## 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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1 (a) (i) $K_{\mathrm{a}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{RCO}_{2}^{-}\right] /\left[\mathrm{RCO}_{2} \mathrm{H}\right]$
(ii) $\mathrm{p} K_{\mathrm{a}}=-\log _{10} K_{\mathrm{a}}$ or $-\log K_{\mathrm{a}}$ or $\log \left[\mathrm{H}^{+}\right]^{2} /\left[\mathrm{RCO}_{2} \mathrm{H}\right]$ NOT ln ;
(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 $\mathrm{O}-\mathrm{H}$ bond $\mathrm{NOT} \mathrm{H}^{+}$more available
(ii) chlorine atom is further away (from O-H) in no. 4, so has less influence
(iii) either: $\mathrm{pH}=1 / 2\left(\mathrm{p} K_{\mathrm{a}}-\log _{10}[\right.$ acid $\left.]\right)$ or $K_{\mathrm{a}}=10^{-\mathrm{p} K a}=1.259 \times 10^{-3}$

$$
\begin{array}{ll}
=1 / 2(4.9+2) & {\left[\mathrm{H}^{+}\right]=\sqrt{ }\left(K_{\mathrm{a}} . \mathrm{c}\right)=3.55 \times 10^{-4}} \\
=3.4 \text { (allow 3.5) } & \mathrm{pH}=3.4 \tag{1}
\end{array}
$$

([1] for correct expression \& values; [1] for correct working)
(c) (i) catalyst
(ii) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}+\mathrm{Cl}_{2} \longrightarrow \mathrm{CH}_{2} \mathrm{CHClCO}_{2} \mathrm{H}+\mathrm{HCl}$
(iii) nucleophilic substitution NOT addition/elimination
(iv) $\mathrm{M}_{\mathrm{r}}\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}\right)=74 \quad \mathrm{M}_{\mathrm{r}}\left(\mathrm{CH}_{2} \mathrm{CH}\left(\mathrm{NH}_{2}\right) \mathrm{CO}_{2} \mathrm{H}\right)=89$
$\therefore 10.0 \mathrm{~g}$ should give $10 \times 89 / 74=12.03 \mathrm{~g}$
$\therefore$ percentage yield $=100 \times 9.5 / 12.03=79 \%$
(d) ${ }^{+} \mathrm{NH}_{3}-\mathrm{CH}\left(\mathrm{CH}_{3}\right)-\mathrm{CO}_{2}^{-}$

Allow charges on $\mathrm{H}^{2} \mathrm{H}_{3} \mathrm{~N}$, and - COO but not - $\mathrm{C}-\mathrm{O}-\mathrm{O}$

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2 (a) solubility decreases (down Group II)
lattice energy decreases
solvation/hydration energy (of cation) decreases
but more so than does lattice energy/is not able to overcome LE
$\Delta \mathrm{H}_{\text {soln }}$ becomes more endothermic/positive/less exothermic
(b) identities of $\mathbf{A}$ and $\mathbf{B}$
$\mathrm{Mg}(\mathrm{OH})_{2}+\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \longrightarrow \mathrm{MgC}_{2} \mathrm{O}_{4}(\mathrm{aq})+2 \mathrm{H}_{2} \mathrm{O}$
(A)
$\mathrm{MgC}_{2} \mathrm{O}_{4}(\mathrm{aq})+\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2} \longrightarrow \mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2}+\mathrm{CaC}_{2} \mathrm{O}_{4}(\mathrm{~s})$
(B)
(c) (i) $\left(K_{s p}=\right)\left[\mathrm{Mg}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2}$
units are $\mathrm{mol}^{3} \mathrm{dm}^{-9}$
(ii) $\quad\left(\right.$ call $\left.\left[\mathrm{Mg}(\mathrm{OH})_{2}(\mathrm{aq})\right]=\left[\mathrm{Mg}^{2+}\right]=\mathrm{x}\right) \quad \therefore K_{\mathrm{sp}}=2 \times 10^{-11}=\mathbf{4 \mathbf { x } ^ { 3 }}$

$$
\begin{equation*}
\therefore \mathrm{x}=1.71 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3} \tag{1}
\end{equation*}
$$

(iii) less soluble because of the common ion effect
or the equilibrium $\mathrm{Mg}(\mathrm{OH})_{2}(\mathrm{~s}) \rightleftharpoons \mathrm{Mg}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq})$ is moved to the left

