UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS

GCE Advanced Subsidiary Level and GCE Advanced Level

MARK SCHEME for the October/November 2010 question paper for the guidance of teachers

9701 CHEMISTRY

9701/42 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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UNIVERSITY of CAMBRIDGE
International Examinations

1 **(a)** $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ (1)

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ (or giving H_2SiO_3, $Si(OH)_4$ etc.) (1) **[2]**

(b) bond energies: S-S = 264 kJ mol^{-1}
Cl-Cl = 244 kJ mol^{-1}
S-Cl = 250 kJ mol^{-1}

$\Delta H = 8 \times 264 + 8 \times 244 - 16 \times 250 = +64$ kJ mol^{-1} (2) **[2]**

(c) **(i)** +2 (1)

(ii) (half) the sulfur goes up by +2, (1)
(the other half) goes down by –2 (1)

(iii) HCl (can be read into **(iv)**) (1)

(iv) $2SCl_2 + 2H_2O \rightarrow S + SO_2 + 4HCl$ (1)

(v) (+ $AgNO_3$) white ppt. (1)
(+ $K_2Cr_2O_7$) solution turns green (1) **[7]**

[Total: 11]

2 **(a)** **(i)** A ligand is a species that contains a lone pair of electrons, *or* that can form a dative bond (to a transition element) (1)

(ii)

species	can be a ligand	cannot be a ligand
OH^-	✓	
NH_4^+		✓
CH_3OH	✓	
CH_3NH_2	✓	

(4 × ½) **[3]**

(b) **(i)** **C** is $[Cu(NH_3)_6]^{2+}$ SO_4^{2-} (allow $[Cu(NH_3)_4]^{2+}$ SO_4^{2-} (1)
D is CuO (1)
E is Na_2SO_4 (1)
F is $BaSO_4$ (1)

(ii) acid-base *or* neutralisation (1) **[5]**

(c) **(i)** any **two** from:
brown fumes or vapour evolved / gas relights glowing splint / black solid formed (2)

(ii) $2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$ (1) **[3]**

[Total: 11 max 10]

3 **(a)** **(i)** $Cu(s) - 2e^- \rightarrow Cu^{2+}(aq)$ allow electrons on RHS (1)

(ii) $E^\ominus$ for Ag^+/Ag is +0.80V which is more positive than +0.34V for Cu^{2+}/Cu, (1) so it's less easily oxidised (owtte) (1)

(iii) $E^\ominus$ for Ni^{2+} is –0.25V, (1) Ni is readily oxidised and goes into solution as $Ni^{2+}(aq)$ (1) [Mark **(ii)** and **(iii)** to max 3]

(iv) $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (1)

(v) $E^\ominus$ for Zn^{2+}/Zn is negative / = –0.76V, so Zn^{2+} is not easily reduced. (1)

(vi) The blue colour fades because $Cu^{2+}(aq)$ is being replaced by $Zn^{2+}(aq)$ *or* $Ni^{2+}(aq)$ *or* $[Cu^{2+}]$ decreases (1) **[7]**

(b) amount of copper = 225/63.5 = **3.54**(3) mol (1)
amount of electrons needed = 2 × 3.54 = **7.08/9** (7.087) mol (1)

no. of coulombs = 20 × 10 × 60 × 60 = 7.2×10^5 C
no. of moles of electrons = $7.2 \times 10^5 / 9.65 \times 10^4$ = **7.46** mol (1)

percentage "wasted" = 100 × (7.461 – 7.087)/7.461 = 5.01 (**5.0**)% (accept 4.98–5.10) (1) **[4]**

(c) $E^\ominus$ data: Ni^{2+}/Ni = –0.25V
Fe^{2+}/Fe = –0.44V (1)

Because the Fe potential is more negative than the Ni potential, the iron will dissolve (1) **[2]**

[Total: 13]

4 **(a)** **(i)** SnO_2 Can be read into equation (1)
$2NaOH + SnO_2 \rightarrow Na_2SnO_3 + H_2O$ (1)

(ii) PbO Can be read into equation (1)
$PbO + 2HCl \rightarrow PbCl_2 + H_2O$ (1)

[4]

(b) moles of oxygen = 9.3/16 = 0.581 mol
moles of lead = 90.7/207 = 0.438 mol <u>(both 3 s.f.)</u> (1)

so formula is Pb_3O_4 (1) **[2]**

(c) **(i)** $K_{sp} = [Pb^{2+}][Cl^-]^2$ (1) units = $mol^3\,dm^{-9}$ (1)

