Cambridge International Advanced Subsidiary and Advanced Level

## CHEMISTRY

Paper 4 A Level Structured Questions
MARK SCHEME
Maximum Mark: 100

## Published

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| Question | Answer | Marks |
| :---: | :---: | :---: |
| 1(a) | $\mathrm{N}+2$ to +3 (and oxidised) | 1 |
|  | $\mathrm{Br}_{2} / \mathrm{BrO}$ to -1 (and reduced) | 1 |
| 1(b) |  |  |
|  | 3 bonding pairs around N (in a structure involving NOBr ) | 1 |
|  | rest of molecule correct | 1 |
| 1(c)(i) | the power to which a concentration of a reactant is raised in the rate equation | 1 |
| 1(c)(ii) | using expt. 2 and 3 <br> $\mathrm{a}=2$ or [ NO ] 2nd order <br> and conc $\times 3$ rate $\times 9$ or $6.1 \times 10^{-2} / 6.8 \times 10^{-3}=(0.09 / 0.03)^{\text {a }}$ | 1 |
|  | using expt. 1 and 2 <br> $\mathrm{b}=1$ or $\left[\mathrm{Br}_{2}\right] 1^{\text {st }}$ order <br> and conc $\times 2$ rate $\times 2$ or $6.8 \times 10^{-3} / 3.4 \times 10^{-3}=(0.04 / 0.02)^{b}$ | 1 |
| (c)(iii) | initial rate $=0.16$ (32) | 1 |
| 1(c)(iv) | $\begin{aligned} & \left(0.0034=k(0.03)^{2}(0.02)\right) \\ & k=188.9 \end{aligned}$ | 1 |
|  | $\mathrm{mol}^{-2} \mathrm{dm}^{6} \mathrm{~s}^{-1}$ | 1 |
| 1(c)(v) | $k$ decreases (as rate decreases) | 1 |


| Question | Answer | Marks |
| :---: | :--- | :---: |
| $1(\mathrm{~d})$ | $m=2$ and $n=0$ | 1 |


| Question | Answer | Marks |
| :---: | :---: | :---: |
| 2(a) | it/solubility decreases down the group and $K_{\text {sp }}$ decreases | 1 |
| 2(b)(i) | $\mathrm{MgCO}_{3}(\mathbf{s}) \rightleftharpoons \mathrm{Mg}^{2+}(\mathrm{aq})+\mathrm{CO}_{3}{ }^{2-}(\mathrm{aq})$ | 1 |
| 2(b)(ii) | (white) solid appears/precipitation (of $\mathrm{MgCO}_{3}$ ) | 1 |
|  | as $\left[\mathrm{CO}_{3}{ }^{2-}\right]$ increases shifting equilibrium to the LHS (precipitating out $\mathrm{MgCO}_{3}$ ) | 1 |
| 2(c) | solubility $=\sqrt{ } 1.0 \times 10^{-5}=3.16 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$ | 1 |
|  | solubility $=3.2 \times 10^{-3} \times 84.3=0.27 \mathrm{~g} \mathrm{dm}^{-3}$ | 1 |
| 2(d)(i) | $\mathrm{Mg}^{2+}$ ion is smaller than $\mathrm{Ba}^{2+}$ ion or ionic radii increase down group ora | 1 |
|  | $\left(\mathrm{Mg}^{2+}\right)$ distorts / polarises/ the anion/ nitrate group/nitrate ion/ $\mathrm{NO}_{3}{ }^{(1)-} / \mathrm{NO}_{3}$ ion more easily (than $\mathrm{Ba}^{2+}$ ) ora | 1 |
| 2(d)(ii) | $\mathrm{Ba}\left(\mathrm{NO}_{3}\right)_{2} \rightarrow \mathrm{BaO}+2 \mathrm{NO}_{2}+1 / 2 \mathrm{O}_{2}$ | 1 |
| 2(d)(iii) | $\mathrm{BaO}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Ba}(\mathrm{OH})_{2}$ | 1 |
|  | $\mathrm{Ba}(\mathrm{OH})_{2}+\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{BaSO}_{4}+2 \mathrm{H}_{2} \mathrm{O}$ | 1 |


