

**MARK SCHEME for the October/November 2007 question paper**

**9701 CHEMISTRY**

**9701/04**

Paper 4 (Theory 2), maximum raw mark 100

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All Examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

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- 1 (a) (i)  $K_a = \frac{[H^+][RCO_2^-]}{[RCO_2H]}$  [1]
- (ii)  $pK_a = -\log_{10}K_a$  or  $-\log K_a$  or  $\log \frac{[H^+]^2}{[RCO_2H]}$  NOT  $\ln$ ; [1]  
[2]
- (b) (i) acid strength increases from no. 1 to no. 3 or down the table or as Cls increase due to the electron-withdrawing effect/electronegativity of chlorine (atoms) stabilising the anion or weakening the O-H bond NOT  $H^+$  more available [1]  
[1]  
[1]
- (ii) chlorine atom is further away (from O-H) in no. 4, so has less influence [1]
- (iii) either:  $pH = \frac{1}{2}(pK_a - \log_{10}[\text{acid}])$  or  $K_a = 10^{-pK_a} = 1.259 \times 10^{-3}$   
 $= \frac{1}{2}(4.9 + 2)$   $[H^+] = \sqrt{K_a \cdot c} = 3.55 \times 10^{-4}$  [1]  
 $= 3.4$  (allow 3.5)  $pH = 3.4$  ecf [1]  
 ([1] for correct expression & values; [1] for correct working) [6]
- (c) (i) catalyst [1]
- (ii)  $CH_3CH_2CO_2H + Cl_2 \longrightarrow CH_2CHClCO_2H + HCl$  [1]
- (iii) nucleophilic substitution NOT addition/elimination [1]
- (iv)  $M_r(CH_3CH_2CO_2H) = 74$   $M_r(CH_2CH(NH_2)CO_2H) = 89$  [1]  
 $\therefore 10.0 \text{ g should give } 10 \times 89/74 = 12.03 \text{ g}$   
 $\therefore \text{percentage yield} = 100 \times 9.5/12.03 = 79\%$  ecf [1]  
 ([2] for correct answer) [5]
- (d)  $^+NH_3-CH(CH_3)-CO_2^-$  correct atoms [1]  
 Allow charges on H of  $H_3N$ , and  $-COO$  but not  $-C-O-O$  correct charges [1]  
 [2]

[Total: 15]

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- 2 (a) solubility **decreases** (down Group II) [1]  
lattice energy decreases [1]  
solvation/hydration energy (of cation) decreases [1]  
but more so than does lattice energy/is not able to overcome LE [1]  
 $\Delta H_{\text{soln}}$  becomes more endothermic/positive/less exothermic [1]  
**[max 4]**
- (b) identities of **A** and **B** 2 x [1]  
 $\text{Mg(OH)}_2 + \text{H}_2\text{C}_2\text{O}_4 \longrightarrow \text{MgC}_2\text{O}_4(\text{aq}) + 2\text{H}_2\text{O}$  [1]  
**(A)**
- $\text{MgC}_2\text{O}_4(\text{aq}) + \text{Ca(NO}_3)_2 \longrightarrow \text{Mg(NO}_3)_2 + \text{CaC}_2\text{O}_4(\text{s})$  [1]  
**(B)**  
**[max 3]**
- (c) (i) ( $K_{\text{sp}} =$ )  $[\text{Mg}^{2+}][\text{OH}^-]^2$  [1]  
units are  $\text{mol}^3\text{dm}^{-9}$  ecf from  $K_{\text{sp}}$  [1]
- (ii) (call  $[\text{Mg(OH)}_2(\text{aq})] = [\text{Mg}^{2+}] = x$ )  $\therefore K_{\text{sp}} = 2 \times 10^{-11} = 4x^3$  [1]  
 $\therefore x = 1.71 \times 10^{-4} \text{ mol dm}^{-3}$  ecf [1]
- (iii) less soluble because of the common ion effect [1]  
or the equilibrium  $\text{Mg(OH)}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$  is moved to the left [1]  
**[5]**  
**[Total: 12]**

