

UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS

GCE Advanced Subsidiary Level and GCE Advanced Level

**MARK SCHEME for the May/June 2009 question paper
for the guidance of teachers**

9701 CHEMISTRY

9701/04

Paper 4 (A2 Structured Questions), 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, which would have considered the acceptability of alternative answers.

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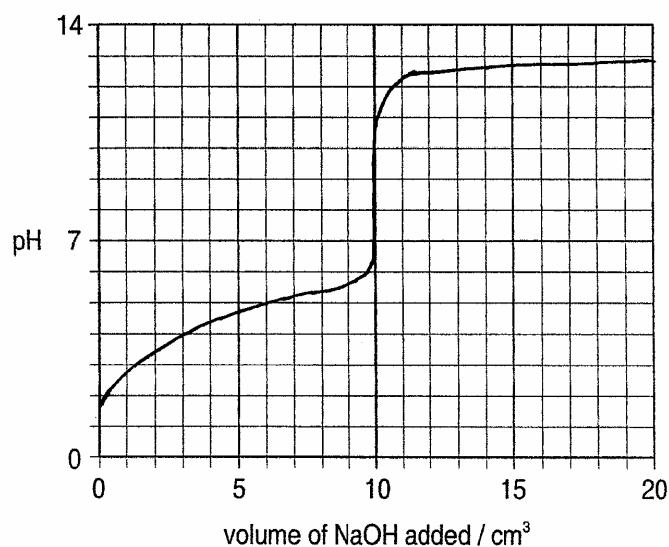
Section A

- 1 (a) acids are proton/ H^+ donors [1]
 bases are proton/ H^+ acceptors [1] [2]

- (b) (i) more *Cl* atoms produce a **stronger acid** or the larger the K_a the **stronger the acid** [1]
 (NOT just “the more *Cl* atoms, the larger the K_a ” – must refer to acid strength) [1]
 because the anion/ RCO_2^- is more stable or the O-H bond is weaker/polarised [1]
 due to the electronegativity/electron-withdrawing effect of *Cl* [1]

- (ii) $[H^+] = \sqrt{K_a \cdot c} = 0.0114 \text{ (mol dm}^{-3}\text{)}$ [1]
 pH = **1.94** (allow 1.9) ecf from $[H^+]$ [1]
 (correct answer = [2])

(iii)



- start at pH = 1.94 (ecf from (ii) and goes up > 2 pH units before steep portion) [1]
 steep portion (over at least 3 pH units) at $V = 10 \text{ cm}^3$ [1]
 flattens off at pH 12–13 [1] [8]

- (c) (i) $CH_3CO_2H + OH^- \longrightarrow CH_3CO_2^- + H_2O$ [1]
 $CH_3CO_2^- + H^+ \longrightarrow CH_3CO_2H$ [1]

- (ii) $pK_a = -\log_{10}(1.7 \times 10^{-5}) = 4.77$ or $[H^+] = 8.5 \times 10^{-6} \text{ (mol dm}^{-3}\text{)}$ [1]
 $pH = pK_a + \log_{10}(0.2/0.1) = 5.07$ (allow 5.1) [1]
 (correct answer = [2]) [4]

[Total: 14]

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- 2 (a) NaCl: steamy fumes [1]
 $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}$ (or ionic, i.e. without the Na^+)
 or $2\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ [1]
- NaBr: orange/brown fumes [1]
 $2\text{NaBr} + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2 + \text{Br}_2$
 or $2\text{HBr} + \text{H}_2\text{SO}_4 \longrightarrow 2\text{H}_2\text{O} + \text{SO}_2 + \text{Br}_2$
 (ignore equations producing HBr) [1] [4]

- (b) relevant E^\ominus quoted: Cl_2/Cl^- , 1.36; Br_2/Br^- , 1.07; ($\text{H}_2\text{SO}_4/\text{SO}_2$, 0.17 – not required) [1]

Br^- is more easily oxidised because its E^\ominus is more negative
 or Cl_2 is more oxidising because its E^\ominus is more positive [1] [2]

- (c) Allow almost any reducing agent from the Data Booklet (see below) with E^\ominus less than 1.07 V.

