UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS

GCE Advanced Level

MARK SCHEME for the May/June 2012 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.

- Cambridge will not enter into discussions or correspondence in connection with these mark schemes.

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1 (a) (i) enthalpy/energy change/released when 1 mol of ions… [1]
in the gas phase (are dissolved in) water [1]

(ii) $Mg^{2+}(g)$ + aq (*or* H_2O) $\rightarrow$ $Mg^{2+}(aq)$ *or* $[Mg(H_2O)_6]^{2+}$ [1]

(iii) Mg^{2+} has a smaller radius/size or greater charge density than Ca^{2+} (**ions** required) [1]

(iv) O^{2-} reacts with water to give OH^- *or equation*: $O^{2-} + H_2O \rightarrow 2OH^-$ [1]
[5]

(b) (apparatus: "insulated" calorimeter, water and thermometer)
- measure (known volume/mass of) water *or* stated volume of water (into calorimeter)
- take the temperature (of the water – NOT the $MgCl_2$)
- weigh out known mass of $MgCl_2$ *or* stated mass of $MgCl_2$
- take final/highest/constant temperature *or* record temperature change/rise 4 × [1]

[4]

(c) (i) $\Delta H^{\ominus}_{sol} = 641 - 801 = -160$ kJ mol^{-1} [1]

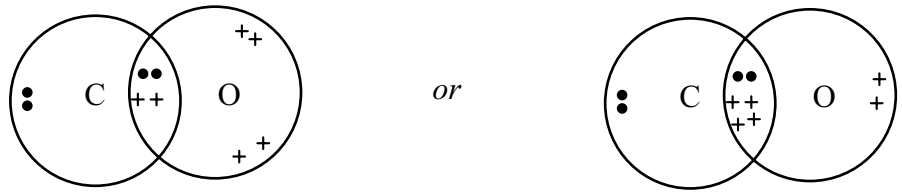
(ii) $\Delta H^{\ominus}_{hyd} = (1890 - 2526 - 160)/2 = -398$ kJ mol^{-1} [2]
[3]

(d)
- solubility: $MgSO_4 > BaSO_4$ *or* decreases down the group
- because ΔH_{sol} is more endothermic for $BaSO_4$ *or* more exothermic for $MgSO_4$
- due to larger r_{ion} *or* smaller charge density of Ba^{2+} (ion has to be mentioned)
- leading to smaller LE and HE *or* LE and HE decrease
- but difference in HE (between Mg^{2+} and Ba^{2+}) is larger than the difference in LE (between $MgSO_4$ and $BaSO_4$)
  or HE is dominant *or* HE decreases more than LE any 4 points [4]

[4]

[Total: 16]

2 (a) (i)



[1]

(ii) incomplete combustion (of hydrocarbon fuels) *or* insufficient O_2/air [1]

(iii) $NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$
or $CO + \frac{1}{2}O_2 \rightarrow CO_2$
equation needs to be balanced [1]
[3]

(b) $\Delta H = 394 - 2 \times 111 = (+)172$ kJ mol^{-1} [2]
[2]

(c) (i) ligand exchange/displacement/replacement/substitution [1]

(ii)

- d-orbitals are split (by the ligand field) *or* orbitals near ligands are at higher energy
- the splitting/energy gap depends on the ligands (surrounding the ion) *or* the metal (ion)
- when an electron moves from lower to higher orbital/energy level *or* is promoted/ excited
- light/a photon is absorbed *or* colour seen/reflected/transmitted is complement of colour absorbed ("emitted" contradicts this mark)
- different energy gap means different frequency absorbed means different colour

5 × [1]

(iii) from rows 1 and 3: rate3/rate1 = 2.0 which also equals $[[complex]_3]/[[complex]_1]$ [1]
(*or* this working mark can be awarded for any valid calculation that shows that order w.r.t. complex is 1)
Thus order w.r.t. [complex] = 1 **and** order w.r.t. [CO] is zero [1]
rate equation: **rate = k[complex]** [1]

(iv) mechanism 2 [1]
it's the only one that does **not** involve CO in the rate determining step *or* rate depends on [complex] only. [1]
[11 max 10]

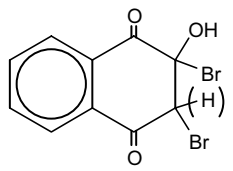
[Total: 15]