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3 (a) $\mathrm{K}=22.4 / 39.1=0.573$
thus ratio is: 1
$\mathrm{Cr}=29.8 / 52.0=0.573$
1
$\mathrm{Cl}=20.3 / 35.5=0.572$
1
$\mathrm{O}=27.5 / 16.0=1.719$
3 or $\mathrm{KCrClO}_{3}$ (scores 2)
[1]
[1]
(b) $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}+2 \mathrm{HCl} \longrightarrow 2 \mathrm{KCrClO}_{3}+\mathrm{H}_{2} \mathrm{O}$
(c) (i) redox or oxidation
(ii) $\mathrm{E}^{\ominus}$ data and half equations:
$\begin{array}{ll}\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}+14 \mathrm{H}^{+}+6 \mathrm{e}^{-} \longrightarrow 2 \mathrm{Cr}^{3+}+7 \mathrm{H}_{2} \mathrm{O} & \begin{array}{l}\mathrm{E}^{\ominus}=1.33 \mathrm{~V} \\ \mathrm{Cl}_{2}+2 \mathrm{e}^{-} \longrightarrow 2 \mathrm{C} t\end{array} \\ \mathrm{E}^{\ominus}=1.36 \mathrm{~V}\end{array}$
overall ionic equation:
$\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+6 \mathrm{C} t+14 \mathrm{H}^{+} \longrightarrow 2 \mathrm{Cr}^{3+}+3 \mathrm{Cl}_{2}+7 \mathrm{H}_{2} \mathrm{O}$
(iii) (dilution will) lower $\mathrm{E}^{\ominus}$ for $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-} / \mathrm{Cr}^{3+}$ or raise $\mathrm{E}^{\ominus}$ for $\mathrm{Cl}_{2} / \mathrm{C} t$
or lower $[\mathrm{C} T]$ or $\left[\mathrm{H}^{+}\right]$will shift equilibrium in eqn to the left hand side J
(iv) $\mathrm{Br}_{2} / \mathrm{Br}^{-}=+1.07 \mathrm{~V}$, so $\mathrm{Cr}(\mathrm{VI})$ would oxidise $\mathrm{Br}^{-}$(easily)

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4 (a) $\mathrm{CC}_{4}$ 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. $\mathrm{SiCl}_{4}+2 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{SiO}_{2}+4 \mathrm{HCl}$
(or $\mathrm{GeCl}_{4}$ etc) or $\mathrm{Si}(\mathrm{OH})_{2} \mathrm{Cl}_{2}$
or $\mathrm{Si}(\mathrm{OH})_{4}$
(allow balanced equations for partial hydrolysis)
(b) (i) $\mathrm{E}(\mathrm{Cl}-\mathrm{Cl})=244 \mathrm{~kJ} \mathrm{~mol}^{-1} ; \quad 2 \mathrm{E}(\mathrm{C}-\mathrm{Cl})=2 \times 340=680 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$\therefore \Delta \mathrm{H}=\mathbf{- 4 3 6}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$
(ii) $\Delta \mathrm{H}=359-329=+\mathbf{3 0}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$
(iii) since reaction (ii) is endothermic, the +4 oxidation state is less stable or the +2 oxidation state is more stable (down the group)

5 (a) $2 \mathrm{MnO}_{4}^{-}+5 \mathrm{H}_{2} \mathrm{O}_{2}+\mathbf{6} \mathrm{H}^{+} \longrightarrow 2 \mathrm{Mn}^{2+}+8 \mathrm{H}_{2} \mathrm{O}+5 \mathrm{O}_{2}$
(b) $E_{\text {cell }}^{\ominus}=1.52-0.68=+\mathbf{0 . 8 4}(\mathrm{V})$
(c) (i) (as $\mathrm{KMnO}_{4}$ is added), colour changed (from purple) to colourless - NOT pink or effervescence/bubbles (of $\mathrm{O}_{2}$ ) are produced at end-point, change is to (first) pink
(ii) $n\left(\mathrm{MnO}_{4}^{-}\right)=0.02 \times 15 / 1000=3 \times 10^{-4}$
since $\mathrm{H}_{2} \mathrm{O}_{2}: \mathrm{MnO}_{4}^{-}=5: 2$,
$\Rightarrow \mathrm{n}\left(\mathrm{H}_{2} \mathrm{O}_{2}\right)=(5 / 2) \times 3 \times 10^{-4}=7.5 \times 10^{-4}$ in $25 \mathrm{~cm}^{3}$
$\therefore\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]=7.5 \times 10^{-4} \times 1000 / 25=3.0 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3}$

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6 (a) (i)

C is
 allow ONa but no covalent O-Na bond
(ii) amide, ester
(iii) $\mathrm{CO}_{2}$ or $\mathrm{H}_{2} \mathrm{CO}_{3}$ or $\mathrm{Na}_{2} \mathrm{CO}_{3}$
$\mathrm{CH}_{3} \mathrm{NH}_{2}$ or $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+} \mathrm{C} t$

