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

This mark scheme is published as an aid to teachers and candidates, to indicate the requirements of the examination. It shows the basis on which Examiners were instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began.

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.

Mark schemes must be read in conjunction with the question papers and the report on the examination.

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

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

(b) (i) acid strength increases from no. 1 to no. 3 *or* down the table *or* as C*l*s 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) $[H^+] = \sqrt{(K_a . c)} = 3.55 \times 10^{-4}$ [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)
lattice energy decreases
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]

$Mg(OH)_2 + H_2C_2O_4 \longrightarrow MgC_2O_4(aq) + 2H_2O$ [1]
(A)

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

(c) **(i)** (K_{sp} =) $[Mg^{2+}][OH^-]^2$ [1]
units are $\underline{mol^3dm^{-9}}$ 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))
no d-orbitals *or* available/low-lying empty orbitals in carbon *or* unable to expand octet
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(C*l*-C*l*) = 244 kJ mol^{-1}; 2 E(C-C*l*) = 2 x 340 = 680 kJ mol^{-1}
$\therefore \Delta H$ = **–436** (kJ mol^{-1}) [1]

(ii) $\Delta H = 359 - 329 =$ **+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]

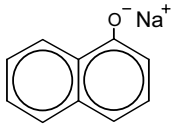
5 **(a)** **2** MnO_4^- + **5** H_2O_2 + **6** $H^+ \longrightarrow$ **2** Mn^{2+} + **8** H_2O + **5** O_2 [1]
[1]

(b) $E^{\ominus}_{cell} = 1.52 - 0.68 =$ **+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 $H_2O_2 : MnO_4^- = 5:2$,
$\Rightarrow n(H_2O_2) = (5/2) \times 3 \times 10^{-4} = 7.5 \times 10^{-4}$ in 25 cm^3
$\therefore [H_2O_2] = 7.5 \times 10^{-4} \times 1000/25 =$ **3.0 x 10^{-2}** mol dm^{-3} [1]
[4]
[Total: 6]

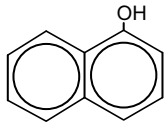
6 (a) (i)

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]



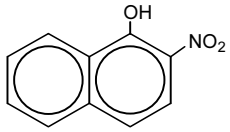
[1]

(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]

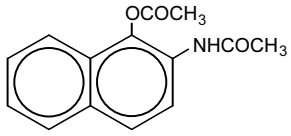
(c) (i)

D is 

[1]

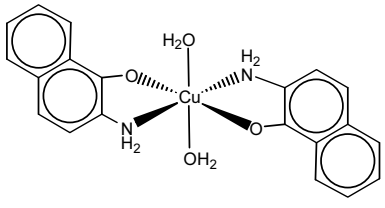
(ii) tin/Fe + HC*l* *NOT* LiA*l*H_4 [1]

(iii)



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

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



penalise missing H on NH_2 [1]

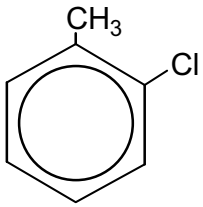
(ii) $[Cu(NH_3)_4]^{2+}$ *or* $[Cu(NH_3)_4(H_2O)_2]^{2+}$ *NOT* $[Cu(NH_3)_6]^{2+}$ [1]

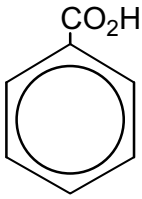
(iii) ligand substitution/exchange [1]
[3]
[Total: max 15]

7 **(a)** $HNO_3 + H_2SO_4$
at 50 – 60°C (*or* ≤ 60°C) not dilute or (aq)

(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: C*l*$_2$ + A*l*C*l*$_3$/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: C*l*$_2$ + A*l*C*l*$_3$/accept other halogen carriers *NOT* aq, *nor* u.v.

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

[Total: 7]

8 (a) (i) Two interlinked spirals *or* chains *or* strands woven round each other

(ii) By hydrogen bonds between bases [1]

(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) $\rightarrow$ 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
Needs to mention applied magnetic field/electron transfer negates
Indication that energy difference is in the radio frequency range
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 $E^{\ominus}$

$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$
If conversion to Fe^{3+} given, E_{cell} is –0.38 [1]

(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 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 A*l* [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]