UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS

Pre-U Certificate

MARK SCHEME for the May/June 2012 question paper

for the guidance of teachers

9791 CHEMISTRY

9791/02 Paper 1 (Part A Written), 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)** $n(Mg) = 9.0\ g / 24.3\ g\ mol^{-1} = 0.37\ mol$ (1) [1]
Allow two or more significant figures.

(b) $n(H_2O)$ reacted = 2 × n(Mg) = 0.74 mol (1)
Mass of water reacted = 0.74 mol × 18 g mol^{-1} = 13.3 g
Mass of excess water = 30 g – 13.3 g = 16.7 g (1) [2]
Allow two or more significant figures.

(c) Vol of H_2 = 0.37 mol × 24 $dm^3\ mol^{-1}$ = 8.9 dm^3 (1) [1]
Allow two or more significant figures.

(d) $\Delta_r H^{\ominus} = -924.5 kJ\ mol^{-1} - (2 \times -285.8 kJ\ mol^{-1}) = -352.9\ kJ\ mol^{-1}$ [2]
1 mark for correct signs; 1 mark for multiplying value for water by 2
Allow two or more significant figures.

(e) Heat energy = 352.9 kJ mol^{-1} × 0.37 mol= 131 kJ (1) [1]
Allow two or more significant figures.

(f) Heat energy = (60 − 15) K × 150 g × 4.2 J $g^{-1}K^{-1}$ = 28 kJ (1) [1]
Allow up to 4 significant figures.

(g) The same amount of heat energy is released from the lumps (1)
The rate of reaction (or the rate of heat generation) is slower and so a lower temperature will be reached (due to imperfect insulation) (1) / Allow temperature reached being the same if there is the stated assumption that the system is perfectly insulated. (1)
VALID ALTERNATIVE: not all of the magnesium reacts as it becomes covered in insoluble magnesium hydroxide. (1)
Therefore less energy released and lower temperature reached. (1) [2]

(h) **(i)** $CaO + H_2O \rightarrow Ca(OH)_2$ (1)
$7 < pH \leq 12$ (1) [2]

(ii) $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ OR $P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$ (1)
$0 \leq pH < 7$ (1) [2]

(iii) $6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$ OR $3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$ (1) [1]
Ignore state symbols.

[Total: 15]

2 **a** **(i)** Energy change to <u>break</u> <u>one mole of bonds</u> in the <u>gas</u> phase.
1 mark for each underlined point. [3]

(ii) $\Delta_r H^{\ominus} = 2 \times (413 + 243 - 346 - 432)$ kJ mol^{-1} = –244kJ mol^{-1}
1 mark for bonds broken; 1 mark for bonds made;
1 mark for correct sign if the answer is correct [3]

(b) **(i)** Energy change = (4405 + 3966 – (2 × 4180))cm^{-1} = 11 cm^{-1} [1]

(ii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ [1]
Superscripts must be used.

(iii) At least one K 4s atomic orbital labelled (1)
Labelled <u>sigma</u> bond below labelled <u>sigma</u> antibond (1)
(A single electron (spinning in either sense) in each atomic orbital and) two spin-paired electrons in the sigma bond (1) [3]
Electrons must be shown with a single- or double-headed arrow.

(iv) The outer electron in K is closer to the nucleus than the outer electron in Rb (1)
There is less shielding of the nucleus for the K outer electron than the Rb outer electron. (1)
(Despite the extra nuclear charge in rubidium) there is a weaker attraction of the electron to the nucleus (1)
Allow the opposite statements with respect to Rb. [3]

(v) Labelled Rb 5s orbital shown higher in energy than labelled K 4s orbital (1)
Sigma bond is lower in energy than K 4s orbital and the antibond is higher in energy than the Rb 5s orbital (1)
The bonding and antibonding orbitals must be labelled for the second mark. [2]

(vi) E = 11 cm^{-1} × h c N_A × 100 cm m^{-1} / 1000 J kJ^{-1} = 0.13 kJ mol^{-1} (1) [2]
Two marks for correct answer. Deduct one mark for each error.
One mark if final answer is out by a factor of N_A i.e. 2.19×10^{-25}
Allow two or more sig figs.

