UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS

Pre-U Certificate

MARK SCHEME for the May/June 2011 question paper

for the guidance of teachers

9791 CHEMISTRY

9791/02 Paper 2 (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.

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

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UNIVERSITY of CAMBRIDGE
International Examinations

1 (a) (i)

s	d_{z^2}	p_y
$d_{x^2-y^2}$ (allow $d_{y^2-x^2}$)	p_x	d_{yz} (allow d_{yz})
d_{xy} (allow d_{yx})	p_z	d_{xz} (allow d_{zx})

The first three marks are for correctly identifying the orbitals with the relevant subshell: 1 for the s, 1 for identifying the three p, and 1 for the five d orbitals. These marks are awarded regardless of the orbital subscripts offered.

1 mark is awarded for the correct subscripts on the p orbitals. This mark can only be awarded if the correct orbitals were identified as p orbitals.

1 mark is awarded for the correct subscripts on the d orbitals. This mark can only be awarded if the correct orbitals were identified as d orbitals.

Do not penalise subscript labels if they are not subscripted (e.g. if they are superscripts or normal text)
If all orbitals given the same subshell label then credit is given for identifying that one subshell. [5]

(ii) Copper (1)
Zinc (1)
Do not penalise a symbol if used instead of a name. [2]

(b) (i) A p_z orbital drawn on each atom (both needed for the mark) [1]

(ii) Either a p_x or a p_y orbital drawn on each atom (both needed and both of the same type for the mark) [1]

(c) (i) $4s^1\ 3d^5$ or $3d^5\ 4s^1$
No credit if the 1 or 5 given as a subscript, but don't penalise if the numbers are normal text size. [1]

(ii) d_{z^2} or $3d_{z^2}$
Allow ecf from a mislabelled orbital in part **(a)**. Same lenience with naming orbitals as in part **(a)**. [1]

(iii) Pi: d_{xz} and d_{yz} (1) (both needed for the mark)
Delta: d_{xy} and $d_{x^2-y^2}$ (1) (both needed for the mark)
Allow ecf from a mislabelled orbital in part **(a)**. Same lenience with naming orbitals as in part **(a)**. [2]

[Total: 13]

2 **(a)** Bonds broken = 4E(C−F) + 4E(Si−H) = ((4 × 467) + (4 × 318)) kJ mol^{-1} = 3140 kJ mol^{-1} (1)
Bonds made = 4E(C−H) + 4E(Si−F) = ((4 × 413) + (4 × 553)) kJ mol^{-1} = 3864 kJ mol^{-1} (1)
Enthalpy change = bonds broken – bonds made = (3140 − 3864) kJ mol^{-1} = −724 kJ mol^{-1} (1)
Allow ecf from the bonds made or broken to the final answer.
+724 kJ mol^{-1} scores 2 marks.
Otherwise −1 mark per error, including no units, to a minimum of zero.
Do not penalise significant figures. [3]

(b) **(i)** $(C_2H_5)_3SiH + C_6F_5CF_3 \rightarrow (C_2H_5)_3SiF + C_6F_5CF_2H$
No credit if the ions are included. [1]

(ii) A catalyst (1)