(ii) if $[Pb^{2+}] = x$, $K_{sp} = 4x^3$, so $x = \sqrt[3]{K_{sp}/4}$
$[Pb^{2+}] = \sqrt[3]{2 \times 10^{-5}/4}$ = $\mathbf{1.71 \times 10^{-2}}$ $mol\,dm^{-3}$ (1)

(iii) $[Pb^{2+}] = 2 \times 10^{-5}/(0.5)^2$ = $\mathbf{8.0 \times 10^{-5}}$ $mol\,dm^{-3}$ (1)

(iv) common ion effect, or increased $[Cl^-]$ forces solubility equilibrium over to the left (1)

[Max 4]

[Total: 10]

5 **(a)** **(i)** ester (1)

(ii) H is nitrobenzene – structure needed here (1)
J is phenyldiazonium chloride – structure needed here (1)

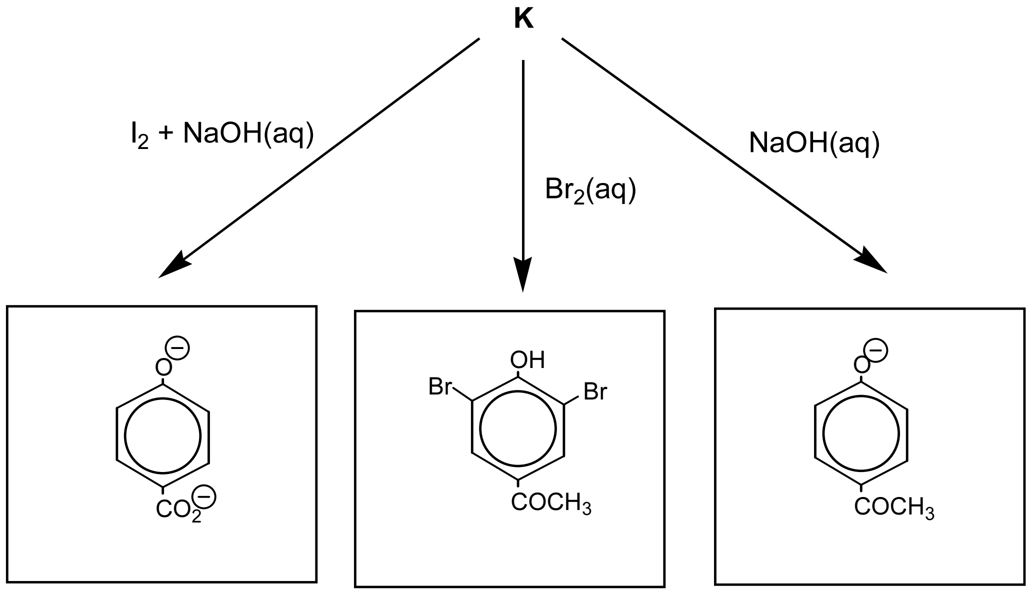
(iii) step 2 Sn/Zn + HC*l* / H_2 + named cat / $NaBH_4$ / $LiAlH_4$ / Na + ethanol (1)
step 3 $HNO_2/NaNO_2$ + HC*l* at T = 10°C or less (1)
step 4 heat/warm to T > 10°C (1)
step 5 CH_3COCl / $CH_3COCOCOCH_3$ (1) **[7]**

(b) **(i)** compounds that have the same molecular formula, but different structures (1)

(ii) phenol (NOT hydroxy) (1)
(methyl) ketone *or* carbonyl (1)

(iii) K is 4-ethanoylphenol, HO-C_6H_4-$COCH_3$ (must be 1,4- disubstituted isomer) (1)

(iv)

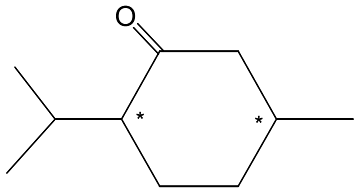


((1) for CO_2^-; (1) for $–O^-$) In any positions | (2 × Br needed) | (anion needed)

[4]
[8 max 7]

[Total: 14]

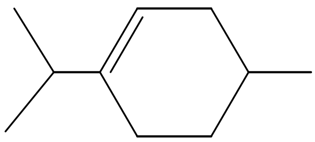
6 (a)



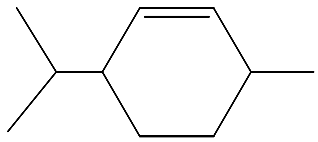
(1) for each centre – more than 2 centres shown deduct 1 mark **[2]**