[Total: 18]

3 **(a)** **(i)** Point plotted corrected (must be within the correct small square in the grid) [1]

(ii) Bonding is intermediate-covalent-ionic-metallic [1]

(b) **(i)** $NO_2^- + 3e^- + 4H^+ \rightarrow \frac{1}{2} N_2 + 2H_2O$ OR $2NO_2^- + 6e^- + 8H^+ \rightarrow N_2 + 4H_2O$ [2]
1 mark for correct number of electrons on the left hand side
1 mark for the rest of the balanced half equation (ignoring charge)

(ii) $3CH_4 + 8NO_2^- + 8H^+ \rightarrow 3CO_2 + 4N_2 + 10H_2O$ [1]

(iii) Enzyme catalysis [1]

(c) **(i)** Oxidation state = {(2 × 112) – 8} / 36 = (+)6 [1]

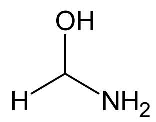
(ii) $[Mo_9O_{28}(H_2O)_4]^{2-}$ OR $[Mo_9O_{32}H_8]^{2-}$ [1]

[Total: 8]

4 **(a)** Carbon atom circled or otherwise indicated [1]

(b) Nucleophile [1]
Allow Nucleophilic or Lewis base or Lone-pair donor

(c) Any unambiguous structure of the hemiaminal [1]



No mark if atom connectivity isn't correct, e.g. $OH-CH_2NH_2$

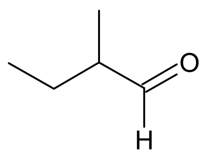
(d) Addition [1]
No credit for "Electrophilic addition"
Allow Nucleophilic addition or Reduction.

(e) Methanal (allow any carbonyl compound) [1]

(f) Hydrolysis [1]
Allow Hydration + Elimination but not Substitution + Elimination

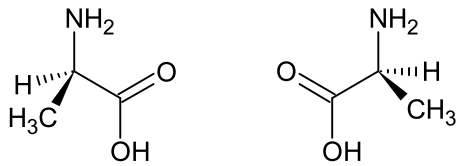
(g) Methanal: FGL 2 (1)
After Reaction 2: FGL 2 (1)
After Reaction 3: FGL 1 (1) [3]
Accept equivalent names for the functional group levels.

(h) **(i)** Allow any unambiguous structure for **z**. [1]



(ii) 2-methylbutanal [1]
Ignore incorrect use of spaces/hyphens but do not allow 2-methylbutan-1-al

(i) 1 mark for a correct structure



2nd mark for showing two optical isomers clearly with hashed and wedge bonds. [2]

[Total: 13]

5 **(a)** Mass of HCl = ¼ × 55.6 mol × 36.5 g mol^{-1} = 507 g [1]
No sig figs or units penalties.

(b) Amount of NaOH = 0.02475 dm^3 × 0.0500 mol dm^{-3} = 0.0012375 mol (1)
Amount of HCl in volumetric flask = 10 × 0.0012375 mol = 0.012375 mol (1)
[HCl] = 0.012375 mol / 0.00100 dm^3 = 12.4 mol dm^{-3} (1)
Final answer to 3 sig figs (1) [4]

(c) **(i)** $H_2SO_4 + NaCl \rightarrow HCl + NaHSO_4$ [1]
Ignore state symbols.
Allow $H_2SO_4 + 2NaCl \rightarrow 2HCl + Na_2SO_4$

(ii) $H_2SO_4 + 2HBr \rightarrow Br_2 + SO_2 + 2H_2O$ [1]
Ignore state symbols
Allow $H_2SO_4 + 2HBr \rightarrow Br_2 + H_2SO_3 + H_2O$

(iii) Sulfuric acid is the oxidising agent (1)
No credit for S being the oxidising agent.
The oxidation number of bromine increases (from −1 to 0) OR the oxidation number of sulfur decreases (from +6 to +4) (1) [2]

(d) **(i)** Bond strength decreases because the bonds gets longer OR because there is greater shielding of the bonding electrons from the halogen nucleus due to the additional inner shells of electrons. [1]
No credit for answers based on electronegativity or ionic radii.

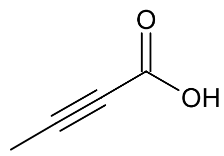
(ii) Acidic strength increases because the H−Hal bond gets weaker. [1]

(iii) Increasing boiling point for HCl → HBr → HI due to increasing van der Waals (permanent) dipole – (permanent) dipole forces. (1)
HF boiling point higher than HCl due to hydrogen bonding. (1) [2]

[Total: 13]

6 **(a)** Molecular formula = $C_4H_4O_2$ [1]

(b) Correct structure (1)



Name = but-2-ynoic acid (1) [2]
No mark for name if it is inconsistent with the structure given.

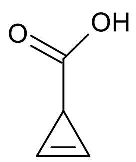
(c) %C = (24/42) × 100% = 57.1%
%H = (2/42) × 100% = 4.8%
%O = (16/42) × 100% = 38.1% [2]
2 marks all correct. 1 mark for two out of three correct.
Don't penalise two or more significant figures. Allow 5% for H.