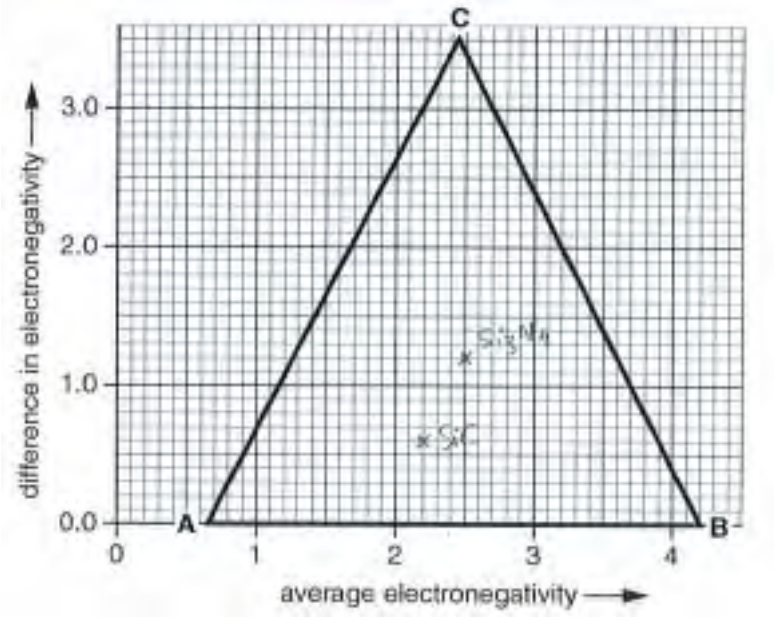
It accepts a fluoride ion and is regenerated in the following step
OR It lowers the activation energy of the reaction (1)
Ignore providing an alternative pathway or being regenerated. [2]

(c) The Si−F bond is more polar or related comments to do with electronegativity difference or ionic character.
OR there is some pi bonding between lone pairs on the fluorine atoms and vacant d orbitals on the silicon atom.
Accept opposite argument relating to the C−F bond. [1]

(d) SiF_4 is more reactive than CF_4 because of lower activation energies or words to this effect relating to the mechanism.
OR silicon, being larger than carbon, can expand its coordination number beyond 4 (which creates the potential for mechanisms with lower activation energies). Just silicon being larger than carbon is insufficient for the mark.
OR d orbitals can participate in the reaction with SiF_4 (which creates the potential for mechanisms with lower activation energies)
Accept arguments relating to steric hindrance around carbon.
Accept arguments that relate to the empty d orbitals in silicon or silicon expanding its octet. [1]

[Total: 8]

3 (a)



1 mark for each point correctly plotted. Points should be within half a square on each axis of the true position. [2]

(b) **B** is covalent **C** is ionic 1 mark for both correct [1]

(c) SiC is more metallic [1]

(d) SiC is intermediate between metallic and covalent [1]

(e) AlN is the most clearly intermediate between all three extremes [1]

(f) The triangle takes no account of oxidation number of an element (1)
It takes no account of the allotropy of an element (1)
It takes no account of the temperature of the compound (1)

Allow related comment about the pressure of the compound but no mark in addition to the temperature mark.
No credit for points relating to the stoichiometry of compounds.
Ignore comments about compounds made from more than two elements. [3]

[Total: 9]

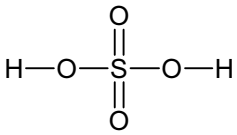
4 (a) (i) Trigonal bipyramidal structure of PCl_5 (1)
At least one equatorial wedged bond and at least one equatorial hashed bond.
(Give this mark if it is clear that the three chlorine atoms are equatorial.) (1)
Bond angles of 120° and 90° (both required for the mark). (1)
Name: trigonal bipyramidal or trigonal bipyramid (both words needed for the mark) (1) [4]

(ii) Hydrolysis
Accept Substitution + Elimination (both processes required) [1]

(iii) (+)5 OR (+)V [1]

(iv) It is not an oxidising agent OR it is less oxidising than H_2SO_4. [1]

(v)



Accept structures with –OH or HO− but not −HO or OH−.
Allow an ionic bond between O and H, i.e. $–O^{-}\ ^{+}H$ [1]

(b) (i) $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$
Ignore state symbols. Equation must be balanced. [1]

(ii) step 2 $PCl_4OH + H_2O \rightarrow PCl_3(OH)_2 + HCl$ (1)
step 3 $PCl_3(OH)_2 \rightarrow POCl_3 + H_2O$ (1)
Be tolerant with the use of brackets, e.g. allow $PCl_4(OH)$ [2]

