UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS

GCE Advanced Subsidiary Level and GCE Advanced Level

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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UNIVERSITY of CAMBRIDGE
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1 **(a)** **(i)** $K_a = [H^+][RCO_2^-]/[RCO_2H]$ [1]

(ii) $pK_a = -\log_{10}K_a$ *or* $-\log K_a$ *or* $\log [H^+]^2/[RCO_2H]$ NOT ln; [1]

[2]

(b) **(i)** acid strength <u>increases</u> from no. 1 to no. 3 *or* down the table *or* as Cls increase [1]
due to the electron-withdrawing effect/electronegativity of chlorine (atoms) [1]
stabilising the anion *or* weakening the O-H bond NOT H^+ more available [1]

(ii) chlorine atom is further away (from O-H) in no. 4, so has less influence [1]

(iii) *either:* pH = ½ (pK_a – $\log_{10}$[acid]) *or* $K_a = 10^{-pKa} = 1.259 \times 10^{-3}$
= ½ (4.9 + 2) $[H^+] = \surd(K_a.\ c) = 3.55 \times 10^{-4}$ [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]
∴ 10.0 g should give 10 x 89/74 = 12.03 g
∴ percentage yield = 100 x 9.5/12.03 = **79%** ecf [1]
([2] for correct answer)

[5]

(d) $^+NH_3\text{-}CH(CH_3)\text{-}CO_2^-$ correct atoms [1]
Allow charges on H of H_3N, and –COO but not –C-O-O correct charges [1]

[2]

[Total: 15]

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]
ΔH_{soln} becomes more endothermic/positive/less exothermic [1]
[max 4]

(b) identities of **A** and **B** 2 x [1]
$Mg(OH)_2 + H_2C_2O_4 \longrightarrow \underset{\textbf{(A)}}{MgC_2O_4(aq)} + 2H_2O$ [1]

$MgC_2O_4(aq) + Ca(NO_3)_2 \longrightarrow Mg(NO_3)_2 + \underset{\textbf{(B)}}{CaC_2O_4(s)}$ [1]
[max 3]

(c) **(i)** (K_{sp} =) $[Mg^{2+}][OH^-]^2$ [1]
units are <u>mol^3dm^{-9}</u> ecf from K_{sp} [1]

(ii) (call $[Mg(OH)_2(aq)] = [Mg^{2+}] = x$) $\therefore K_{sp} = 2 \times 10^{-11} = \mathbf{4x^3}$ [1]

$\therefore x = \mathbf{1.71 \times 10^{-4}}$ mol dm^{-3} ecf [1]

(iii) less soluble <u>because</u> of the common ion effect
or the equilibrium $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ is moved to the left [1]
[5]
[Total: 12]

3 **(a)** K = 22.4/39.1 = 0.573 thus ratio is: 1
Cr = 29.8/52.0 = 0.573 1
C*l* = 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:
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ $E^\ominus = 1.33$ V [1]
$Cl_2 + 2e^- \longrightarrow 2\,Cl^-$ $E^\ominus = 1.36$ 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) $Br_2/Br^- = +1.07$ V, so Cr(VI) would oxidise Br^- (easily) [1]
[6]
[Total: 9]

4 **(a)** 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. $SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$

(*or* $GeCl_4$ etc) *or* $Si(OH)_2Cl_2$

or $Si(OH)_4$

(allow balanced equations for partial hydrolysis) [1]

[3]

(b) **(i)** E(Cl-Cl) = 244 kJ mol^{-1}; 2 E(C-Cl) = 2 x 340 = 680 kJ mol^{-1}

$\therefore$ ΔH = **–436** (kJ mol^{-1}) [1]

(ii) ΔH = 359 – 329 = **+30** (kJ mol^{-1}) [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)** $\mathbf{2}\,MnO_4^- + \mathbf{5}\,H_2O_2 + \mathbf{6}\,H^+ \longrightarrow \mathbf{2}\,Mn^{2+} + \mathbf{8}\,H_2O + \mathbf{5}\,O_2$ [1]

[1]

(b) $E^{\text{e}}_{\text{cell}}$ = 1.52 – 0.68 = **+0.84** (V) [1]

[1]

(c) **(i)** (as $KMnO_4$ is added), colour changed (from purple) to colourless – *NOT* pink *or* effervescence/bubbles (of O_2) are produced [1]

at end-point, change is to (first) pink [1]

