\mathrm{P}^{77} \mathrm{C} l^{77} \mathrm{C} l \end{aligned}$ | 1 1 1 |  |
| :---: | :---: | :---: | :---: |
| (ii) | 9:6:1 | 1 | [4] |
| (b) (i) | $\mathrm{PC}_{5} 5$ bonding pairs around P | 1 |  |
| (ii) |   | $\begin{aligned} & 1 \\ & 1 \end{aligned}$ | [3] |
| (c) (i) |  <br> $\mathrm{P}_{4} \mathrm{O}_{6}$ structure where each P has three $\mathrm{P}-\mathrm{O}$ bonds and each O has two $\mathrm{P}-\mathrm{O}$ bonds e.g. | 1 |  |
| (ii) | (molecule/ion/species) that donates a lone pair of electrons (to a central transition metal atom or ion) | 1 | [2] |
| (d) (i) | $K_{\text {sp }}=\left[\mathrm{Ca}^{2+}\right]^{3}\left[\mathrm{PO}_{4}{ }^{3-}\right]^{2}$ | 1 |  |


| (ii) | $\begin{aligned} & {\left[\mathrm{Ca}^{2+}\right]=3 \times 2.50 \times 10^{-6}=7.50 \times 10^{-6} \mathrm{~mol} \mathrm{dm}^{-3}} \\ & {\left[\mathrm{PO}_{4}^{3-}\right]=2 \times 2.50 \times 10^{-6}=5.00 \times 10^{-6} \mathrm{~mol} \mathrm{dm}^{-3}} \\ & =\left(7.50 \times 10^{-6}\right)^{3}\left(5.00 \times 10^{-6}\right)^{2} \\ & =1.05(1.1) \times 10^{-26} \\ & \mathrm{~mol}^{5} \mathrm{dm}^{-5} \end{aligned}$ | 1 1 1 | [4] |
| :---: | :---: | :---: | :---: |
| (e) (i) | (enthalpy change) when 1 mole of an ionic compound is formed from its gaseous ions | 1 1 |  |
| (ii) | $\mathrm{Mg}^{2+}$ has a smaller (ionic) radii than $\mathrm{Ca}^{2+}$ OR $\mathrm{Mg}^{2+}$ is smaller than $\mathrm{Ca}^{2+}$ | 1 | [3] |
| Total |  |  | [16] |
| 4 (a) (i) | $\begin{aligned} & 2 \mathrm{H}_{2} \mathrm{SO}_{4}+\mathrm{HNO}_{3} \rightarrow 2 \mathrm{HSO}_{4}^{-}+\mathrm{NO}_{2}^{+}+\mathrm{H}_{3} \mathrm{O}^{+} \\ & \mathrm{OR} \mathrm{H}_{2} \mathrm{SO}_{4}+\mathrm{HNO}_{3} \rightarrow \mathrm{HSO}_{4}^{-}+\mathrm{NO}_{2}^{+}+\mathrm{H}_{2} \mathrm{O} \end{aligned}$ | 1 |  |


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| (ii) | any three of <br> - curly arrow from inside the benzene ring to $\mathrm{NO}_{2}{ }^{+}$group <br> - intermediate - penalise $\mathrm{NO}_{2}$ connectivity or missing methyl group (once) <br> - curly arrow from C-H bond into ring <br> - product $+\mathrm{H}^{+}$(or as diagram $-\mathrm{H}^{+}$) <br> allow 2- and 3-substituted nitromethylbenzene) | 3 | [4] |
| :---: | :---: | :---: | :---: |
| (b) (i) <br> (ii) | acidity of $\mathrm{ClCH} \mathrm{CO}_{2} \mathrm{H}>\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ AND $\left(\mathrm{ClCH}_{2} \mathrm{CO}_{2} \mathrm{H}\right)$ as an electronegative/electron withdrawing Cl <br> acidity of phenol $>\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ AND electrons on oxygen (on phenol) delocalised into ring OR benzene ring withdraws electrons from oxygen stronger acid linked to weakening O-H bond/anion being stabilised | 1 1 1 | [3] |