3 (a) (i) ketone, alcohol, alkene, arene/aryl/benzene/phenyl. any three [2]
(if more than 3 are given, mark the first 3 the candidate has written)

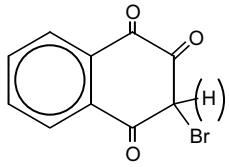
(ii) (2,4-)DNPH/Brady's *or* $FeCl_3$ (aq or neutral) *or* Br_2(**aq**) [1]
Lawsone ⇒ orange/red, (not yellow) ppt *or* purple/violet with **A**, *or* white ppt with **A**,
and A ⇒ nothing *or* **and** nothing with Lawsone *or* **and** decolourises with Lawsone [1]

(iii) $NaBH_4$ *or* $LiAlH_4$ *or* $SnCl_2$ *or* Na + ethanol *or* any suitable reducing agents with $E^{\ominus} < 0.2\,V$, e.g. SO_2. **NOT** H_2 + Ni etc. [1]

(iv)



or



(One of the Br atoms in either formula could be an OH group instead.
Br on the **benzene** ring negates this mark)

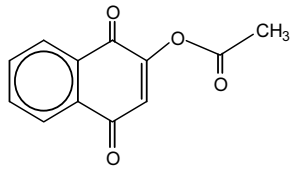
[1]
[6]

(b) (i) E_{cell} = 1.33 – 0.36 = **(+)0.97 (V)** [1]

(ii) $Cr_2O_7^{2-} + 8H^+ + 3C_{10}H_8O_3 \rightarrow 2Cr^{3+} + 7H_2O + 3C_{10}H_6O_3$
3:1 ratio [1]
balancing [1]

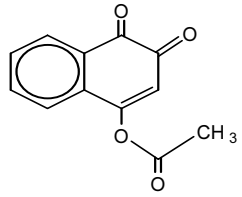
(iii) = 0.05 × 7.5/1000 = 3.75×10^{-4} mol [1]
n(**A**) = $3 \times 3.75 \times 10^{-4}$
= 1.125×10^{-3} in 20 cm^3
[**A**] = **5.63×10^{-2}** mol dm^{-3} (allow 5.6, 5.62, 5.625 etc.) [1]
[5]

(c) (i) compound **C** is [1]

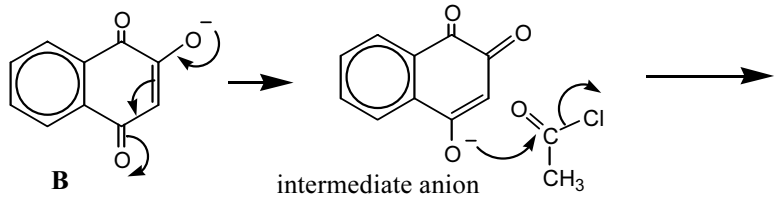


or -OCOCH$_3$
or -OOCCH$_3$

(ii) compound **D** is [1]



(iii) mechanism: 3 curly arrows in **B** *or* correct intermediate anion [1]
a curly arrow from an O^- or an oxygen with a lone pair to the carbon of the C=O group in CH_3COCl, and a second curly arrow breaking the C-C*l* bond [1]



[4 max 3]

[Total: 14]

4 **(a)** volatility: $Cl_2 > Br_2 > I_2$ *or* boiling points: $Cl_2 < Br_2 < I_2$ *or* Cl_2 is (g); Br_2 is (l); I_2 is (s) [1]
more <u>electrons</u> in X_2 down the group *or* more shells/bigger cloud <u>of electrons</u> [1]
so there's greater van der Waals/dispersion/id-id/induced/temporary dipole force/attraction [1]
[3]

(b) **(i)** $H_2O > H_2S$ *(see * below for mark)*
due to H-bonding in H_2O (none in H_2S) [1]
diagram minimum is: $H_2O^{\delta-}\cdots^{\delta+}H\text{-}OH$ *or* $H_2O{:}\cdot H\text{-}OH$ [allow (+) for δ+] [1]

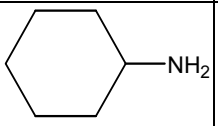
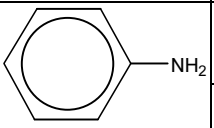
(ii) $CH_3\text{-}O\text{-}CH_3 > CH_3CH_2CH_3$ *(see * below for mark)*
due to dipole in $CH_3\text{-}O\text{-}CH_3$ (O is $\delta-$ not needed, but O is $\delta+$ negates) *or* CH_3OCH_3 is polar [1]
* correct comparison of boiling points for **both** [1]
[4]

