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**CHEMISTRY** **9701/41**

Paper 4 A Level Structured Questions **October/November 2017**

MARK SCHEME

Maximum Mark: 100

**Published**

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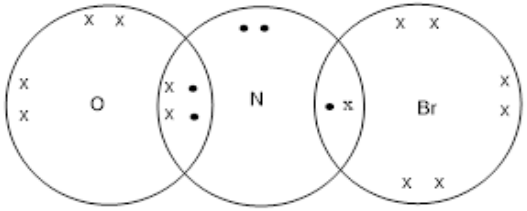
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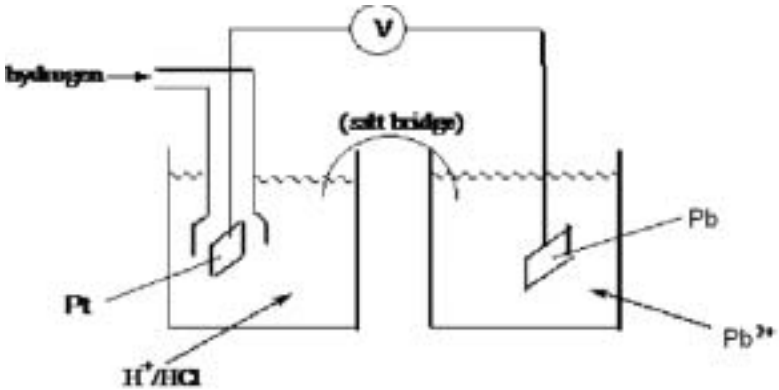
| Question | Answer | Marks |
|---|---|---|
| 1(a) | N +2 to +3 (and oxidised) | **1** |
| | $Br_2$ / Br 0 to –1 (and reduced) | **1** |
| 1(b) |   | |
| | 3 bonding pairs around N (in a structure involving NOBr) | **1** |
| | rest of molecule correct | **1** |
| 1(c)(i) | the **power** to which a concentration of a reactant is raised in the **rate equation** | **1** |
| 1(c)(ii) | using expt. 2 and 3<br>a = 2 **or** [NO] 2nd order<br>**and** conc × 3 rate × 9 **or** $6.1 \times 10^{-2} / 6.8 \times 10^{-3} = (0.09 / 0.03)^a$ | **1** |
| | using expt. 1 and 2<br>b = 1 **or** $[Br_2]$ 1st order<br>**and** conc × 2 rate × 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) | $(0.0034 = k(0.03)^2(0.02))$<br>k = **188.9** | **1** |
| | $mol^{-2}\,dm^6\,s^{-1}$ | **1** |
| 1(c)(v) | *k* decreases (as rate decreases) | **1** |

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| Question | Answer | Marks |
|---|---|---|
| 1(d) | m = 2 **and** n = 0 | **1** |

| Question | Answer | Marks |
|---|---|---|
| 2(a) | it / solubility **decreases** down the group **and** $K_{sp}$ decreases | **1** |
| 2(b)(i) | $MgCO_3$**(s)** ⇌ $Mg^{2+}$**(aq)** + $CO_3^{2-}$**(aq)** | **1** |
| 2(b)(ii) | (white) solid appears / precipitation (of $MgCO_3$) | **1** |
| | as [$CO_3^{2-}$] increases shifting equilibrium to the LHS (precipitating out $MgCO_3$) | **1** |
| 2(c) | solubility = $\sqrt{1.0 \times 10^{-5}} = 3.16 \times 10^{-3}$ mol dm$^{-3}$ | **1** |
| | solubility= $3.2 \times 10^{-3} \times 84.3 =$ **0.27** g dm$^{-3}$ | **1** |
| 2(d)(i) | $Mg^{2+}$ ion is smaller than $Ba^{2+}$ ion **or** ionic radii increase down group ora | **1** |
| | ($Mg^{2+}$) distorts / polarises / the anion / nitrate group / nitrate **ion** / $NO_3^{(1)-}$ / $NO_3$ ion more easily (than $Ba^{2+}$) ora | **1** |
| 2(d)(ii) | $Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + ½O_2$ | **1** |
| 2(d)(iii) | $BaO + H_2O \rightarrow Ba(OH)_2$ | **1** |
| | $Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$ | **1** |

