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.

Mark schemes must be read in conjunction with the question papers and the report on the examination.

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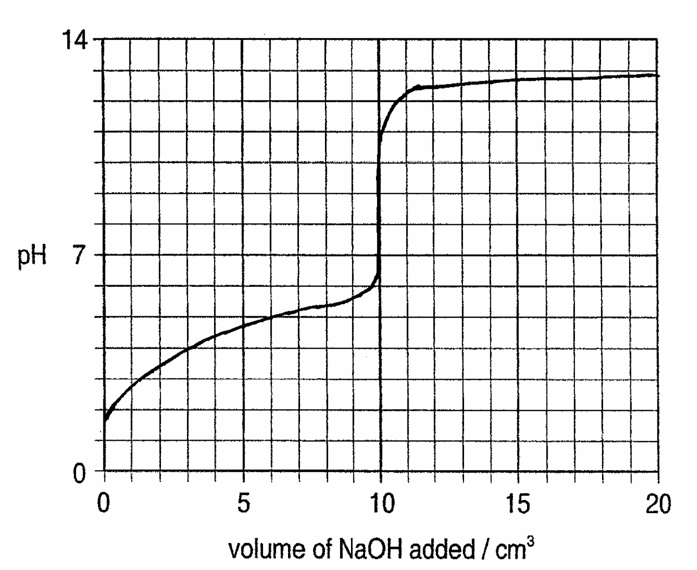
Section A

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

(b) (i) more C*l* atoms produce a **stronger acid** *or* the larger the K_a the **stronger the acid**
(NOT just "the more C*l* 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 C*l* [1]

(ii) $[H^+] = \sqrt{(K_a.c)}$ = 0.0114 (mol dm^{-3}) [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 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* $[H^+] = 8.5 \times 10^{-6}$ (mol dm^{-3}) [1]
pH = $pK_a + \log_{10}(0.2/0.1)$ = **5.07** (allow 5.1) [1]
(correct answer = [2]) **[4]**

[Total: 14]

2 **(a)** NaC*l*: steamy fumes [1]

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$ (*or* ionic, i.e. without the Na^+)

or $2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$ [1]

NaBr: orange/brown fumes [1]

$2NaBr + 3H_2SO_4 \longrightarrow 2NaHSO_4 + 2H_2O + SO_2 + Br_2$

or $2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 + Br_2$

(ignore equations producing HBr) [1] **[4]**

(b) relevant $E^\ominus$ quoted: Cl_2/Cl^-, 1.36; Br_2/Br^-, 1.07; (H_2SO_4/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]
$E^\ominus = 1.07 - (E^\ominus$ of reductant$) =$ **x.xx (V)** (see below) [1] **[2]**

[Total: 8]

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

reductant	$E^\ominus_{cell}$/V	reductant	$E^\ominus_{cell}$/V	reductant	$E^\ominus_{cell}$/V
Ag	0.27	$Fe \Rightarrow Fe^{2+}$	1.51	Na	3.78
A*l*	2.73	$Fe \Rightarrow Fe^{3+}$	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	$S_2O_3^{2-}$	0.98
$Cr \Rightarrow Cr^{2+}$	1.98	K	3.99	Sn	1.21
$Cr \Rightarrow Cr^{3+}$	1.81	Li	4.11	Sn^{2+}	0.92
Cr^{2+}	1.48	Mg	3.45	V	2.27
$Cu \Rightarrow Cu^+$	0.55	Mn	2.25	V^{2+}	1.33
$Cu \Rightarrow Cu^{2+}$	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+}: $Sn^{2+} + Br_2 \longrightarrow Sn^{4+} + 2Br^-$ [1]
$E^\ominus = 1.07 - 0.15 =$ **0.92** V [1]
(*or* similarly for other suitable reagents)

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 ⇒) blue/cyan **solid/ppt**.(*or* (s) in the formula) [1]

(blue ppt. is) $Cu(OH)_2$ *or* copper hydroxide [1]

