## 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)  $M_r = 233$ , so  $0.945 \text{ mol} = 0.945 \times 233 = 220g \Rightarrow 100 \times 220/250 = 88(.07)\%$  (or  $0.9475 \text{ mol} \Rightarrow 220.8g \Rightarrow 88(.3)\%$ ) [1] If RTP used answer is 90(.0)%
  - (c) (i) from data booklet,  $1^{st}$  IE = 502;  $2^{nd}$  IE = 966; sum = 1468 kJ mol<sup>-1</sup> so -460 = 1468 + 180 + 279 - 200 + 640 + LE -460 = 2367 + LELE = -2827 kJ mol<sup>-1</sup> ( -1 for each error)
    - (ii) LE of BaS should be smaller than that of BaO, since S<sup>2-</sup> is bigger than O<sup>2-</sup>. [1]

[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 <sub>3</sub> (aq) is added	observation when dilute NH₃(aq) is added	observation when concentrated NH <sub>3</sub> (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]

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

(d) (i)  $K_c = [Ag(RNH_2)_2^+]/[Ag^+][RNH_2]^2$  [1] units are mol<sup>-2</sup> dm<sup>6</sup> [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<sup>-3</sup>

(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]

[Total: 13]

[3]

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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

[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<sup>2+</sup>(aq)/in a pipette and place in (conical) flask

Add an excess of (dil) H<sub>2</sub>SO<sub>4</sub>

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) 
$$2 \text{ MnO}_4^- + 5 \text{ SO}_2 + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ Mn}^{2+} + 5 \text{ SO}_4^{2-} + 4 \text{ H}^+$$
 [2]

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

(ii) 
$$1 \text{ Cr}_2 \text{O}_7^{2-} + 6 \text{ NO}_2 + 2 \text{ H}^+ \rightarrow 2 \text{ Cr}^{3+} + 6 \text{ NO}_3^- + 1 \text{ H}_2 \text{O}$$
 [2]

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

([2] marks for each equation: [1] for balancing of redox species,

[1] for total balancing: i.e. H<sub>2</sub>O and H<sup>+</sup>)

[6]

(d) Fe<sup>3+</sup> is a homogeneous (catalyst)

Fe<sup>3+</sup> oxidised I<sup>-</sup> (and is reduced to Fe<sup>2+</sup>) Fe<sup>2+</sup> reduces  $S_2O_8^{2-}$  (and is oxidised to Fe<sup>3+</sup>)

or equations showing this

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

[3]

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

$$6 E(CI-F) -328 = 3 \times 158 + 244$$
  
  $E(CI-F) = +174 (kJ mol^{-1})$ 

[2] [2]

[Total: 7]

5 (a)

,			
	compound	all carbon atoms can be coplanar	not all carbon atoms coplanar
	Α	✓	
	В		<b>√</b>
	С	✓	
	D	✓	
	E	✓	

all 5 correct [3]

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

[3]

(b) reaction I: Cl<sub>2</sub> + AlCl<sub>3</sub> / FeCl<sub>3</sub> / Fe / or bromides of Al or Fe [1] reaction II: Cl<sub>2</sub> + heat / light / uv / hf [1]

[2]

(c) (i) H is  $C_6H_5CH_2CI$ [1]

(ii) reaction III: KMnO<sub>4</sub> + heat (+ OH<sup>-</sup>) [1] reaction V: NaOH in water + heat [1] reaction VI: conc H<sub>2</sub>SO<sub>4</sub> + heat [1]

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

[Total: 11]

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(a)	L is CH <sub>3</sub> CH M is CH <sub>3</sub> CC N is CH <sub>3</sub> CH Q is CH <sub>3</sub> CH P is CH <sub>3</sub> CH	O <sub>2</sub> H I <sub>2</sub> NH <sub>2</sub> I <sub>2</sub> CO <sub>2</sub> H	
		DNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	[7] <b>[7]</b>
(b)	reaction II:	KCN, heat NOT H <sup>+</sup> OR HCN aq negates SOCl <sub>2</sub> or PCl <sub>5</sub> or PCl <sub>3</sub> BUT aq negates H <sub>2</sub> + Ni or LiAlH <sub>4</sub> or NaBH <sub>4</sub> NOT Sn + HCl	[1] [1] [1] <b>[3]</b>
(c)	reaction IV: reaction VI:	reduction nucleophilic substitution <i>or</i> condensation reaction	[1] [1] <b>[2]</b>
(d)	(i) amide		[1]
	(ii) amine		[1] <b>[2]</b>
			[Total: 14]
(a)	Primary:	Covalent bond (ignore amide, peptide etc.) Diagram showing peptide bond: (-CHR-)CONH(-CHR-)	[1] [1]
	Secondary:	Hydrogen bonds (NOT between side chains" Diagram showing N-H···O=C	[1] [1]
	Tertiary:	<ul> <li>Two of the following:</li> <li>hydrogen bonds (diagram must show H-bonds other than tor β-pleated sheet – e.g. ser-ser)</li> <li>electrostatic/ionic attraction,</li> <li>Van der Waals'/hydrophobic forces/bonds,</li> </ul>	hose in α-helix
		(covalent) disulphide (links/bridges)	[1] + [1]
		Suitable diagram of <b>one</b> of the above (for disulphide: S-S <b>not</b> S=S or SH-SH)	[1] [max 6]
(b)	Substrate bir	nds to the active site of the enzyme	[1]
(~)	Interaction w	ith site causes a specific bond to be weakened, (which breaks) shape weakens bond(s) / lowers activation energy	[1] <b>[2]</b>
(c)	Non-competi Rate never re		[1] [1] <b>[2]</b>
			[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 - 8xHence x = 0.0044(g) [1]

- (c) (i) Ratio would be 3:1 [1]
  - (ii) Each chlorine at could be <sup>35</sup>C/ or <sup>37</sup>C/
    Only way of getting M+4 is for both chlorines to be <sup>37</sup>C/ (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]

[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] [1] (d) (i) Resistance to corrosion / reaction [1] (ii) Ability to kill bacteria / prevent bacteria multiplying (iii) Very much larger surface area means they dissolve more readily [1] [3]