(iv) $\mathrm{H}_{3} \mathrm{O}^{+}$and heat $>80^{\circ}$ or $\mathrm{OH}^{-}(\mathrm{aq})$ and heat $>80^{\circ}$
(b) (i) $\mathrm{Br}_{2}(\mathrm{aq})$ (or other suitable solvent)
(ii) dilute/aqueous $\mathrm{HNO}_{3}$
(c) (i)

D is

(ii) $\mathrm{tin} / \mathrm{Fe}+\mathrm{HCl} \mathrm{NOT}_{\mathrm{LiAlH}}^{4}$
(iii)

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

penalise missing H on $\mathrm{NH}_{2}$
(ii) $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ or $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+} \mathrm{NOT}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$
(iii) ligand substitution/exchange

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7 (a) $\mathrm{HNO}_{3}+\mathrm{H}_{2} \mathrm{SO}_{4}$
at $50-60^{\circ} \mathrm{C}\left(\right.$ or $\left.\leq 60^{\circ} \mathrm{C}\right)$ not dilute or (aq)
(b) $2 \mathrm{H}_{2} \mathrm{SO}_{4}+\mathrm{HNO}_{3} \longrightarrow 2 \mathrm{HSO}_{4}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{NO}_{2}^{+}$ (allow equ. with only one $\mathrm{H}_{2} \mathrm{SO}_{4}$, giving $\mathrm{H}_{2} \mathrm{O}$ )
(c)
$\mathbf{G}$ is
 $\mathbf{H}$ is

reaction I: $\quad \mathrm{Cl}_{2}+\mathrm{AlCl}_{3} /$ accept other halogen carriers $N O T$ aq, nor u.v.
reaction II: $\mathrm{KMnO}_{4}+\mathrm{H}^{+} \mathrm{NOT} \mathrm{HCl}$ nor $\mathrm{HNO}_{3}$
reaction III: $\mathrm{KMnO}_{4}+\mathrm{H}^{+} \mathrm{NOT} \mathrm{HCl}$ nor $\mathrm{HNO}_{3}$
reaction IV: $\quad \mathrm{Cl}_{2}+\mathrm{AlCl}_{3} /$ accept other halogen carriers $N O T$ aq, nor u.v.

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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

- (2)strand is used as a template
- (3)mRNA reads the sequence on this strand/ produces complementary strand

Translation - (4)mRNA binds to the ribosome [1]

- (5)tRNA translates the codon from mRNA
- (6)tRNA carries amino acids to ribosome/adds a.a. to chain
(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)
(ii) The covalent/peptide bonds in the (protein) chain are too strong
(d) Energy is provided by the breakdown/hydrolysis of adenosine triphosphate (ATP)

ATP is produced during respiration/Krebs cycle/oxidation of glucose, fats or proteins/ in mitochondria/ADP is recycled

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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 ${ }^{1} \mathrm{H}$
(b) They do not damage tissues/X-rays harmful/NMR of lower energy

They are not obscured by bones/skeleton
They can be tuned to examine particular tissues/tumours/organs/protons
(c) (i) $\mathrm{M}: \mathrm{M}+1=100 /(1.1 \mathrm{n})$
$\mathrm{n}=\frac{0.66 \times 200}{14.5 \times 1.1}=\frac{66}{15.95}=4.14=4$ carbon atoms
Check for 1.1 in divisor, if missing, penalise
(ii) Singlet at $\delta 2$ suggests methyl adjacent to $\mathrm{C}=\mathrm{O}$

Quartet at $\delta 4$ suggests a $-\mathrm{CH}_{2}$ - group (adjacent to a -methyl group)
(allow $-\mathrm{OCH}_{2}$ - )
Triplet at $\delta 1.2$ suggests a methyl group (adjacent to a $-\mathrm{CH}_{2}$-)
$\mathbf{G}$ is ethyl ethanoate (or structure)/if methyl propanoate given here cannot score first marking point

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10 (a) Iron is higher in the reactivity series than copper (owtte)/allow use of $E^{\circ}$
$\mathrm{Cu}^{2+}(\mathrm{aq})+\mathrm{Fe}(\mathrm{s}) \rightarrow \mathrm{Cu}(\mathrm{s})+\mathrm{Fe}^{2+}(\mathrm{aq})$
If conversion to $\mathrm{Fe}^{3+}$ given, $\mathrm{E}_{\text {cell }}$ is -0.38
(b) It does not require investment in machinery/labour

It requires little energy
accept it produces little/no pollution/noise
Do not accept comparison with electrolytic method
(c) The process takes a long time/requires smaller workforce
(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)
(ii) $450 \times 0.17=76.5$ tonnes (accept 77)
or $1125 \times 0.17=191.25$ tonnes (accept 191) - this is an ecf if 675 not in (i)
(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
(f) Control the pH (greater than pH 6.0 )

Bioremediation/growth of special plants (to remove heavy metals)
Other reasonable suggestions such as displacement by a more reactive metal/ precipitation/ion exchange