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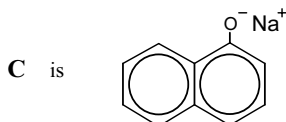
- 3 (a)  $K = 22.4/39.1 = 0.573$  thus ratio is: 1  
 $Cr = 29.8/52.0 = 0.573$  1  
 $Cl = 20.3/35.5 = 0.572$  1  
 $O = 27.5/16.0 = 1.719$  3 or  $KCrClO_3$  (scores 2)  
[1] [1] [2]
- (b)  $K_2Cr_2O_7 + 2HCl \longrightarrow 2KCrClO_3 + H_2O$  [1]  
[1]
- (c) (i) redox or oxidation [1]
- (ii)  $E^\ominus$  data and half equations:  
 $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$   $E^\ominus = 1.33\text{ V}$  [1]  
 $Cl_2 + 2e^- \longrightarrow 2Cl^-$   $E^\ominus = 1.36\text{ V}$  [1]  
overall ionic equation:  
 $Cr_2O_7^{2-} + 6Cl^- + 14H^+ \longrightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$  [1]
- (iii) (dilution will) lower  $E^\ominus$  for  $Cr_2O_7^{2-}/Cr^{3+}$  or raise  $E^\ominus$  for  $Cl_2/Cl^-$  }  
or lower  $[Cl^-]$  or  $[H^+]$  will shift equilibrium in eqn to the left hand side } [1]
- (iv)  $Br_2/Br^- = +1.07\text{ V}$ , so Cr(VI) would oxidise  $Br^-$  (easily) [1]  
[6]  
[Total: 9]

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- 4 (a)  $\text{CCl}_4$  is unreactive. (The rest react (with increasing vigour)) [1]  
 no d-orbitals *or* available/low-lying empty orbitals in carbon *or* unable to expand octet [1]  
 e.g.  $\text{SiCl}_4 + 2\text{H}_2\text{O} \longrightarrow \text{SiO}_2 + 4\text{HCl}$   
 (*or*  $\text{GeCl}_4$  etc) *or*  $\text{Si(OH)}_2\text{Cl}_2$   
*or*  $\text{Si(OH)}_4$   
 (allow balanced equations for partial hydrolysis) [1]  
**[3]**
- (b) (i)  $E(\text{C}-\text{Cl}) = 244 \text{ kJ mol}^{-1}$ ;  $2 E(\text{C}-\text{Cl}) = 2 \times 340 = 680 \text{ kJ mol}^{-1}$   
 $\therefore \Delta H = -436 \text{ (kJ mol}^{-1}\text{)}$  [1]
- (ii)  $\Delta H = 359 - 329 = +30 \text{ (kJ mol}^{-1}\text{)}$  [1]
- (iii) since reaction (ii) is endothermic, the +4 oxidation state is less stable  
*or* the +2 oxidation state is more stable (down the group) [1]  
**[3]**  
**[Total: 6]**
- 5 (a)  $2 \text{MnO}_4^- + 5 \text{H}_2\text{O}_2 + 6 \text{H}^+ \longrightarrow 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O} + 5 \text{O}_2$  [1]  
**[1]**
- (b)  $E_{\text{cell}}^\ominus = 1.52 - 0.68 = +0.84 \text{ (V)}$  [1]  
**[1]**
- (c) (i) (as  $\text{KMnO}_4$  is added), colour changed (from purple) to colourless – *NOT* pink [1]  
*or* effervescence/bubbles (of  $\text{O}_2$ ) are produced [1]  
 at end-point, change is to (first) pink [1]
- (ii)  $n(\text{MnO}_4^-) = 0.02 \times 15/1000 = 3 \times 10^{-4}$  [1]  
 since  $\text{H}_2\text{O}_2 : \text{MnO}_4^- = 5:2$ ,  
 $\Rightarrow n(\text{H}_2\text{O}_2) = (5/2) \times 3 \times 10^{-4} = 7.5 \times 10^{-4} \text{ in } 25 \text{ cm}^3$   
 $\therefore [\text{H}_2\text{O}_2] = 7.5 \times 10^{-4} \times 1000/25 = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$  [1]  
**[4]**  
**[Total: 6]**