(then produces a) deep blue *or* purple **solution** [1]

which contains $[Cu(NH_3)_4]^{2+}$ *or* $[Cu(NH_3)_4(H_2O)_2]^{2+}$ [1]

formed by ligand replacement [1] **[5]**

(e) $2VO_3^- + 8H^+ + Cu \longrightarrow 2VO^{2+} + 4H_2O + Cu^{2+}$

or $2VO_2^+ + 4H^+ + Cu \longrightarrow 2VO^{2+} + 2H_2O + Cu^{2+}$

correct species [1]

balancing [1]

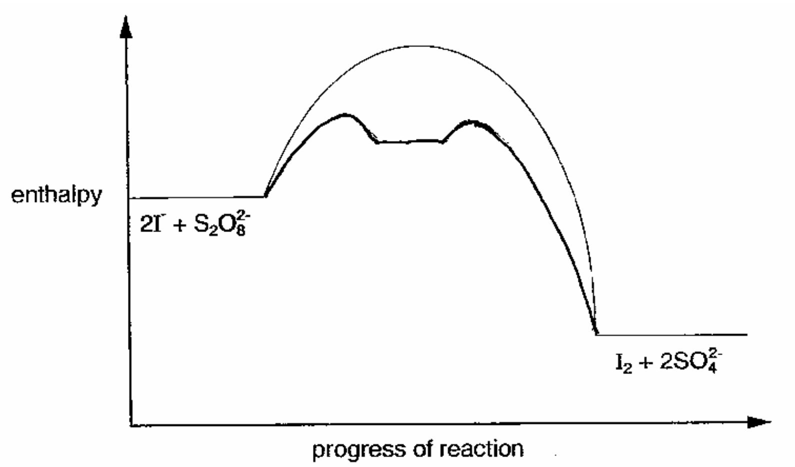
(award only [1] for just the two half-equations) **[2]**

[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]**

(b) **(i)** SO_3 produces acid rain *or* $SO_3 + H_2O \longrightarrow H_2SO_4$ *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) $SO_2 + NO_2 \longrightarrow SO_3 + NO$ [1]

$NO + \frac{1}{2}O_2 \longrightarrow NO_2$ [1]

[4]

[Total: 9]

5 **(a)** $CH_3CH_2CH_2CH_2CH_2OH$ **A** $CH_3CH_2CH_2CH(OH)CH_3$ **B** $CH_3CH_2CH(OH)CH_2CH_3$ **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) $CHI_3 + CH_3CH_2CH_2CO_2Na$ *or* anion (no credit for the acid, RCO_2H) [1] + [1]

[4]

(d) **A** $\longrightarrow CH_3CH_2CH_2CH_2CO_2H$ [1]

B $\longrightarrow CH_3CH_2CH_2COCH_3$ [1]

C $\longrightarrow CH_3CH_2COCH_2CH_3$ (letters may differ) [1] **[3]**

(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) $\Delta H = 7(1080) + 15(\boldsymbol{436}) - 6(\boldsymbol{350}) - 16(\boldsymbol{410}) - 14(\boldsymbol{460})$
$= \mathbf{-1000}$ 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 + heat *or* Cl_2 + P + heat
[**NOT** $NaCl + H_2SO_4$] [1]
(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°C [1]

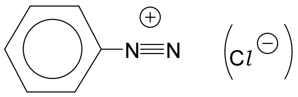
IV: Sn + **conc** HCl [**NOT** $LiAlH_4$ or H_2 + Ni] [1]

(ii) III: electrophilic substitution [1]

IV: reduction *or* redox [1]
[5]

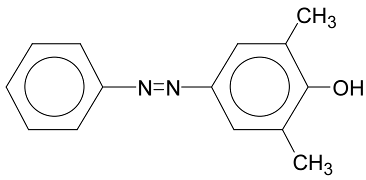
(c) e.g. add bromine water *or* $Br_2(aq)$ (a solvent is needed for the mark) [1]
or add UI solution
phenylamine decolorises the bromine *or* gives a white ppt., hexylamine does not [1]
or hexylamine turns UI blue, with phenylamine it stays green **[2]**

