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

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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]

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

percentage "wasted" = $100 \times (7.461 - 7.087)/7.461$ = 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 $x = \sqrt[3]{\{K_{sp}/4\}}$
$[Pb^{2+}] = \sqrt[3]{\{2 \times 10^{-5}/4\}}$ = **1.71×10^{-2}** mol dm^{-3} (1)

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

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

[Max 4]

[Total: 10]

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5 (a) (i) ester (1)

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

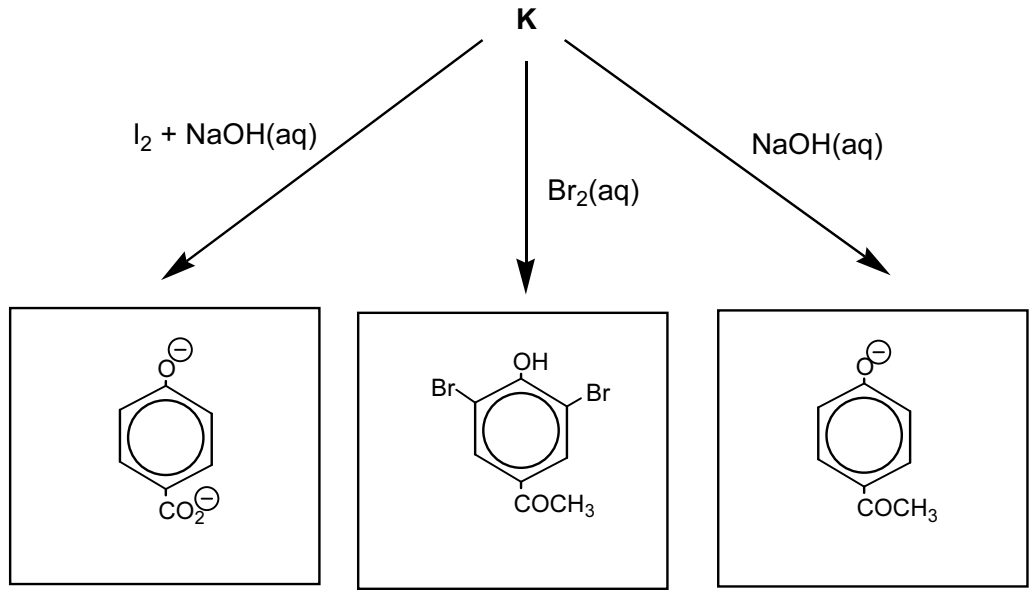
(iii) step 2 Sn/Zn + HC*l* / H_2 + named cat / $NaBH_4$ / $LiAlH_4$ / Na + ethanol (1)
step 3 $HNO_2/NaNO_2$ + HC*l* at T = 10°C or less (1)
step 4 heat/warm to T > 10°C (1)
step 5 CH_3COCl / $CH_3COCOCOCH_3$ (1) **[7]**

(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, $HO\text{-}C_6H_4\text{-}COCH_3$ (must be 1,4- disubstituted isomer) (1)

(iv)



((1) for CO_2^-; (1) for $-O^-$) (2 × Br needed) (anion needed)
In any positions [4]
[8 max 7]

[Total: 14]

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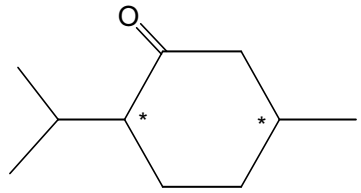
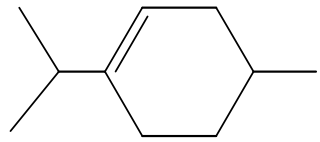
6 (a)



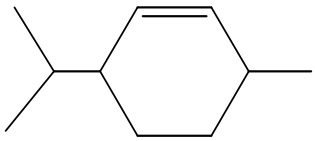
(1) for each centre – more than 2 centres shown deduct 1 mark **[2]**

(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)



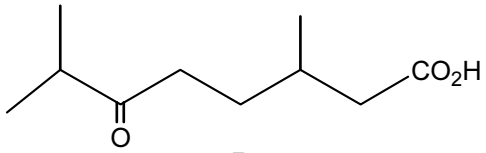
M (1)

(letters may be reversed)

[4]

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

(ii)

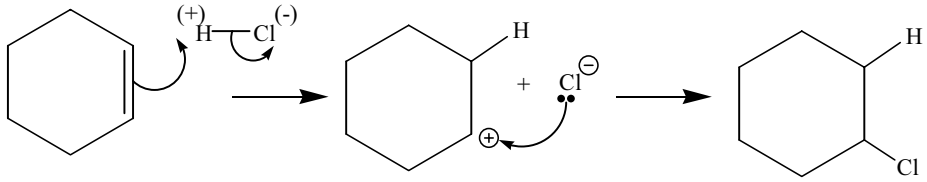


P

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]

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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)

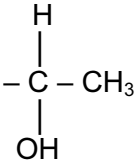
Hence **Y** must be a 2° alcohol (1)

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)



Y is (1)

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

[Total: 11]

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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]

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