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6 (a) (i)



allow ONa but no covalent O-Na bond

[1]

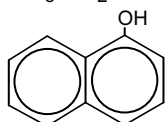
(ii) amide, ester

2 x [1]

(iii)  $\text{CO}_2$  or  $\text{H}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$   
 $\text{CH}_3\text{NH}_2$  or  $\text{CH}_3\text{NH}_3^+\text{Cl}^-$

[1]

[1]



[1]

(iv)  $\text{H}_3\text{O}^+$  and heat  $>80^\circ$  or  $\text{OH}^-(\text{aq})$  and heat  $>80^\circ$

[1]

[7]

(b) (i)  $\text{Br}_2(\text{aq})$  (or other suitable solvent)

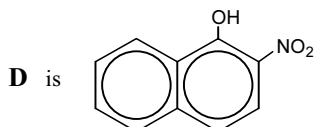
[1]

(ii) dilute/aqueous  $\text{HNO}_3$

[1]

[2]

(c) (i)

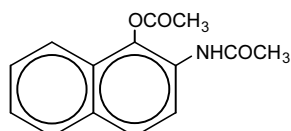


[1]

(ii) tin/Fe + HCl NOT  $\text{LiAlH}_4$

[1]

(iii)

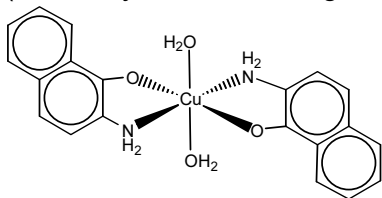


mark each side chain separately

2 x [1]

[4]

(d) (i) (allow any orientation of groups)



penalise missing H on  $\text{NH}_2$

[1]

(ii)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  or  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  NOT  $[\text{Cu}(\text{NH}_3)_6]^{2+}$

[1]

(iii) ligand substitution/exchange

[1]

[3]

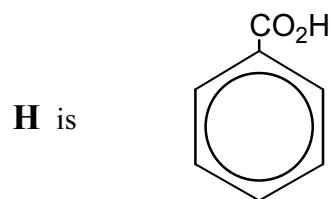
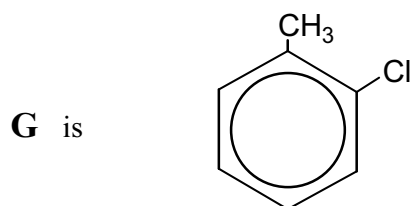
[Total: max 15]

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- 7 (a)  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  [1]  
 at  $50 - 60^\circ\text{C}$  (or  $\leq 60^\circ\text{C}$ ) not dilute or (aq) [1]  
 [2]

- (b)  $2\text{H}_2\text{SO}_4 + \text{HNO}_3 \longrightarrow 2\text{HSO}_4^- + \text{H}_3\text{O}^+ + \text{NO}_2^+$  [1]  
 (allow equ. with only one  $\text{H}_2\text{SO}_4$ , giving  $\text{H}_2\text{O}$ ) [1]

(c)



[1] + [1]

- reaction I:  $\text{Cl}_2 + \text{AlCl}_3$ /accept other halogen carriers *NOT* aq, *nor* u.v.  
 reaction II:  $\text{KMnO}_4 + \text{H}^+$  *NOT*  $\text{HCl}$  *nor*  $\text{HNO}_3$   
 reaction III:  $\text{KMnO}_4 + \text{H}^+$  *NOT*  $\text{HCl}$  *nor*  $\text{HNO}_3$   
 reaction IV:  $\text{Cl}_2 + \text{AlCl}_3$ /accept other halogen carriers *NOT* aq, *nor* u.v.

both I + IV [1]  
both II + III [1]  
 [4]

[Total: 7]

