# MARK SCHEME for the October/November 2009 question paper for the guidance of teachers 

9701 CHEMISTRY<br>9701/42 Paper 42 (A2 Structured Questions), maximum raw mark 100

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1 (a) Sulfates become less soluble down the group
both lattice energy and hydration (are involved)
but hydration energy decreases more than lattice energy or HE becomes less than LE or HE decreases whereas LE is almost constant (due to cationic radius increasing)
(b) (i) $\mathrm{n}(\mathrm{CO})=\mathrm{pV} / \mathrm{RT}=1.01 \times 10^{5} \times 140 \times 10^{-3} /(8.31 \times 450)=\mathbf{3 . 7 8}$
or $\quad=140 \times(273 / 450) / 22.4=3.79$
allow $=140 \times(298 / 450) / 24.0=3.86$
(ii) $\mathrm{n}\left(\mathrm{BaSO}_{4}\right)=\mathrm{n}(\mathrm{CO}) / 4=\mathbf{0 . 9 4 5}$ moles (or 0.9475)

If RTP used answer is $\mathbf{0 . 9 6 6}$
(iii) $\mathrm{M}_{\mathrm{r}}=233$,
so $0.945 \mathrm{~mol}=0.945 \times 233=220 \mathrm{~g} \Rightarrow 100 \times 220 / 250=88(.07) \%$ (or $0.9475 \mathrm{~mol} \Rightarrow 220.8 \mathrm{~g} \Rightarrow 88(.3) \%$ )
If RTP used answer is $90(.0) \%$
(c) (i) from data booklet, $1^{\text {st }} \mathrm{IE}=502 ; 2^{\text {nd }} \mathrm{IE}=966$; sum $=1468 \mathrm{~kJ} \mathrm{~mol}^{-1}$

$$
\begin{align*}
& \text { so }-460=1468+180+279-200+640+\mathrm{LE} \\
& -460=2367+\mathrm{LE} \\
& \mathrm{LE}=-2827 \mathrm{~kJ} \mathrm{~mol} \\
& (-1 \text { for each error }) \tag{3}
\end{align*}
$$

(ii) LE of BaS should be smaller than that of BaO , since $\mathrm{S}^{2-}$ is bigger than $\mathrm{O}^{2-}$.

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2 (a) ethylamine $>\mathrm{NH}_{3}$, but phenylamine $<\mathrm{NH}_{3}$
in ethylamine, the alkyl group donates electrons to the N , making lone pair more available
in phenylamine, the lone pair is delocalised over the ring, so is less available
(b)

| halide | observation when <br> $\mathrm{AgNO}_{3}(\mathrm{aq})$ is <br> added | observation when <br> dilute $\mathrm{NH}_{3}(\mathrm{aq})$ is <br> added | observation when <br> concentrated <br> $\mathrm{NH}_{3}(\mathrm{aq})$ is added |
| :---: | :---: | :---: | :---: |
| chloride | white ppt | dissolves | dissolves |
| bromide | cream ppt | no reaction / <br> slightly dissolves | dissolves |
| iodide | (pale) yellow ppt | no reaction | no reaction |

(c) (i) $\left[\mathrm{Ag}^{+}(\mathrm{aq})\right]=\sqrt{ } \mathrm{K}_{\mathrm{sp}}=\sqrt{ }\left(5 \times 10^{-13}\right)=\mathbf{7 . 1}(\mathbf{7 . 0 7}) \times \mathbf{1 0}^{\mathbf{- 7}} \mathrm{mol} \mathrm{dm}^{-3}$
(ii) AgBr will be less soluble in KBr , due to common ion effect or equilibrium is shifted to the left / or by Le Chatelier's principle
(d) (i) $\mathrm{K}_{\mathrm{c}}=\left[\mathrm{Ag}\left(\mathrm{RNH}_{2}\right)_{2}{ }^{+}\right] /\left[\mathrm{Ag}^{+}\right]\left[\mathrm{RNH}_{2}\right]^{2}$
units are $\mathrm{mol}^{-2} \mathrm{dm}^{6}$
(ii) assume that most of the $\mathrm{Ag}^{+}(\mathrm{aq})$ has gone to the complex, then

$$
\begin{align*}
& {\left[\mathrm{Ag}^{+}(\mathrm{aq})\right]=7.1 \times 10^{-7}} \\
& {\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}^{+}\right]=0.1} \tag{1}
\end{align*}
$$