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| Total |  |  | 13 |
| :---: | :---: | :---: | :---: |
| 5 (a) | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCl}>\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Cl}>\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{Cl}$ <br> any two of: <br> - $\mathrm{C}-\mathrm{Cl}$ bond strength is weakest in $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCl}$ ora <br> - In $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{Cl}$ (no hydrolysis) $\mathrm{C}-\mathrm{Cl}$ bond is part of delocalised system OR p-orbital on Cl overlaps with $\pi$ system OR electrons from Cl overlap with $\pi$ system <br> - $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCl}$ carbon in $\mathrm{C}-\mathrm{Cl}$ bond is more electron deficient since it is also attached to an oxygen atom ora | 1 $1+1$ | [3] |
| (b) | ketone, amine, carboxylic acid two correct 1 mark, all three 2 | 2 | [2] |
| (c) (i) | dipole on C-Br <br> curly arrow breaking $\mathrm{C}-\mathrm{Br}$ bond curly arrow from lone pair on N to carbon in $\mathrm{C}-\mathrm{Br}$ bond | $\begin{aligned} & 1 \\ & 1 \\ & 1 \end{aligned}$ |  |
| (ii) | nucleophilic substitution | 1 |  |
| (iii) | HBr or hydrogen bromide | 1 | [5] |


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| (d) |  | 3 | [3] |
| :---: | :---: | :---: | :---: |
| (e) |  <br> correct displayed amide formula correct polyamide with two repeat units | 1 | [2] |
| Total |  |  | 15 |
| 6 (a) | - (move in different directions) <br> some amino acids have a different charge <br> - (move at different speeds) <br> some amino acids have a different size/different charge <br> - (some amino acids do not move at all) some amino acids exist as a zwitterions/have no net(overall) charge/neutral/both $\mathrm{NH}_{2} / \mathrm{COOH}$ are charged in amino acids | 1 1 1 | [3] |
| (b) (i) | mobile - solvent or water <br> stationary - alumina/silica (supported on glass/plastic/AI) | 1 |  |
| (ii) | by adsorption | 1 | [3] |


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| (c) | any three of: (all can be awarded from a clear, labelled diagram) <br> - (base pairing) A to T OR C to G <br> - H-bonds between bases <br> - two/double stranded/chains <br> - anti-parallel strands <br> - (general structure) sugar-phosphate backbone OR BASE-SUGAR-PHOSPHATE bonded in a diagram | 3 | [3] |
| :---: | :---: | :---: | :---: |
| (d) | van der Waals' forces lost (in val) H -bonding gained (in ser) | 1 | [2] |
| Total |  |  | 11 |
| $7 \quad$ (a) | amide group circled OR indicated as diagram ester group circled OR indicated as diagram | $\begin{aligned} & 1 \\ & 1 \end{aligned}$ | [2] |
| (b) | lower doses of the drug required OR improved activity of the drug OR reduced side effects | 1 | [1] |


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| (c) | decreases enzyme activity OR decreases rate at which product is formed <br> binds with the enzyme's active site OR has a complementary shape to active site OR similar shape to substrate <br> (competitive inhibition can be overcome by) increasing [substrate] OR increasing substrate concentration | 1 <br> 1 <br> 1 | [3] |
| :---: | :---: | :---: | :---: |
| (d) | energy source/carrier OR releases energy when hydrolysed | 1 | [1] |
| Total |  |  | 7 |
| 8 (a) | $\begin{aligned} & \mathrm{M}: \mathrm{M}+1=100 /(1.1 \times \mathrm{n}) \\ & 20.4 / 0.9=100 /(1.1 \times \mathrm{n}) \\ & \mathrm{x}=4 \end{aligned}$ | 1 1 |  |
| (ii) | $\mathrm{C}_{4} \mathrm{H}_{10} \mathrm{O}$ | 1 | [3] |
| (b) (i) | 2-methylpropan-1-ol OR correct structure | 1 |  |
| (ii) | $\begin{array}{ll} 0.9-1.0 & \text { is }(2 \times) \mathrm{CH}_{3} \mathrm{R} / \mathrm{CH}_{3} / \mathrm{RCH} \\ \text { multiplet } / 1.8 & \text { is } \mathrm{CHR} / \mathrm{R}_{3} \mathrm{CH} \\ \text { singlet } / 2.5 & \text { is } \mathrm{OH} \\ 3.4 & \text { is } \mathrm{CH}_{2} \mathrm{O} / \mathrm{CH}_{3} \mathrm{O} \end{array}$ | 1 1 1 1 |  |
| (iii) | doublet <br> 1H/one proton on adjacent carbon | 1 1 |  |


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| (iv) | OH peak or one peak disappears <br> OH proton is labile or exchanges for $D$ of $D_{2} O$ <br> or as an equation e.g. $\mathrm{D}_{2} \mathrm{O}+\mathrm{OH} \rightarrow \mathrm{DOH}+\mathrm{OD}$ as a minimum | 1 | 1 |
| :---: | :--- | :---: | :---: |
| Total |  | 12 |  |
|  |  | 100 |  |