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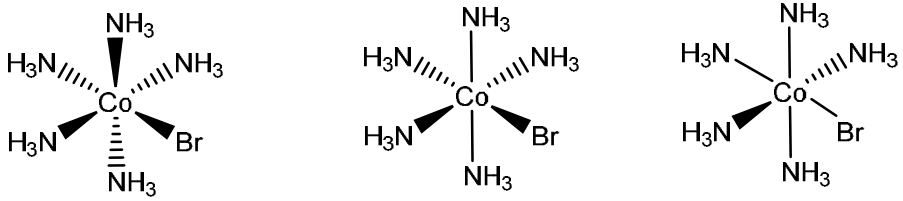
| Question | Answer | Marks |
|---|---|---|
| 3(a) | the potential **difference** between two half-cells / two electrodes (in a cell) | **1** |
| | under standard conditions of 1 atm., 298 K, (all) solutions being 1 mol $dm^{-3}$ | **1** |
| 3(b)(i) | <br>8 marking points, any 2 points for each mark<br><br>$H_2$ / hydrogen<br>correct delivery system for $H_2$<br>$Pb^{2+}$ (aq)<br>Pb electrode<br>Pt electrode<br>$H^+$(aq) solution<br>salt bridge<br>voltmeter / V labelled | **4** |
| 3(b)(ii) | more negative | **1** |
| | shifts $Pb^{2+}$ (+ $2e^-$) ⇋ Pb equilibrium / reaction to the left | **1** |

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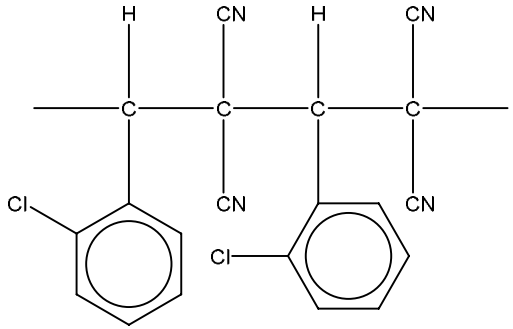
| Question | Answer | Marks |
|---|---|---|
| 3(c)(i) | Q = 0.4 × 80 × 60 = **1920** C **and** use of 96500 / 193000<br>Moles of Pb = 1920 / 193000 = $9.95 \times 10^{-3}$<br>Mass of Pb = $207.2 \times 9.95 \times 10^{-3}$ = **2.1 g**<br><br>**OR**<br>Q = 0.4 × 80 × 60 = **1920** C **and** use of $1.6 \times 10^{-19}$ / $1.2 \times 10^{22}$<br>atoms Pb = $6 \times 10^{21}$; moles of Pb = $6 \times 10^{21} / 6 \times 10^{23}$ = 0.01<br>Mass of Pb = 207.2 × 0.01 = **2.1 g** | **2** |
| 3(c)(ii) | $PbO_2(s) + SO_4^{2-}(aq)$ **+ $4H^+$ + $2e^-$** → $PbSO_4(s)$ **+ $2H_2O$** | **1** |
| 3(d) | reagents / $PbO_2$ / $H_2SO_4$ **and** used up / concentration decreases | **1** |
| | as fuel / hydrogen is being continuously supplied / fuel has not run out | **1** |

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

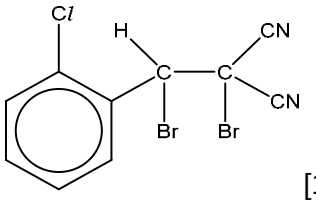
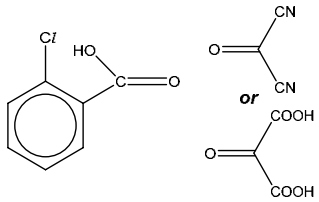
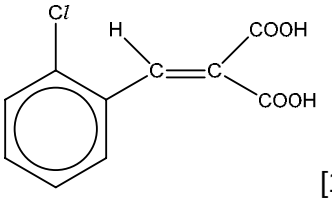
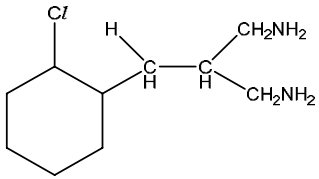
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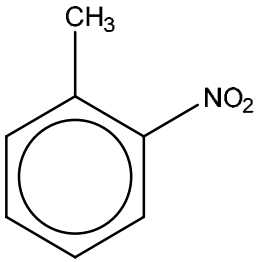
<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>4(c)(ii)</td><td>octahedral AND 3D structure of $[Co(NH_3)_5Br]^{2+}$<br>e.g.<br></td><td>1</td></tr>
<tr><td>4(c)(iii)</td><td>co-ordinate / dative covalent</td><td>1</td></tr>
<tr><td>4(c)(iv)</td><td>+3 for both</td><td>1</td></tr>
<tr><td rowspan="2">4(d)</td><td>($HNO_3$) $Ag^+$ / $AgNO_3$ cream(–yellow) ppt. (of AgBr) and no reaction / white ppt. for other isomer</td><td>1</td></tr>
<tr><td>$Ba(OH)_2$ / $Ba^{2+}(aq)$ / $BaCl_2$ / $Ba(NO_3)_2$ white ppt. (of $BaSO_4$) and no reaction for other isomer</td><td>1</td></tr>
<tr><td rowspan="2">4(e)</td><td>(d-d) energy gap / $\Delta E$ is different</td><td>1</td></tr>
<tr><td><u>absorb</u> different wavelength / frequency (of light)</td><td>1</td></tr>
<tr><td>4(f)</td><td>
<table>
<tr><th></th><th>heterogeneous</th><th>homogeneous</th></tr>
<tr><td>Fe in the Haber process</td><td>✓</td><td></td></tr>
<tr><td>$Fe^{2+}$ in the $I^-$ / $S_2O_8^{2-}$ reaction</td><td></td><td>✓</td></tr>
<tr><td>$NO_2$ in the oxidation of $SO_2$</td><td></td><td>✓</td></tr>
<tr><td>$V_2O_5$ in the Contact process</td><td>✓</td><td></td></tr>
</table>
</td><td>2</td></tr>
</table>