| Question | Answer | Marks |
| :---: | :---: | :---: |
| 3(a) | the potential difference between two half-cells/two electrodes (in a cell) | 1 |
|  | under standard conditions of $1 \mathrm{~atm} ., 298 \mathrm{~K}$, (all) solutions being $1 \mathrm{~mol} \mathrm{dm}^{-3}$ | 1 |
| 3(b)(i) | 8 marking points, any 2 points for each mark <br> $\mathrm{H}_{2}$ / hydrogen <br> correct delivery system for $\mathrm{H}_{2}$ <br> $\mathrm{Pb}^{2+}$ (aq) <br> Pb electrode <br> Pt electrode <br> $\mathrm{H}^{+}(\mathrm{aq})$ solution <br> salt bridge <br> voltmeter/V labelled | 4 |
| 3(b)(ii) | more negative | 1 |
|  | shifts $\mathrm{Pb}^{2+}\left(+2 \mathrm{e}^{-}\right) \leftrightharpoons \mathrm{Pb}$ equilibrium/reaction to the left | 1 |


| Question | Answer | Marks |
| :---: | :---: | :---: |
| 3(c)(i) | $Q=0.4 \times 80 \times 60=1920 C$ and use of $96500 / 193000$ <br> Moles of $\mathrm{Pb}=1920 / 193000=9.95 \times 10^{-3}$ <br> Mass of $\mathrm{Pb}=207.2 \times 9.95 \times 10^{-3}=\mathbf{2 . 1} \mathbf{g}$ <br> OR <br> $Q=0.4 \times 80 \times 60=1920 \mathrm{C}$ and use of $1.6 \times 10^{-19} / 1.2 \times 10^{22}$ <br> atoms $\mathrm{Pb}=6 \times 10^{21}$; moles of $\mathrm{Pb}=6 \times 10^{21} / 6 \times 10^{23}=0.01$ <br> Mass of $\mathrm{Pb}=207.2 \times 0.01=\mathbf{2 . 1} \mathrm{g}$ | 2 |
| 3(c)(ii) |  | 1 |
| 3(d) | reagents $/ \mathrm{PbO}_{2} / \mathrm{H}_{2} \mathrm{SO}_{4}$ and used up/concentration decreases | 1 |
|  | as fuel/hydrogen is being continuously supplied/fuel has not run out | 1 |


| Question | Answer | Marks |
| :---: | :--- | :---: |
| $4(\mathrm{a})$ | density is higher and melting point is higher |  |
|  | (density) due to $A_{r}$ being larger and smaller atomic radii <br> or (Co) atoms / ions heavier and smaller | $\mathbf{1}$ |
|  | (melting point) due to stronger attraction to cations as more delocalised electrons | $\mathbf{1}$ |
|  | (a molecule or ion) formed by a central metal atom/ion surrounded by (one or more) ligands | $\mathbf{1}$ |
| $4(\mathrm{c})(\mathrm{i})$ | same number and type of atoms and different structural formula | $\mathbf{1}$ |


| Question | Answer |  |  | Marks |
| :---: | :---: | :---: | :---: | :---: |
| 4(c)(ii) | octahedral AND 3D structure of $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Br}\right]^{2+}$ e.g. |  |  | 1 |
| 4(c)(iii) | co-ordinate/dative covalent |  |  | 1 |
| 4(c)(iv) | +3 for both |  |  | 1 |
| 4(d) | $\left(\mathrm{HNO}_{3}\right) \mathrm{Ag}^{+} / \mathrm{AgNO}_{3}$ cream(-yellow) ppt. (of AgBr ) and no reaction/white ppt. for other isomer |  |  | 1 |
|  | $\mathrm{Ba}(\mathrm{OH})_{2} / \mathrm{Ba}^{2+}(\mathrm{aq}) / \mathrm{BaCl}_{2} / \mathrm{Ba}\left(\mathrm{NO}_{3}\right)_{2}$ white ppt. (of $\mathrm{BaSO}_{4}$ ) and no reaction for other isomer |  |  | 1 |
| 4(e) | (d-d) energy gap / $\Delta E$ is different |  |  | 1 |
|  | absorb different wavelength/frequency (of light) |  |  | 1 |
| 4(f) |  | heterogeneous | homogeneous | 2 |
|  |  | $\checkmark$ |  |  |
|  |  |  | $\checkmark$ |  |
|  |  |  | $\checkmark$ |  |
|  |  | $\checkmark$ |  |  |