But do not allow reducing agents that require conditions that would react with Br_2 in the absence of the reducing agent (e.g. NH_3 or OH^-), and also do not allow "reducing agents" that could produce, or act as, oxidising agents (e.g. MnO_4^{2-} and H_2O_2)

balanced equ. showing reduction of Br_2 by the chosen reducing agent
 (either ionic or molecular) [1]

$E^\ominus = 1.07 - (E^\ominus \text{ of reductant}) = \mathbf{x.xx (V)}$ (see below) [1] [2]

[Total: 8]

List of acceptable reductants with resulting E^\ominus_{cell} values

reductant	$E^\ominus_{\text{cell}}/\text{V}$	reductant	$E^\ominus_{\text{cell}}/\text{V}$	reductant	$E^\ominus_{\text{cell}}/\text{V}$
Ag	0.27	$\text{Fe} \Rightarrow \text{Fe}^{2+}$	1.51	Na	3.78
Al	2.73	$\text{Fe} \Rightarrow \text{Fe}^{3+}$	1.11	Ni	1.32
Ba	3.97	Fe^{2+}	0.30	Pb	1.20
Ca	3.94	H_2	1.07	SO_2	0.90
Co	1.35	I^-	0.53	$\text{S}_2\text{O}_3^{2-}$	0.98
$\text{Cr} \Rightarrow \text{Cr}^{2+}$	1.98	K	3.99	Sn	1.21
$\text{Cr} \Rightarrow \text{Cr}^{3+}$	1.81	Li	4.11	Sn^{2+}	0.92
Cr^{2+}	1.48	Mg	3.45	V	2.27
$\text{Cu} \Rightarrow \text{Cu}^+$	0.55	Mn	2.25	V^{2+}	1.33
$\text{Cu} \Rightarrow \text{Cu}^{2+}$	0.73	NO_2	0.26	V^{3+}	0.73
Cu^+	0.92	HNO_2	0.13	VO^{2+}	0.07
		NH_4^+	0.20	Zn	1.83

e.g. for Sn^{2+} : $\text{Sn}^{2+} + \text{Br}_2 \longrightarrow \text{Sn}^{4+} + 2\text{Br}^-$ [1]

$$E^\ominus = 1.07 - 0.15 = \mathbf{0.92 V}$$

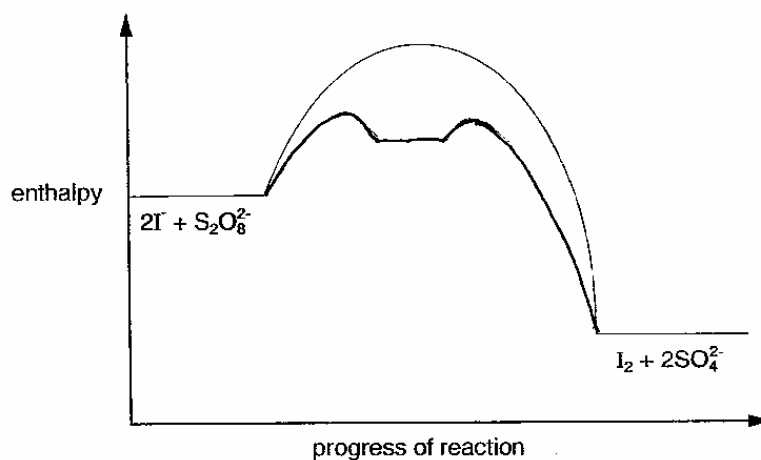
(or similarly for other suitable reagents) [1]

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- 3 (a) a (d-block) element forming stable ions/compounds/oxidation states with incomplete/partially filled [NOT empty] d-orbitals [1] [1]
- (b) (i) $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^3 4s^2$ [1]
(ii) $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^9$ [1] [2]
- (c) (+)2, (+)3, (+)4, (+)5 or II, III, IV, V [1] [1]
- (d) (pale blue solution \Rightarrow) blue/cyan **solid/ppt.**(or (s) in the formula) [1]
(blue ppt. is) $\text{Cu}(\text{OH})_2$ or copper hydroxide [1]
(then produces a) deep blue or purple **solution** [1]
which contains $[\text{Cu}(\text{NH}_3)_4]^{2+}$ or $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ [1]
formed by ligand replacement [1] [5]
- (e) $2\text{VO}_3^- + 8\text{H}^+ + \text{Cu} \longrightarrow 2\text{VO}^{2+} + 4\text{H}_2\text{O} + \text{Cu}^{2+}$
or $2\text{VO}_2^+ + 4\text{H}^+ + \text{Cu} \longrightarrow 2\text{VO}^{2+} + 2\text{H}_2\text{O} + \text{Cu}^{2+}$
correct species [1]
balancing [1]
(award only [1] for just the two half-equations) [2]