and $\left[\mathrm{NH}_{3}\right]=\sqrt{ }\left\{\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}^{+}\right] /\left(\mathrm{K}_{\mathrm{c}}\left[\mathrm{Ag}^{+}\right]\right)\right\}=\sqrt{ }\left\{0.1 /\left(1.7 \times 10^{7} \times 7.1 \times 10^{-7}\right)\right\}$
$=0.091 \mathrm{~mol} \mathrm{dm}^{-3}$
(iii) When $\mathrm{R}=\mathrm{C}_{2} \mathrm{H}_{5}, \mathrm{~K}_{\mathrm{c}}$ is likely to be greater, since the ethyl group will cause the lone pair on N to be more available / nucleophilic / increases basicity
[Total: 13]

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3 (a) Any two from: high(-ish) density of metal variable oxidation states ability to form complexes formation of coloured compounds incomplete d subshell
high m.p. / b.p.
(b) equ: $\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+5 \mathrm{Fe}^{2+} \longrightarrow \mathrm{Mn}^{2+}+5 \mathrm{Fe}^{3+}+4 \mathrm{H}_{2} \mathrm{O}$
method: Take a known volume of $\mathrm{Fe}^{2+}(\mathrm{aq})$ /in a pipette and place in (conical) flask
Add an excess of (dil) $\mathrm{H}_{2} \mathrm{SO}_{4}$
Titrate until end point is reached and note volume used
End point is first permanent pink colour
Repeat titration \& take average of consistent readings
any 3 points
[3]
(c) (i) $2 \mathrm{MnO}_{4}^{-}+5 \mathrm{SO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{Mn}^{2+}+5 \mathrm{SO}_{4}{ }^{2-}+4 \mathrm{H}^{+}$
$\begin{array}{lllll}\text { oxidation numbers: } & \mathbf{+ 7} & \mathbf{+ 4} & \mathbf{+ 2} & \mathbf{+ 6}\end{array}$
(ii) $1 \mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+6 \mathrm{NO}_{2}+2 \mathrm{H}^{+} \rightarrow 2 \mathrm{Cr}^{3+}+6 \mathrm{NO}_{3}^{-}+1 \mathrm{H}_{2} \mathrm{O}$
$\begin{array}{lllll}\text { oxidation numbers: } & \mathbf{+ 6} & \mathbf{+ 4} & \mathbf{+ 3}\end{array}$
([2] marks for each equation: [1] for balancing of redox species,
[1] for total balancing: i.e. $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{H}^{+}$)
(d) $\mathrm{Fe}^{3+}$ is a homogeneous (catalyst)
$\mathrm{Fe}^{3+}$ oxidised $\mathrm{I}^{-}$(and is reduced to $\mathrm{Fe}^{2+}$ )
$\mathrm{Fe}^{2+}$ reduces $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}$ (and is oxidised to $\mathrm{Fe}^{3+}$ )
or equations showing this any two points
[Total: 14]

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4 (a) The energy required to break....
..... 1 mole of bonds in the gas phase
(b) HCl : nothing happens AND HI : purple fumes (at a low temperature)
purple is iodine formed (or in an equation: $2 \mathrm{HI} \longrightarrow \mathrm{H}_{2}+\mathrm{I}_{2}$ )
$\mathrm{H}-\mathrm{X}$ bond energy becomes smaller/weaker down the group
(c) data needed: F-F = 158

$$
\begin{equation*}
\mathrm{Cl}-\mathrm{Cl}=244 \tag{2}
\end{equation*}
$$

$6 \mathrm{E}(\mathrm{Cl}-\mathrm{F})-328=3 \times 158+244$
$\mathrm{E}(\mathrm{Cl}-\mathrm{F})=\boldsymbol{+ 1 7 4}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$
[Total: 7]

5 (a)

| compound | all carbon atoms <br> can be coplanar | not all carbon <br> atoms coplanar |
| :---: | :---: | :---: |
| A | $\checkmark$ |  |
| B |  | $\checkmark$ |
| C | $\checkmark$ |  |
| D | $\checkmark$ |  |
| E | $\checkmark$ |  |

all 5 correct
(4 correct: [2], 3 correct: [1]. <3 correct: [0])
(b) reaction I: $\mathrm{Cl}_{2}+\mathrm{AlCl}_{3} / \mathrm{FeCl}_{3} / \mathrm{Fe} /$ or bromides of Al or Fe
reaction II: $\mathrm{Cl}_{2}+$ heat / light / uv / hf
(c) (i) $\mathbf{H}$ is $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{Cl}$
(ii) reaction III: $\mathrm{KMnO}_{4}+$ heat (+ $\mathrm{OH}^{-}$)
reaction V : NaOH in water + heat
reaction VI: conc $\mathrm{H}_{2} \mathrm{SO}_{4}+$ heat
(iii) reaction III: oxidation
reaction V: hydrolysis or nucleophilic substitution