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| Question | Answer | Marks |
|---|---|---|
| 5(a) | nitrile; alkene; chloro; benzene / arene | **2** |
| 5(b) |  | **1** |
| | addition (polymerisation) | **1** |

| Question | Answer | Marks |
|---|---|---|
| 5(c) | | **8** |

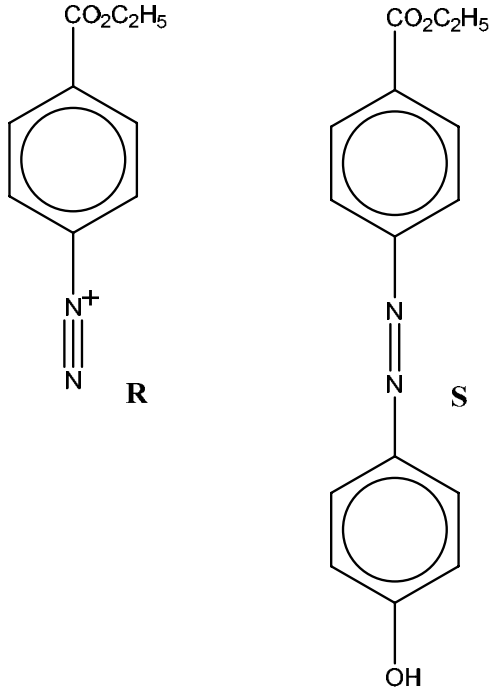
| reagent | structure of product | type of organic reaction |
|---|---|---|
| excess $Br_2(aq)$ |  [1] | (electrophilic) addition |
| excess hot, conc. $MnO_4^-(aq)$ |  [1] + [1] | oxidation |
| excess hot, aqueous HCl |  [1] | hydrolysis |
| excess $H_2$ / Pt catalyst |  both $CH_2NH_2$ formed [1]<br>both arene and alkene reduced [1] | reduction / hydrogenation |
| | structures [6] | 2 correct for 1 mark<br>total [2] |

| Question | Answer | Marks |
|---|---|---|
| 6(a)(i) |   | **1** |
| 6(a)(ii) | $HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$ | **1** |
| 6(a)(iii) | **any three** from:<br><br>Point 1: bonds / electrons are **partially** delocalised in **T**<br>**or** delocalised / π system / π bonding extends over only five carbons<br><br>Point 2: four π-electrons in the (delocalised system of **T**)<br>**or** methylbenzene has (two) more π-electrons / (two) more delocalised electrons<br><br>Point 3: contains a carbon that is $sp^3$ hybridised in **T**<br>***or*** (all the) carbons are $sp^2$ hybridised in methylbenzene<br><br>Point 4**:** one carbon has a bond angle of 109.5° / tetrahedral (in **T)**<br>***or*** (C-C) bond strengths / lengths are not all the same<br>**or** not all the bond angles are 120° (in **T**) | **3** |
| 6(b)(i) | 4-aminobenzoic acid | **1** |
| 6(b)(ii) | step 1 Sn + HC*l* [1] concentrated / reflux / heat [1]<br>step 2 $CH_3COCl$ [1]<br>step 3 $KMnO_4$ / manganate(VII) / $MnO_4^-$ (acidified / alkaline) **and** heat [1]<br>step 4 aqueous HC*l* **and** heat [1]<br>step 5 ethanol, $H_2SO_4$, concentrated / reflux / heat [1] | **6** |