(b) (i) step 1 LiAlH$_4$ *or* NaBH$_4$ *or* Na + ethanol *or* H_2 + Ni (1)
step 2 heat with Al_2O$_3$ / porous pot or conc. H_2SO_4 / H_3PO_4 (1)

(ii)



L (1)



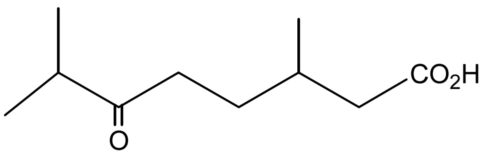
M (1)

(letters may be reversed)

[4]

(c) (i) **M** (no mark)

(ii)

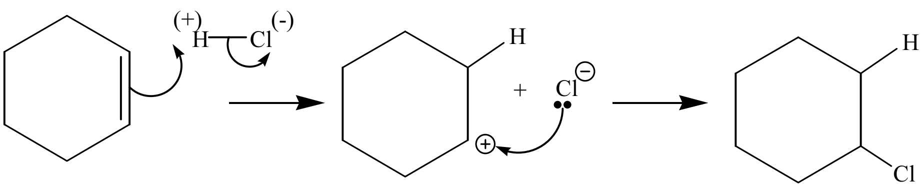


P

i.e. 3,7-dimethyl-6-oxo-octanoic acid (1)

(iii) 2,4-DNPH (1) orange ppt. with **P** (none with **N**) (1)
Mark ecf from candidates' P **[3]**

(d)



2 curly arrows (1)
carbocation intermediate + Cl^- (1)
lone pair on Cl^- and last curly arrow (1) **[3]**

[Total: 12]

7 **(a)** **(i)** Disulfide bond / group / bridge (1)

(ii) The tertiary structure (1)

(iii) The substrate will no longer bond to / fit into the active site (1)
or shape of active site is changed **[3]**

(b) **(i)** Acid-base / proton donor / neutralisation / salt formation (1)

(ii) The ability of the $–CO_2H$ group to form hydrogen bonds (1) and ionic interactions (1)

The $–CO_2H/–CO_2^-$ group is no longer able to interact with $–NH_2/–NH_3^+$ (1)

The Ag^+ forms a strong bond with $–COO^-$ (1) **[5] max [4]**

(c) **(i)** 8 but allow $4O_2$ if specified as molecules (1)

(ii) Dative / co-ordinate (1)

(iii) Octahedral / 6 co-ordinate (1) **[3]**

[Total: 10]

8 **(a)** Protons (1)
in NMR, energy is absorbed due to the two spin states (1)
Electrons (1)
in X-ray crystallography, X-rays are diffracted (by regions of high electron density) (1) **[4]**

(b) **(i)** 1 – no mark
The spectrum of alcohol / **Y** contains different peaks
Alcohol / **Y** contains different chemical environments
Spectrum 2 contains only one peak (1)

(ii) Spectrum 2 only shows 1 peak so **Z** must be a ketone (1)

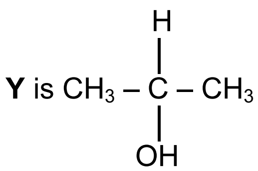
Hence **Y** must be a 2° alcohol (1)

Number of carbon atoms present $= \dfrac{0.6 \times 100}{17.6 \times 1.1} = 3$ (1)

Thus **Z** must be CH_3COCH_3 (1)

Hence **Y** must be propan-2-ol, $CH_3CH(OH)CH_3$ (1)

(iii)



(1)

(iv) All of the protons in **Z** are in the same chemical environment (1) **[8] max [7]**

[Total: 11]

9 **(a)** **(i)** A few nanometres (accept 0.5–10 nm) (1)

(ii) Graphite/graphene (1)

(iii) van der Waals' (1)
Carbon atoms in the nanotubes are joined by covalent bonds (1)
(as are the hydrogen atoms in a hydrogen molecule)
or no dipoles on C or H_2 *or* the substances are non-polar **[4]**

(b) More hydrogen can be packed into the same space/volume (1) **[1]**

(c) If a system at equilibrium is disturbed, the equilibrium moves in the direction which tends to reduce the disturbance (owtte) (1)

When H_2 is removed the pressure drops and more H_2 is released from that adsorbed (1)

The equilibrium $H_{2adsorbed} \rightleftharpoons H_{2gaseous}$ (1)

Equilibrium shifts to the right as pressure drops (1) **[4]**

[Total: 9]