(ii) $n(MnO_4^-) = 0.02 \times 15/1000 = 3 \times 10^{-4}$ [1]

since $H_2O_2 : MnO_4^-$ = 5:2,

$\Rightarrow$ $n(H_2O_2)$ = (5/2) x 3 x 10^{-4} = 7.5 x 10^{-4} in 25 cm^3

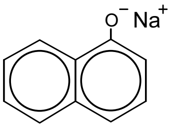
$\therefore$ $[H_2O_2]$ = 7.5 x 10^{-4} x 1000/25 = **3.0 x $\mathbf{10^{-2}}$** mol dm^{-3} [1]

[4]

[Total: 6]

6 **(a)** **(i)**

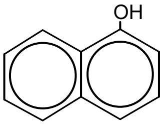
C is



allow ONa but no covalent O-Na bond [1]

(ii) amide, ester 2 x [1]

(iii) CO_2 *or* H_2CO_3 *or* Na_2CO_3 [1]
CH_3NH_2 *or* $CH_3NH_3^+Cl^-$ [1]



[1]

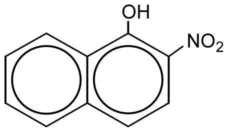
(iv) H_3O^+ and heat >80° *or* OH^-(aq) and heat >80° [1]
[7]

(b) **(i)** Br_2(aq) (or other suitable solvent) [1]

(ii) dilute/aqueous HNO_3 [1]
[2]

(c) **(i)**

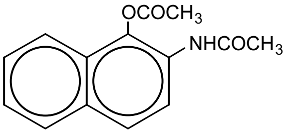
D is



[1]

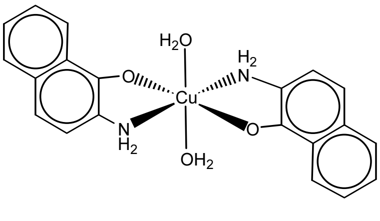
(ii) tin/Fe + HCl *NOT* $LiAlH_4$ [1]

(iii)



mark each side chain separately 2 x [1]
[4]

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



penalise missing H on NH_2 [1]

(ii) $[Cu(NH_3)_4]^{2+}$ *or* $[Cu(NH_3)_4(H_2O)_2]^{2+}$ *NOT* $[Cu(NH_3)_6]^{2+}$ [1]

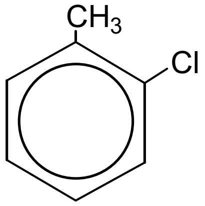
(iii) ligand substitution/exchange [1]
[3]
[Total: max 15]

7 **(a)** $HNO_3 + H_2SO_4$ [1]
at 50 – 60°C (*or* $\leq$ 60°C) not dilute or (aq) [1]
[2]

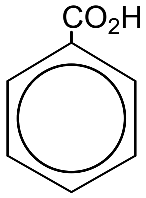
(b) $2H_2SO_4 + HNO_3 \longrightarrow 2HSO_4^- + H_3O^+ + NO_2^+$
(allow equ. with only one H_2SO_4, giving H_2O) [1]
[1]

(c)

G is



H is



[1] + [1]

reaction I: $Cl_2 + AlCl_3$/accept other halogen carriers *NOT* aq, *nor* u.v.
reaction II: $KMnO_4 + H^+$ *NOT* HC*l* *nor* HNO_3
reaction III: $KMnO_4 + H^+$ *NOT* HC*l* *nor* HNO_3
reaction IV: $Cl_2 + AlCl_3$/accept other halogen carriers *NOT* aq, *nor* u.v.

<u>both</u> I + IV [1]
<u>both</u> II + III [1]
[4]

[Total: 7]

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_2O) → ADP + P_i (+ 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]

9 **(a)** Suitable diagram showing origin of two energy states/or description [1]
Needs to mention applied magnetic field/electron transfer negates
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 ^{1}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 δ 2 suggests methyl adjacent to C=O [1]
Quartet at δ 4 suggests a $-CH_2-$ group *(*adjacent to a –methyl group*)* [1]
(allow $-OCH_2-$)
Triplet at δ 1.2 suggests a methyl group *(*adjacent to a $-CH_2-$*)* [1]
G is ethyl ethanoate (or structure)/if methyl propanoate given here cannot score first marking point [1]
[5]

[Total: 10]

10 **(a)** Iron is higher in the reactivity series than copper (owtte)/allow use of $E^\ominus$ [1]

$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$ [1]
If conversion to Fe^{3+} given, E_{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 <u>not</u> 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 x 0.6 = 675 tonnes (accept 680) [1]

(ii) 450 x 0.17 = 76.5 tonnes (accept 77) [1]
or 1125 x 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]