(c) SF_6 has 6 bonding pairs/bonds and <u>no lone pairs</u> (bonds can be read into a diagram e.g. S-F, but 'no lone pairs' can *only* be read into a diagram showing 6 <u>bonded pairs of electrons</u>. [1]
<u>clear</u> diagram *or* 'shape is octahedral' [1]
[2]

[Total: 9]

5 **(a)** acidities: $CHCl_2CO_2H > CH_2ClCO_2H > CH_3CO_2H$ [1]
due to Cl being (more) electronegative/electron withdrawing (than H). [1]
this stabilises the <u>anion</u> *or* weakens the O-H bond [1]
[3]

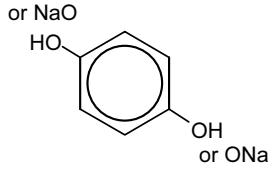
(b)

first compound	second compound	test	observation with first compound	observation with second compound
		Br_2(aq) [not (l)]	none	decolourises/ white ppt.
		$NaNO_2$ + HC*l or* HNO_2 followed by phenol (+ NaOH)	none	yellow/orange/red ppt.
CH_3CH_2COCl	CH_3COCH_2Cl	$AgNO_3$(aq)	(immediate) white ppt.	none
		add H_2O/ROH	steamy/misty/ white fumes	none
		(2,4-)DNPH	none	orange ppt.
		I_2/OH^-	none	yellow ppt./ antiseptic smell
CH_3CH_2CHO	CH_3COCH_3	I_2/OH^-	none	yellow ppt./ antiseptic smell
		Fehling's/Benedict's solution + warm	red ppt.	none
		Tollens' reagent + warm	silver/black ppt.	none
		$Cr_2O_7^{2-}$ + H^+ + warm	turns green	no change
		MnO_4^- + H^+ + warm	decolourises	no change

three correct reagents [3]
three correct positive results [3]
three × 'none' [1]
[7]

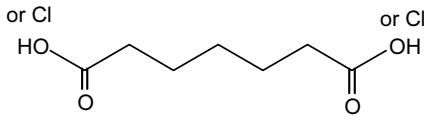
(c) (i) condensation [1]

(ii) *(in parts **(ii)** and **(iii)**, allow structural formulae instead of skeletal formulae)* [1] + [1]



E

and

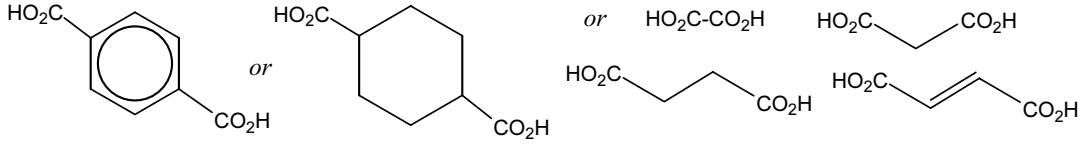


F

(N.B. letters **E** and **F** may be reversed.)

(iii) make acyl chloride from **F** (if not already there) [1]
add that to a solution of **E** in NaOH(aq) [1]

(iv) **F** (or **E**, i.e. the alphatic di-acid) should be changed to something less flexible, e.g.



(any size ring with n < 6; any orientation) (but not $HO_2C(CH_2)_3CO_2H$ or longer)

(ignore side chains: length of chain is the important feature)

or allow a tri-carboxylic acid (or triphenol), i.e. one that will allow cross linking [1]

[6]

[Total: 16]

6 (a)

amino acid	structure	type of interaction
alanine	$H_2NCH(CH_3)CO_2H$	van der Waals' (NOT hydrophobic)
cysteine	$H_2NCH(CH_2SH)CO_2H$	disulfide bonds *or* S-S
lysine	$H_2NCH((CH_2)_4NH_2)CO_2H$	ionic/electrovalent hydrogen/H bonds
serine	$H_2NCH(CH_2OH)CO_2H$	hydrogen/H bonds

[3]

[3]

(b) Iron – in haemoglobin *or* **red** blood cells; transport of oxygen/CO_2
or in myoglobin; transport of oxygen (in muscle)
or in cytochromes; cell respiration [1]