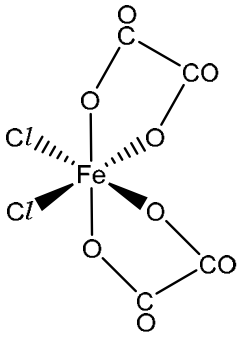
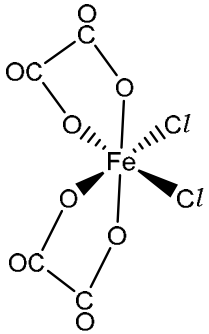
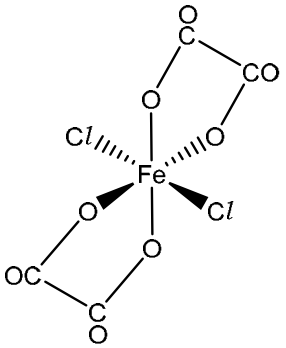
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<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>6(c)</td><td>(benzocaine) is less (basic than ethylamine) AND<br>lone pair (on N) is less available to accept a proton / $H^+$<br><br>since (lone pair on N) is delocalised over the ring<br>or phenyl ring is electron withdrawing group<br><br>OR<br>ethylamine is more basic (than benzocaine) AND<br>lone pair (on N) is more available to accept a proton / $H^+$<br><br>since ethyl / alkyl group is electron-donating group</td><td>2</td></tr>
<tr><td>6(d)(i)</td><td>7 peaks</td><td>1</td></tr>
<tr><td>6(d)(ii)</td><td>$CDCl_3$ will produce no signal in the spectrum<br>or $CHCl_3$ would produce a signal / would be detected</td><td>1</td></tr>
<tr><td>6(d)(iii)</td><td><table>
<tr><th>δ/ppm</th><th>group responsible for the peak</th><th>number of H atoms responsible for the peak</th><th>splitting pattern</th></tr>
<tr><td>1.2</td><td>$CH_{(3)}$</td><td>3</td><td>triplet</td></tr>
<tr><td>3.5</td><td>$CH_{(2)}O$</td><td>2</td><td>quartet</td></tr>
<tr><td>5.5</td><td>$NH_2$</td><td>2</td><td>singlet (broad)</td></tr>
<tr><td>7.1–7.4</td><td>H attached to aromatic / benzene ring</td><td>4</td><td>multiplet</td></tr>
</table></td><td>4</td></tr>
<tr><td>6(d)(iv)</td><td>neighbouring / adjacent carbon atom has two protons / H (attached to it)<br>or there is an adjacent $CH_2(O)$ group</td><td>1</td></tr>
<tr><td>6(d)(v)</td><td>peak at 5.5 / $NH_2$ peak will disappear<br>and<br>$NH_2$ / protons exchange / swap with deuterium</td><td>1</td></tr>
</table>

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| Question | Answer | Marks |
|---|---|---|
| 6(e)(i) | $NaNO_2$ + HC*l* ***or*** $HNO_2$ | **1** |
| 6(e)(ii) |  **R** **S** | |
| | structure of diazonium salt **R** | **1** |
| | structure of azo dye **S** | **1** |

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| Question | Answer | Marks |
|---|---|---|
| 7(a) | Fe atom= $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^6 4s^2$<br><br>$Fe^{3+}$ ion= $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^5$ | **1** |
| 7(b) | $([H^+]^2 = 8.9 \times 10^{-4} \times 0.25$ ***or*** $2.225 \times 10^{-4})$<br>$[H^+] = 0.0149$ | **1** |
| | pH = –log(0.0149) = **1.83** | **1** |
| 7(c)(i) | ($K_{stab}$ is) the **equilibrium constant** for the formation of a complex (ion) (in a solvent from its constituent ions / molecules) | **1** |
| 7(c)(ii) | $[Fe(H_2O)_5F]^{2+}$ **and** $[Hg(H_2O)_5Cl]^+$ | **1** |
| 7(d) | $K_{stab} = \dfrac{[Fe(ed)_2Cl_2^{3-}]}{[Fe(H_2O)_4Cl_2^+][ed]^2}$ | **1** |
| | $mol^{-2}\,dm^6$ | **1** |
| 7(e)(i) |  cis  cis  trans | **3** |

| Question | Answer | Marks |
|---|---|---|
| 7(e)(ii) | any cis isomer **and** the trans isomer identified | **1** |
| 7(e)(iii) | **both** correct cis isomers identified | **1** |
| 7(e)(iv) | trans isomer identified | **1** |

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