UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS

GCE Advanced Subsidiary Level and GCE Advanced Level

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

9701 CHEMISTRY

9701/42 Paper 42 (A2 Structured Questions), maximum raw mark 100

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1 (a) Sulfates become **less soluble** down the group [1]
both lattice energy and hydration (are involved) [1]
but hydration energy decreases more than lattice energy
or HE becomes less than LE *or* HE decreases whereas LE is almost constant [1]
(due to cationic radius increasing)

[3]

(b) (i) $n(CO) = pV/RT = 1.01 \times 10^5 \times 140 \times 10^{-3}/(8.31 \times 450) =$ **3.78**

or $= 140 \times (273/450) / 22.4 =$ **3.79**

allow= $140 \times (298/450) / 24.0 = 3.86$ [1]

(ii) $n(BaSO_4) = n(CO)/4 =$ **0.945** moles (*or* 0.9475) [1]
If RTP used answer is **0.966**

(iii) $M_r = 233$, [1]
so 0.945 mol = $0.945 \times 233 = 220$g $\Rightarrow$ $100 \times 220/250 =$ **88(.07)%**
(*or* 0.9475 mol $\Rightarrow$ 220.8g $\Rightarrow$ 88(.3)%) [1]
If RTP used answer is **90(.0)%**

[4]

(c) (i) from data booklet, 1st IE = 502; 2nd IE = 966; sum = 1468 kJ mol^{-1}

so –460 = 1468 + 180 + 279 – 200 + 640 + LE
–460 = 2367 + LE
LE = **–2827** kJ mol^{-1}
(–1 for each error) [3]

(ii) LE of BaS should be smaller than that of BaO, since S^{2-} is bigger than O^{2-}. [1]

[4]

[Total: 11]

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2 **(a)** ethylamine > NH_3, but phenylamine < NH_3 [1]

in ethylamine, the alkyl group donates electrons to the N, making lone pair more available [1]

in phenylamine, the lone pair is delocalised over the ring, so is less available [1]

[3]

(b)

halide	observation when $AgNO_3(aq)$ is added	observation when dilute $NH_3(aq)$ is added	observation when concentrated $NH_3(aq)$ is added	
chloride	**white ppt**	**dissolves**	**dissolves**	[1]
bromide	**cream ppt**	**no reaction / slightly dissolves**	**dissolves**	[1]
iodide	**(pale) yellow ppt**	**no reaction**	**no reaction**	[1]

[3]

(c) **(i)** $[Ag^+(aq)] = \sqrt{K_{sp}} = \sqrt{(5 \times 10^{-13})} =$ **7.1 (7.07) × 10^{-7}** mol dm^{-3} [1]

(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 [1]

[2]

(d) **(i)** $K_c = [Ag(RNH_2)_2^+]/[Ag^+][RNH_2]^2$ [1]

units are $mol^{-2}\ dm^6$ [1]

(ii) assume that most of the $Ag^+(aq)$ has gone to the complex, then

$[Ag^+(aq)] = 7.1 \times 10^{-7}$

$[Ag(NH_3)_2^+] = 0.1$

and $[NH_3] = \sqrt{\{[Ag(NH_3)_2^+]/(K_c[Ag^+])\}} = \sqrt{\{0.1/(1.7 \times 10^7 \times 7.1 \times 10^{-7})\}}$ [1]

$=$ **0.091** mol dm^{-3} [1]

(iii) When R = C_2H_5, K_c is likely to be greater, since the ethyl group will cause the lone pair on N to be more available / nucleophilic / increases basicity [1]

[5]

[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. [1] + [1]
[2]

(b) equ: $MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ [1]

method: Take a known volume of $Fe^{2+}(aq)$/in a pipette and place in (conical) flask
Add an excess of (dil) H_2SO_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]
[4]

(c) **(i)** **2** MnO_4^- + **5** SO_2 + **2** H_2O → **2** Mn^{2+} + **5** SO_4^{2-} + **4** H^+ [2]

oxidation numbers: **+7** **+4** **+2** **+6** [1]

(ii) **1** $Cr_2O_7^{2-}$ + **6** NO_2 + **2** H^+ → **2** Cr^{3+} + **6** NO_3^- + **1** H_2O [2]

oxidation numbers: **+6** **+4** **+3** **+5** [1]

([2] marks for each equation: [1] for balancing of redox species,
[1] for total balancing: i.e. H_2O and H^+)
[6]

(d) Fe^{3+} is a homogeneous (catalyst)
Fe^{3+} oxidised I^- (and is reduced to Fe^{2+})
Fe^{2+} reduces $S_2O_8^{2-}$ (and is oxidised to Fe^{3+})
or equations showing this any two points [2]
[2]

[Total: 14]

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4 **(a)** The energy required to break.... [1]
.....1 mole of bonds in the gas phase [1]
[2]

(b) HCl: nothing happens AND HI: purple fumes (at a low temperature) [1]
purple is **iodine** formed (*or* in an equation: $2HI \longrightarrow H_2 + \mathbf{I_2}$) [1]
H-X bond energy becomes smaller/weaker down the group [1]
[3]