(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 ferrodoxin	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_2CO_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]**

(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]

$–CH_2\text{-}S\text{-}S\text{-}CH_2\text{-} + 4Hg^+ \rightarrow 2\ –CH_2\text{-}S–Hg + 2Hg^{2+}$
or $R\text{-}S\text{-}S\text{-}R + 4Hg^+ \rightarrow 2\ R\text{-}S\text{-}Hg + 2Hg^{2+}$ *or* $R\text{-}S\text{-}S\text{-}R + Hg^+ \rightarrow 2\ R\text{-}S\text{-}Hg^+$
or $R\text{-}SH + Hg^+ \rightarrow R\text{-}SHg + H^+$ *or* $R\text{-}SH + Hg^{2+} \rightarrow R\text{-}S\text{-}Hg^+ + H^+$
or $2\ R\text{-}SH + Hg^{2+} \rightarrow (R\text{-}S)_2Hg + 2\ H^+$ etc [1]

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

$–CO_2H + Hg^+ \rightarrow –CO_2Hg + H^+$ *or* $2\ RCO_2H + Hg^{2+} \rightarrow (RCO_2)_2Hg + 2H^+$ [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* PC = $[X]_a/[X]_b$
[1]

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

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

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

K_{pc} = 0.02/0.001 = **20** [1]

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

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

hence $x/10 = (10 – 20x)/100$
$100x = 10(10 – 20x)$ or $100x = 100 – 200x$
***x* = 0.33 g** [1]

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

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

hence $y/10 = (3.4 – 20y)/100$
$100y = 10(3.4 – 20y)$ or $100y = 34 – 200y$
***y* = 0.11 g** [1]

total extracted = **0.44** g, *or* difference = **0.04** g *or* **10% more** (is extracted) [1]
(correct answer = [3]) **[5]**

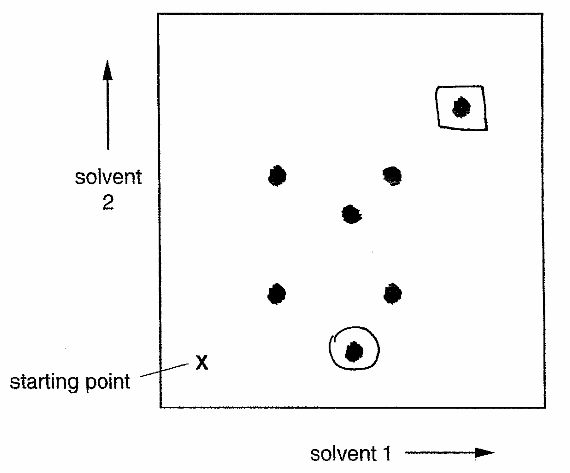
(b) **(i)** berries are aqueous media [1]
PCBs are insoluble/sparingly soluble in water *or* more fat-soluble [1]

(ii) partition coefficient *or* [fat]/[water] is greater than 1 [1]

[3]

(c) **(i)** 4 (four) [1]

(ii)



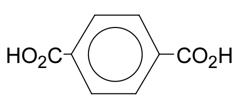
correct spot circled [1]
correct spot squared [1]
[in each case, more than one spot circled or squared negates the mark] **[3]**

[Total: 11]

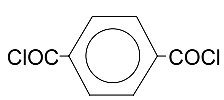
9 **(a)** **(i)** correct diagram showing at least one monomer unit, and at least one N-H and C=O.
i.e. –NH-C_6H_2-NH-CO– *or* –CO-C_6H_4-CO-NH–
(no mark for this, but apply a penalty of –[1] if candidate's diagram does NOT show these points correctly)
one H-bond between N-H of original chain and C=O 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)



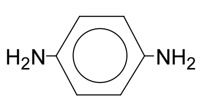
or



[1]

allow HO_2C-
HOOC-
HOCO-

allow ClCO-



[1]

allow NH_2-

[5]

(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]