(d) m/z = 84 [1]

(e) **(i)** Allow wavenumber values from the following ranges
Double bonds: 1500 – 1900 cm^{-1} (inclusive)
Single bonds (no H): ≤1500 cm^{-1}
Single bonds to H: 2500 – 3700 cm^{-1} (inclusive)
Allow a correct range rather than a value.
2 marks for 3 correct responses
1 mark for 1 or 2 correct responses [2]

(ii) Broad OR a wavenumber range given that is at least 500 cm^{-1} across. [1]

(f)



[1]

[Total: 10]

7 **(a)** 1 mark for each correct test; 1 mark for each correct observation; 1 mark for each correct deduction.

Halogenoalkanes: max 5 marks
Testing for the haloalkanes with aqueous silver nitrate or aqueous lead nitrate (1)
White ppt (produced slowly) (1) with the chloroalkane (1)
Yellow ppt (produced quickly) (1) with the iodoalkane (1)
Allow use of NaOH to hydrolyse the halogenoalkane first (though the alkali precipitates out the silver). [5]

Aldehyde: max 3 marks
Tollens' (or Fehling's etc) reagent or ammoniacal silver nitrate (1) used to identify the aldehyde (1)
Silver mirror (or red ppt) produced (1)
Brady's reagent or 2,4-dinitrophenylhydrazine or 2,4-DNP (1) used to identify the aldehyde (1)
Orange ppt (1)
Ignore oxidation of the aldehyde if it has already been identified. [3]

Alcohols: max 6 marks
Identification of alcohols by their oxidation [max 3 marks]
Oxidising agent specified to identify the alcohols (dichromate/ manganate must be acidified) (1)
Colour change specified (1)
Identification of the two alcohols as having given the colour change. (1)

Distinguishing between the two alcohols using their oxidation [max 3 marks]
Test to distinguish the two alcohols, eg distilling off oxidation product (1)
Product of oxidising propan-2-ol distils off readily / is not acidic (1)
Product of oxidising propan-1-ol distils off at higher temperature / is acidic (1)

Lucas reagent method:
Lucas reagent or conc HCl with $ZnCl_2$ catalyst (1)
Very slow cloudiness (1) implies propan-1-ol (1)
Moderately rapid cloudiness (1) implies propan-2-ol (1)

Alternative methods
Sodium (1) specified to identify the alcohols (1)
Effervescence (or hydrogen gas produced) (1)
Glacial ethanoic acid and conc sulfuric acid (1) to identify the alcohols (1)
Sweet / fruity vapour produced (1)
Iodoform test (1) to identify propan-2-ol (1)
Iodoform observations for positive test (1)

If alcohols are identified by a concise clear method, e.g. Lucas reagent, which yields only 5 marks, additional mark to be given for economy of method (1) [6]

Alkane: max 1 mark
Hexane gives no positive results with any of these tests [1]

Give credit to alternative legitimate methods and also to the observations from those methods

[Max. 15 marks]

(b) Reduction (max 5 marks)
Dissolve benzophenone in ethanol (if using $NaBH_4$) or dry ether (if using $LiAlH_4$) (1)
Choice of $NaBH_4$ or $LiAlH_4$ as reducing agent (1)
Dissolve reducing agent in ethanol or water (if using $NaBH_4$) or dry ether (if using $LiAlH_4$) (1) Allow ether as a solvent for $NaBH_4$.
Use excess reducing agent (1)
Heat (under reflux) benzophenone with reducing agent (1)

Separation (max 3 marks)
If using alcohol:
Precipitate product (1) by adding (excess) water (1)
Then filter off product (1)

If using ether:
Add (excess) water (1)
Separate the ether layer (with a separating funnel) (1)
Then distil off ether to recover product (1)

Allow Alternative Separation Method (based on solubility in warm water) (max 3 marks)
Add water and warm mixture (1)
Filter off undissolved X (allow decant) (1)
Evaporate off water or leave to cool to recover Y (1)

Marks for separation reliant on a feasible technique, ie a reasonable sequence of steps that would work.

Purification (max 3 marks)
Wash product with cold water or cold hexane (1)
Recrystallise product from (a minimum of) hot hexane (or water) (1)
Cooling/scratching of glass to aid precipitation (1)

Checking Purity (max 1 mark)
Check purity of product by measuring its melting point
OR by thin-layer chromatography (against starting material) OR infrared (1)

[Max: 8 marks]

[Total: 23]