Potassium – in cell membranes/enzymes; controlling the flow of ions/water into or out of cells
or – in nerves; controlling nerve impulses
or – $Na^+ – K^+$ pump; nerve impulses/control of cell volume/active transport [1]

Zinc acting as a cofactor in enzymes (*or* a named one, e.g. carbonic anhydrase);
or in making of insulin [1]

[3]

(c) **(i)** $ATP + H_2O \rightarrow ADP + Pi$ [1]

(ii) Hydrolysis *or* nucleophilic substitution [1]

[2]

(d) **(i)** Sodium or chloride (sweat is salty) **and** Potassium (water retention in cells) [1]

(ii) Hydrogen bonding **and** reference to water *or* bonding in mucous molecules [1]

[2]

[Total: 10]

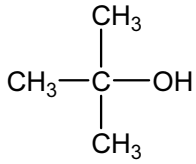
7 (a) (i) + (ii) any two from:

- The nature/electronegativity of the atom the proton is attached to *or* is near *or* the electronic/chemical environment of the proton
- The number/spin states of adjacent protons *or* protons attached to adjacent atoms
- The (strength of) the applied/external magnetic field [1] + [1]

[2]

(b) (i) Peak at 1.26δ = (3 ×) CH_3 *or* methyl **and** Peak at 2.0δ = –O–H *or* alcohol [1]

Structure: [1]



(ii)

Isomer	Isomer	Isomer
$CH_3CH_2CH_2CH_2OH$	$(CH_3)_2CHCH_2OH$	$CH_3CH_2CH(CH_3)OH$
5 groups of peaks	4 groups of peaks	5 groups of peaks

structures of any two isomers (Also allow both stereoisomers of butan-2-ol) [1] + [1]
correct assignation of no. of peaks [1] + [1]

[6]

(c) (i) Phosphorus – it has more electrons *or* high electron density (NOT phosphate) [1]

(ii) H atoms don't have enough electron density to show up *or* they only contain one e^- [1]

[2]

[Total: 10]

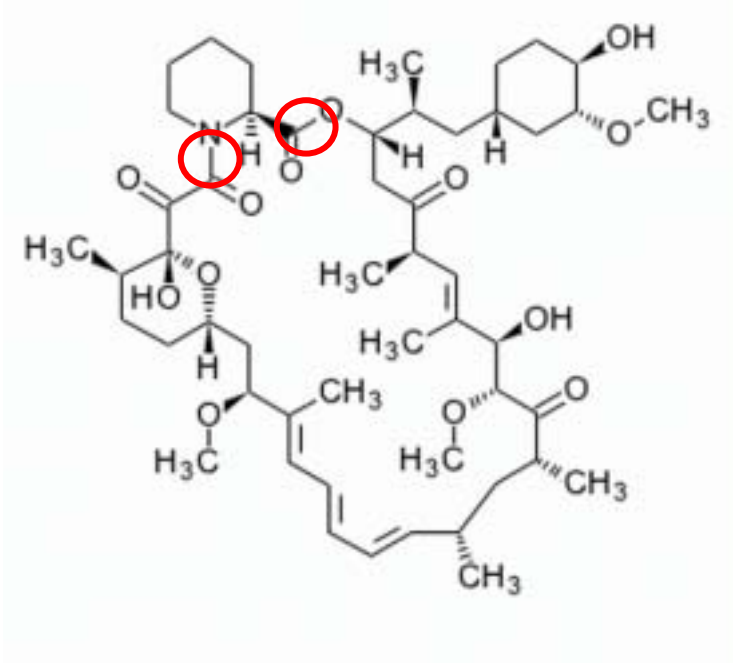
8 (a) (i) hydrophilic in area **C** [1]
fat-soluble in area **B** [1]

(ii) **A** – region would be exposed to the atmosphere/water/enzymes *or* nothing the molecule can attach to at **A** [1]
[3]

(b) (i) amide/peptide *or* ester [1]

(ii) hydrolysis [1]

(iii)



[1] + [1]
[4]

(c) (i) measured in nm, i.e. between 1 and 1000 nm (*or* 10^{-9} – 10^{-6} m). Any quoted value or range between these limits is acceptable [1]

(ii) One or both of the –OH groups (NOT just 'oxygen' or 'O') [1]

(iii) PEG can H-bond (with water) because it is hydrophilic/contains an OH group/contains lots of oxygen atoms [1]
[3]

[Total: 10]