[Total: 11]

- 4 (a) (i) homogeneous [1]
- (ii) ions in 2 and 3 are oppositely charged ions (thus attract each other) or ions in 1 are similarly charged ions (thus repel each other) [1]
- (iii)



- two** contiguous activation humps [1]
both less than the original [1]
starting and finishing at the same points as before [1] [5]

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- (b) (i) SO_3 produces acid rain *or* $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$ *or* a consequence of acid rain, e.g. lower pH of lakes; leaches aluminium from soils; kills fish/plants/rainforests; dissolves/corrodes/damages buildings (NOT global warming) [1]
 (NOT asthma etc – since this is not environmental)
- (ii) the burning of fossil fuels/coal/oil/petrol/gas/diesel/fuel *or* car exhausts *or* roasting of sulphide ores *or* cement manufacture *or* volcanoes [1]
- (iii) $\text{SO}_2 + \text{NO}_2 \longrightarrow \text{SO}_3 + \text{NO}$ [1]
 $\text{NO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{NO}_2$ [1]

[4]

[Total: 9]

- 5 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
A **B** **C**
 all three (any order) [2]
 (2 only = [1]) [2]
- (b) **B** above (may be different letter) ([0] if more than one compound stated) [1] [1]
- (c) (i) **B** above (may be different letter) ([0] if more than one compound stated) [1]
 (ii) (pale) yellow ppt. [1]
 (iii) $\text{CHI}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{Na}$ *or* anion (no credit for the acid, RCO_2H) [1] + [1] [4]
- (d) **A** $\longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ [1]
B $\longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ [1]
C $\longrightarrow \text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ (letters may differ) [1] [3]

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(e) (i) $(C_6H_{10}O_5)_n \longrightarrow 5n H_2 + 5n CO + n C$ correct species and the 5:5:1 ratio [1]
(allow n5 instead of 5n) balancing, i.e. multiplying by n [1]

(ii) $\Delta H = 7(1080) + 15(\mathbf{436}) - 6(\mathbf{350}) - 16(\mathbf{410}) - 14(\mathbf{460})$
 $= -\mathbf{1000} \text{ kJ mol}^{-1}$
 4 correct values from DB (in bold italics above) [1]
 correct multipliers [1]
 correct signs and arithmetic [1]
 (correct answer = [3])

Some ecf values for [2] marks (i.e. 1 error): for [1] mark (i.e. 2 errors):

+1000 (signs reversed)
 -1350 (7 x (C-C) instead of 6) +1350
 +2220 (7 x O-H instead of 14) -2220
 -1410 (17 C-H instead of 16) +1410

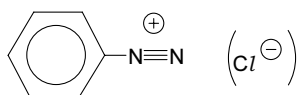
The omission of a type of bond (C-C is the most common one that is omitted) forfeits 2 marks, in addition to any other errors there may be. [5]

[Total: 15]

- 6 (a) (i) I: $SOCl_2$ or PCl_5 or $HCl + ZnCl_2$ or $PCl_3 + \text{heat}$ or $Cl_2 + P + \text{heat}$ [1]
 [NOT $NaCl + H_2SO_4$]
 (mention of aq negates mark)
- II: NH_3 (ignore any conditions stated) [1]
- (ii) nucleophilic substitution or S_N or S_N1 or S_N2 [1]
- (iii) delocalisation of lone pair on Cl over benzene ring produces a stronger C-Cl bond [1] [4]
- (b) (i) III: $HNO_3 + H_2SO_4$ [1]
 both conc., and at $T < 60^\circ C$ [1]
 IV: $Sn + \text{conc } HCl$ [NOT $LiAlH_4$ or $H_2 + Ni$] [1]
- (ii) III: electrophilic substitution [1]
 IV: reduction or redox [1] [5]
- (c) e.g. add bromine water or $Br_2(aq)$ (a solvent is needed for the mark) [1]
 or add UI solution
 phenylamine decolorises the bromine or gives a white ppt., hexylamine does not [1]
 or hexylamine turns UI blue, with phenylamine it stays green [2]