Question
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| :---: | :---: | :---: |
| 6(a)(i) |  | 1 |
| 6(a)(ii) | $\mathrm{HNO}_{3}+2 \mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{NO}_{2}^{+}+2 \mathrm{HSO}_{4}^{-}$ | 1 |
| 6(a)(iii) | any three from: <br> Point 1: bonds/electrons are partially delocalised in T or delocalised $/ \pi$ system $/ \pi$ bonding extends over only five carbons <br> Point 2: four $\pi$-electrons in the (delocalised system of $\mathbf{T}$ ) or methylbenzene has (two) more $\pi$-electrons/(two) more delocalised electrons <br> Point 3: contains a carbon that is $\mathrm{sp}^{3}$ hybridised in $\mathbf{T}$ or (all the) carbons are $\mathrm{sp}^{2}$ hybridised in methylbenzene <br> Point 4: one carbon has a bond angle of $109.5^{\circ} /$ tetrahedral (in T) or (C-C) bond strengths / lengths are not all the same or not all the bond angles are $120^{\circ}$ (in T) | 3 |
| 6(b)(i) | 4-aminobenzoic acid | 1 |
| 6(b)(ii) | ```step 1 Sn + HCl [1] concentrated/reflux/heat [1] step 2 CH3COCl[1] step 3 KMnO step 4 aqueous HCl and heat [1] step 5 ethanol, H2SO4, concentrated/reflux/heat [1]``` | 6 |


| Question | Answer |  |  |  | Marks |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 6(c) | (benzocaine) is less (basic than ethylamine) AND Ione pair (on N ) is less available to accept a proton/ $\mathrm{H}^{+}$ <br> since (lone pair on N ) is delocalised over the ring or phenyl ring is electron withdrawing group <br> OR <br> ethylamine is more basic (than benzocaine) AND Ione pair (on N ) is more available to accept a proton $/ \mathrm{H}^{+}$ <br> since ethyl/alkyl group is electron-donating group |  |  |  | 2 |
| 6(d)(i) | 7 peaks |  |  |  | 1 |
| 6(d)(ii) | $\mathrm{CDCl}_{3}$ will produce no signal in the spectrum or $\mathrm{CHCl}_{3}$ would produce a signal/would be detected |  |  |  | 1 |
| 6(d)(iii) | $\delta / p p m$ group responsible for the peak |  | number of H atoms responsible for the peak | splitting pattern | 4 |
|  | 1.2 | $\mathrm{CH}_{(3)}$ | 3 | triplet |  |
|  | 3.5 | $\mathrm{CH}_{(2)} \mathrm{O}$ | 2 | quartet |  |
|  | 5.5 | $\mathrm{NH}_{2}$ | 2 | singlet (broad) |  |
|  | 7.1-7.4 | H attached to aromatic/benzene ring | 4 | multiplet |  |
| 6(d)(iv) | neighbouring/adjacent carbon atom has two protons/H (attached to it) or there is an adjacent $\mathrm{CH}_{2}(\mathrm{O})$ group |  |  |  | 1 |
| 6(d)(v) | peak at $5.5 / \mathrm{NH}_{2}$ peak will disappear and $\mathrm{NH}_{2}$ /protons exchange/swap with deuterium |  |  |  | 1 |

Question

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| :---: | :---: | :---: |
| 7(a) | $\begin{aligned} & \text { Fe atom }=\left(1 s^{2} 2 s^{2} 2 p^{6}\right) 3 s^{2} 3 p^{6} 3 d^{6} 4 s^{2} \\ & F e^{3+} \text { ion }=\left(1 s^{2} 2 s^{2} 2 p^{6}\right) 3 s^{2} 3 p^{6} 3 d^{5} \end{aligned}$ | 1 |
| 7(b) | $\begin{aligned} & \left(\left[\mathrm{H}^{+}\right]^{2}=8.9 \times 10^{-4} \times 0.25 \text { or } 2.225 \times 10^{-4}\right) \\ & {\left[\mathrm{H}^{+}\right]=0.0149} \end{aligned}$ | 1 |
|  | $\mathrm{pH}=-\log (0.0149)=1.83$ | 1 |
| 7(c)(i) | ( $K_{\text {stab }}$ is) the equilibrium constant for the formation of a complex (ion) (in a solvent from its constituent ions/molecules) | 1 |
| 7(c)(ii) | $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{~F}\right]^{2+}$ and $\left[\mathrm{Hg}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{C}\right\rceil^{+}$ | 1 |
| 7(d) | $K_{\text {stab }}=\frac{\left[\mathrm{Fe}(\mathrm{ed})_{2} \mathrm{Cl}_{2}^{3-}\right]}{\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4} \mathrm{Cl}_{2}^{+}\right][\mathrm{ed}]^{2}}$ | 1 |
|  | $\mathrm{mol}^{-2} \mathrm{dm}^{6}$ | 1 |
| 7(e)(i) |    <br> cis <br> cis <br> trans | 3 |


| Question | Answer | Marks |
| :---: | :--- | :---: |
| $7(e)($ ii $)$ | any cis isomer and the trans isomer identified |  |
| $7(e)$ (iii) | both correct cis isomers identified | $\mathbf{1}$ |
| $7(e)($ iv $)$ | trans isomer identified | $\mathbf{1}$ |