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6 (a) L is $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Br}$
$\mathbf{M}$ is $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$
$\mathbf{N}$ is $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}$
$\mathbf{Q}$ is $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}$
$\mathbf{P}$ is $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$
$J$ is $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CONHCH}_{2} \mathrm{CH}_{3}$
$\mathbf{K}$ is $\mathrm{CH}_{3} \mathrm{CONHCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}$
(b) reaction I: KCN, heat NOT H ${ }^{+}$OR HCN aq negates
reaction II: $\mathrm{SOCl}_{2}$ or $\mathrm{PCl}_{5}$ or $\mathrm{PCl}_{3}$ BUT aq negates
reaction IV: $\mathrm{H}_{2}+\mathrm{Ni}$ or $\mathrm{LiAlH}_{4}$ or $\mathrm{NaBH}_{4}$ NOT $\mathrm{Sn}+\mathrm{HCl}$
(c) reaction IV: reduction
reaction VI: nucleophilic substitution or condensation reaction
(d) (i) amide
(ii) amine
[Total: 14]

7 (a) Primary: Covalent bond (ignore amide, peptide etc.)
Diagram showing peptide bond: (-CHR-)CONH(-CHR-)
Secondary: Hydrogen bonds (NOT between side chains"
Diagram showing $\mathrm{N}-\mathrm{H} \cdots \mathrm{O}=\mathrm{C}$
Tertiary: Two of the following:

- hydrogen bonds (diagram must show H-bonds other than those in $\alpha$-helix or $\beta$-pleated sheet - e.g. ser-ser)
- electrostatic/ionic attraction,
- Van der Waals'/hydrophobic forces/bonds,
- (covalent) disulphide (links/bridges)

Suitable diagram of one of the above
(for disulphide: S-S not S=S or SH-SH)
(b) Substrate binds to the active site of the enzyme

Interaction with site causes a specific bond to be weakened, (which breaks)
Or change in shape weakens bond(s) / lowers activation energy
(c) Non-competitive inhibition

Rate never reaches $V_{\text {max }}$

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8 (a) Ratio of the concentrations of a solute / distribution of solute [1] in two immiscible liquids
(b) $K_{\mathrm{c}}=\frac{\text { [pesticide in hexane] }}{\text { [pesticide in water] }}$ hence $8.0=\frac{\text { [pesticide in hexane] }}{0.0050-[\text { [pesticide in hexane }]}$

Therefore [pesticide in hexane] $x=0.040-8 x$
Hence $\mathrm{x}=0.0044(\mathrm{~g})$
(c) (i) Ratio would be 3:1
(ii) Each chlorine at could be ${ }^{35} \mathrm{C} /$ or ${ }^{37} \mathrm{C} /$

Only way of getting $\mathrm{M}+4$ is for both chlorines to be ${ }^{37} \mathrm{Cl}$ (1 in 9 chance)
$\begin{array}{ccc}\text { Ratio of peaks } M & M+2 & M+4 \\ 9 & 6 & 1\end{array}$
(d) (i) Accept dioxins and furans (without specifying)
(ii) PCBs (but don't penalise non-specified dioxins and furans)
(iii) Allow : pollution control / environmental legislation / removal of dioxins and furans / mill closed down (owtte)
(iv) Five
[Total: 11]

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9 (a) Length of DNA nanosphere diameter cell diameter 3 1 2

Both marks for correct sequence, [1] for cell smaller than DNA
(b) (i) Gaps in structure of shaft much smaller, hence less prone to fracture / more flexible
(ii) Composites and carbon nanotubes less dense than metal (of comparable strength)
(c) Wavelength of infrared energy is longer than that of light
Gaps between nano-sized particles allow light to pass through, but reflect infrared energy
(d) (i) Resistance to corrosion / reaction
(ii) Ability to kill bacteria / prevent bacteria multiplying
(iii) Very much larger surface area means they dissolve more readily