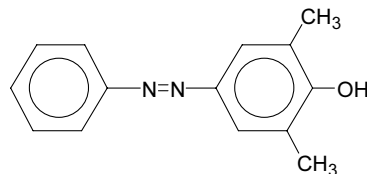
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(d)



(allow + charge on either N)
(allow double or triple bond)

[1]



(phenylazo group must be at 4-position to -OH)
(N=N must be double bond, not triple)

[1]

[2]

[Total: 13]

Section B

- 7 (a) For each element, award [1] mark for each column in one particular line in the table below. The [2] marks awardable for each element are not conditional on each other, but don't take the location from one line and the role from another.

element	location	role
iron	red blood cells/haemoglobin	to bind to/carry/transfer oxygen (to cells) or CO ₂ (away from cells)
	muscle (cells)/myoglobin	to bind to/carry/transfer oxygen (to muscles) or CO ₂ (away from muscles)
	in mitochondria/cytochromes	to aid redox reactions or to help oxidise NADH etc
	in iron-sulphide proteins	to aid redox reactions
	in ferredoxin	to aid redox reactions
sodium	in nerve cells/nerves/nervous system/neurones or in cell membranes/phospholipid bilayers	Na ⁺ /K ⁺ pump or ion pump or active transport or transmission/regulation of nerve impulses
	in kidneys	to help re-absorb glucose
zinc	in blood ("cells" not needed, but "plasma" negates) or carbonic anhydrase	as an enzyme co-factor/prosthetic group or to help the hydration/removal of CO ₂ or production of H ₂ CO ₃ /HCO ₃ ⁻
	in the gut/carboxypeptidase	as an enzyme co-factor/prosthetic group or to help hydrolyse polypeptides
	in the liver/alcohol dehydrogenase	as an enzyme co-factor/prosthetic group or to help oxidise/break down alcohol

[1]

+

[1] for each element

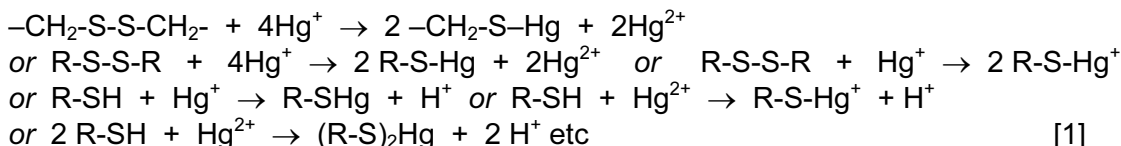
[6]

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- (b) (i) manufacture of NaOH *or* manufacture of batteries *or* manufacture of felt *or* gold extraction
or (mercury) fungicides *or* (mercury) compounds used in timber preservation [1]

(ii) ***In each case below, a balanced equation is worth [2] marks***

breaks disulphide bonds/linkages *or* Hg bonds to S-H groups (*or* in an unbalanced equation) [1]



bonds to carboxyl side chains (in amino acids) (*or* in an unbalanced equation) [1]



[5]

[11 max 10]

- 8 (a) (i) Partition coefficient (PC) is an equilibrium constant representing the distribution of a solute between two solvents.
or PC = ratio of the concentrations of the solute in the two solvents *or* $\text{PC} = \frac{[\text{X}]_a}{[\text{X}]_b}$ [1]

- (ii) If 0.4 g has been extracted, 0.1 g remain in the aqueous layer.

$$\text{the concentration in the hexane layer} = \frac{0.4}{20} = 0.02 \text{ g cm}^{-3}$$

$$\text{the concentration in the aqueous layer} = \frac{0.1}{100} = 0.001 \text{ g cm}^{-3}$$

$$K_{\text{pc}} = 0.02/0.001 = \mathbf{20} \quad [1]$$

- (iii) *1st extraction:* hexane $x/10 \text{ g cm}^{-3}$ water $(0.50-x)/100 \text{ g cm}^{-3}$

$$K_{\text{pc}} = \frac{x/10}{(0.5-x)/100} = 20$$

$$\begin{aligned} \text{hence } x/10 &= (10 - 20x)/100 \\ 100x &= 10(10 - 20x) \text{ or } 100x = 100 - 200x \end{aligned}$$

$$\mathbf{x = 0.33 \text{ g}} \quad [1]$$

- 2nd extraction:* hexane $y/10 \text{ g cm}^{-3}$ water $(0.17 - y)/100 \text{ g cm}^{-3}$

$$K_{\text{pc}} = \frac{y/10}{(0.17-y)/100} = 20$$

$$\begin{aligned} \text{hence } y/10 &= (3.4 - 20y)/100 \\ 100y &= 10(3.4 - 20y) \text{ or } 100y = 34 - 200y \end{aligned}$$