(c) data needed: F-F = 158
Cl-Cl = 244

$6\ E(Cl\text{-}F) - 328 = 3\times158 + 244$
$E(Cl\text{-}F) = \mathbf{+174}\ (kJ\ mol^{-1})$ [2]
[2]

[Total: 7]

5 **(a)**

compound	all carbon atoms can be coplanar	not all carbon atoms coplanar
A	✓	
B		✓
C	✓	
D	✓	
E	✓	

all 5 correct [3]
(4 correct: [2], 3 correct: [1]. <3 correct: [0])
[3]

(b) reaction **I:** $Cl_2 + AlCl_3 / FeCl_3$ / Fe / or bromides of Al or Fe [1]
reaction **II:** Cl_2 + heat / light / uv / hf [1]
[2]

(c) **(i)** **H** is $C_6H_5CH_2Cl$ [1]

(ii) reaction **III:** $KMnO_4$ + heat (+ OH^-) [1]
reaction **V:** NaOH in water + heat [1]
reaction **VI:** conc H_2SO_4 + heat [1]

(iii) reaction **III:** oxidation [1]
reaction **V:** hydrolysis *or* nucleophilic substitution [1]
[6]

[Total: 11]

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6 **(a)** **L** is CH_3CH_2Br
M is CH_3CO_2H
N is $CH_3CH_2NH_2$
Q is $CH_3CH_2CO_2H$
P is $CH_3CH_2CH_2NH_2$
J is $CH_3CH_2CONHCH_2CH_3$
K is $CH_3CONHCH_2CH_2CH_3$ [7]
[7]

(b) reaction **I:** KCN, heat NOT H^+ OR HCN aq negates [1]
reaction **II:** $SOCl_2$ *or* PCl_5 *or* PCl_3 BUT aq negates [1]
reaction **IV:** H_2 + Ni *or* $LiAlH_4$ *or* $NaBH_4$ NOT Sn + HCl [1]
[3]

(c) reaction **IV:** reduction [1]
reaction **VI:** nucleophilic substitution *or* condensation reaction [1]
[2]

(d) **(i)** amide [1]

(ii) amine [1]
[2]

[Total: 14]

7 **(a)** Primary: Covalent bond (ignore amide, peptide etc.) [1]
Diagram showing peptide bond: (-CHR-)CONH(-CHR-) [1]

Secondary: Hydrogen bonds (NOT between side chains" [1]
Diagram showing N-H···O=C [1]

Tertiary: **Two** of the following:
- hydrogen bonds (diagram **must** show H-bonds *other* than those in α-helix *or* β-pleated sheet – e.g. ser-ser)
- electrostatic/ionic attraction,
- Van der Waals'/hydrophobic forces/bonds,
- (covalent) disulphide (links/bridges) [1] + [1]

Suitable diagram of **one** of the above [1]
(for disulphide: S-S **not** S=S or SH-SH)
[max 6]

(b) Substrate binds to the active site of the enzyme [1]
Interaction with site causes a specific bond to be weakened, (which breaks)
Or change in shape weakens bond(s) / lowers activation energy [1]
[2]

(c) Non-competitive inhibition [1]
Rate never reaches V_{max} [1]
[2]

[Total: 10]

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8 **(a)** Ratio of the concentrations of a solute / distribution of solute [1] in two immiscible liquids [1]
[2]

(b) $K_c = \frac{\text{[pesticide in hexane]}}{\text{[pesticide in water]}}$ hence $8.0 = \frac{\text{[pesticide in hexane]}}{0.0050 - \text{[pesticide in hexane]}}$ [1]

Therefore [pesticide in hexane] $x = 0.040 - 8x$
Hence x = 0.0044(g) [1]
[2]

(c) **(i)** Ratio would be 3 : 1 [1]

(ii) Each chlorine at could be ^{35}Cl or ^{37}Cl
Only way of getting M+4 is for both chlorines to be ^{37}Cl (1 in 9 chance) [1]
Ratio of peaks M M+2 M+4
9 6 1 [1]
[3]

(d) **(i)** Accept dioxins and furans (without specifying) [1]

(ii) PCBs (but don't penalise non-specified dioxins and furans) [1]

(iii) Allow : pollution control / environmental legislation / removal of dioxins and furans / mill closed down (owtte) [1]

(iv) Five [1]
[4]

[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

[2]

(b) (i) Gaps in structure of shaft much smaller, hence less prone to fracture / more flexible [1]

(ii) Composites and carbon nanotubes less dense than metal (of comparable strength) [1]
[2]

(c) Wavelength of infrared energy is longer than that of light [1]
Gaps between nano-sized particles allow light to pass through, but reflect infrared energy [1]
[2]

(d) (i) Resistance to corrosion / reaction [1]

(ii) Ability to kill bacteria / prevent bacteria multiplying [1]

(iii) Very much larger surface area means they dissolve more readily [1]
[3]

[Total: 9]

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