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- 8 (a) (i) Two interlinked spirals *or* chains *or* strands woven round each other [1]  
(ii) By hydrogen bonds between bases [1]  
[2]
- (b) Transcription – (1)DNA/RNA/nucleic acid unravels [1]  
– (2)strand is used as a template [1]  
– (3)mRNA reads the sequence on this strand/  
produces complementary strand [1]
- Translation – (4)mRNA binds to the ribosome [1]  
– (5)tRNA translates the codon from mRNA [1]  
– (6)tRNA carries amino acids to ribosome/adds a.a. to chain [1]  
[**max 4**]
- (c) (i) Disruption of the secondary/tertiary/quaternary/3D structure of the protein  
(could be answered in terms of bonds e.g. hydrogen bonds break) [1]
- (ii) The covalent/peptide bonds in the (protein) chain are too strong [1]  
[2]
- (d) Energy is provided by the breakdown/hydrolysis of adenosine triphosphate (ATP) [1]  
ATP (+ H<sub>2</sub>O) → ADP + P<sub>i</sub> (+ energy) or in words [1]  
ATP is produced during respiration/Krebs cycle/oxidation of glucose, fats or proteins/  
in mitochondria/ADP is recycled [1]  
[3]
- [**Total: 11**]



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- 9 (a) Suitable diagram showing origin of two energy states/or description [1]  
Needs to mention applied magnetic field/electron transfer negates [1]  
Indication that energy difference is in the radio frequency range [1]  
Indication that frequency of absorption *or* gap between the 2 energy states depends on the nature of nearby atoms *or* the chemical environment of the <sup>1</sup>H [1]  
**[3]**
- (b) They do not damage tissues/X-rays harmful/NMR of lower energy [1]  
They are not obscured by bones/skeleton [1]  
They can be tuned to examine particular tissues/tumours/*organs*/protons [1]  
**[max 2]**
- (c) (i)  $M : M+1 = 100/(1.1n)$   

$$n = \frac{0.66 \times 200}{14.5 \times 1.1} = \frac{66}{15.95} = 4.14 = 4 \text{ carbon atoms}$$
 [1]  
Check for 1.1 in divisor, if missing, penalise
- (ii) Singlet at  $\delta$  2 suggests methyl adjacent to C=O [1]  
Quartet at  $\delta$  4 suggests a –CH<sub>2</sub>- group (adjacent to a –methyl group) [1]  
(allow –OCH<sub>2</sub>- )  
Triplet at  $\delta$  1.2 suggests a methyl group (adjacent to a –CH<sub>2</sub>-) [1]  
**G** is ethyl ethanoate (or structure)/if methyl propanoate given here cannot score first marking point [1]  
**[5]**

**[Total: 10]**

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- 10 (a)** Iron is higher in the reactivity series than copper (owtte)/allow use of  $E^\ominus$  [1]
- $\text{Cu}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Fe}^{2+}(\text{aq})$  [1]
- If conversion to  $\text{Fe}^{3+}$  given,  $E_{\text{cell}}$  is  $-0.38$  [2]
- (b)** It does not require investment in machinery/labour [1]
- It requires little energy [1]
- accept it produces little/no pollution/noise [1]
- Do not accept comparison with electrolytic method [max 2]
- (c)** The process takes a long time/requires smaller workforce [1]
- [1]
- (d) (i)** 0.75% is 7.5 kg in every tonne of ore
- Hence 150,000 tonnes of ore yield  $\frac{7.5 \times 150000}{1000}$  tonnes
- or 1,125 tonnes Cu
- $1125 \times 0.6 = 675$  tonnes (accept 680) [1]
- (ii)**  $450 \times 0.17 = 76.5$  tonnes (accept 77) [1]
- or  $1125 \times 0.17 = 191.25$  tonnes (accept 191) – this is an ecf if 675 not in (i) [2]
- (e)** Aluminium is too high in the reactivity series/very reactive/aluminium forms bonds with oxygen which are too strong/aluminium ore doesn't exist as sulphide /Fe unable to displace Al [1]
- [1]
- (f)** Control the pH (*greater* than pH 6.0) [1]
- Bioremediation/growth of special plants (to remove heavy metals)
- Other reasonable suggestions such as displacement by a more reactive metal/precipitation/ion exchange [1]
- [2]
- [Total: 9]