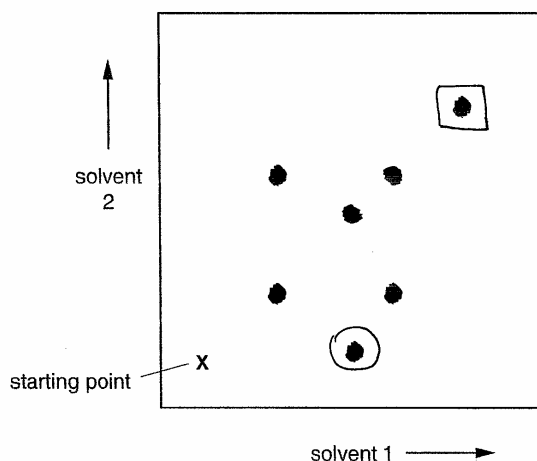
$$\mathbf{y = 0.11 \text{ g}} \quad [1]$$

total extracted = **0.44 g**, *or* difference = **0.04 g** *or* **10% more** (is extracted) [1]
(correct answer = [3])

[5]

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- (b) (i) berries are aqueous media [1]
 PCBs are insoluble/sparingly soluble in water or more fat-soluble [1]
- (ii) partition coefficient or $[\text{fat}]/[\text{water}]$ is greater than 1 [1]
- [3]**
- (c) (i) 4 (four) [1]
- (ii)

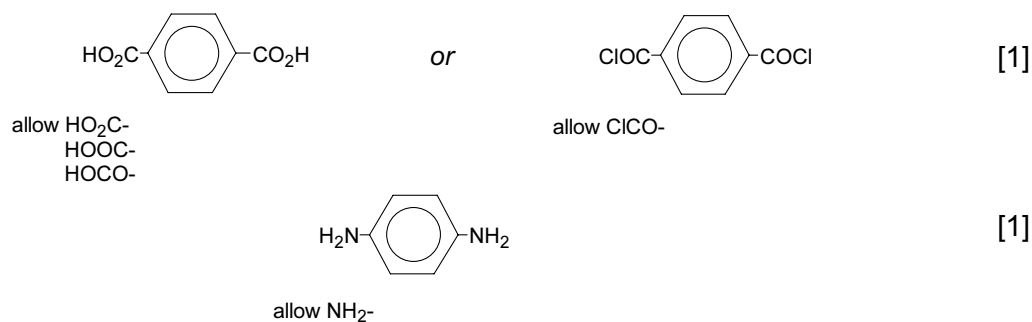


- correct spot circled [1]
 correct spot squared [1]
 [in each case, more than one spot circled or squared negates the mark] **[3]**

[Total: 11]

- 9 (a) (i) correct diagram showing at least one monomer unit, and at least one N-H and C=O.
 i.e. $-\text{NH}-\text{C}_6\text{H}_2-\text{NH}-\text{CO}-$ or $-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{NH}-$
 (no mark for this, but apply a penalty of $-[1]$ if candidate's diagram does NOT show these points correctly)
 one H-bond between N-H of original chain and C=O group of new chain [1]
 one H-bond between C=O of original chain and N-H group of new chain [1]
- (ii) hydrogen bonds or H-bonds (in words; can be written on diagram)
 (ignore ref to v d W) [1]

(iii)



[5]

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- (b) (i) Water-hating/fearing/repelling/resistant *or* can't form bonds with water (molecules) [1]
[NOT insoluble *or* does not dissolve in water, also NOT "non-polar"]
- (ii) Fluorine-containing groups form van der Waals bonds (with the oil molecules)... [1]
...but cannot form hydrogen bonds (with the water molecules) [1]
- (iii) Teflon/PTFE [1]
- [4]
- [Total: 9]