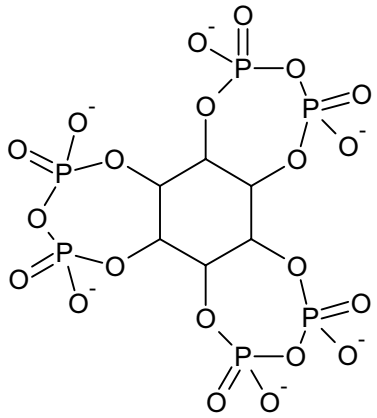
(c) (i) Correct basic structure, i.e. $(HO)_2P(=O)–O–P(=O)(OH)_2$, not worrying about the 3-dimensional aspect
Penalise −HO or OH− only if penalty wasn't incurred in **(a)(v)**. [1]

(ii) Tetraphosphoric acid $H_6P_4O_{13}$ [1]

(iii) $H_{n+2}P_nO_{3n+1}$ [1]

(d) (i) CH_2O (Allow COH_2) [1]

(ii)



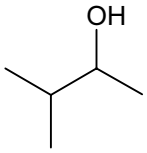
Biphosphates linking adjacent oxygens on the ring (1)
Correct negative charge on each phosphate ester (1) [2]

[Total: 17]

5 (a) C of C−Mg bond labelled as δ− and Mg as δ+ [1]

(b) Nucleophile (1) (but contradicted by Electrophile)
Reducing agent (1) (but contradicted by Oxidising agent)
Base (1) (but contradicted by Acid) [3]

(c) (i)



Accept any unambiguous structure
Allow the alkoxide ion or the intermediate compound with −MgC*l*. [1]

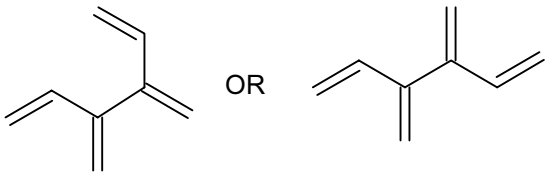
(ii) Just the C−OH carbon is chiral
Allow ecf from **(c)(i)**. If there is no chiral carbon in **(c)(i)** response then it must be stated explicitly. [1]

(iii) Name: 3-methylbutan-2-ol (don't penalise hyphens/spaces and allow 3-methyl-2-butanol)
No credit for 2-methylbutan-3-ol or other near misses.
Allow ecf from **(c)(i)** [1]

(d) Propane. Accept name or formula or structure. [1]

(e) (i) C_6H_8 [1]

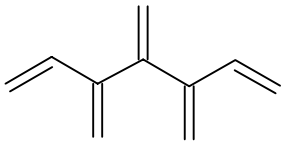
(ii) The organic product is:



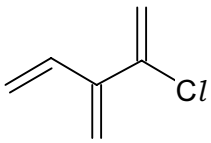
(1)

Accept other equivalents, bearing in mind that the C−C single bonds can rotate.
The inorganic product is $MgCl_2$ (1) [2]

(iii)



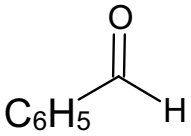
Correct product – as drawn or another rotamer. Allow partially skeletal formula.
Just one mark if there's no skeletal part to the structure.
One mark only awarded for the intermediate or a rotamer of it:



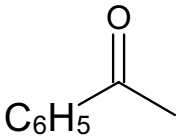
[2]

[Total: 13]

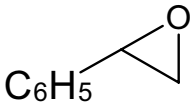
6 (a) Structure **A**:



Structure **B**:



Structure **C**:

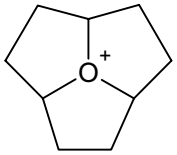


Allow any unambiguous structure. 1 mark each. Ignore any name written. [3]

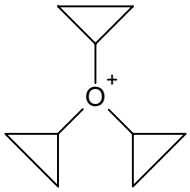
(b) (i) Correct dot-cross diagram. H and O electrons must be represented by different symbols and one of the O−H bonds must be dative. (1)
A positive charge must be shown either on the O or the H of the dative bond or outside brackets. (1) [2]

(ii) ionic molecular formula $C_9H_{21}O^+$ (+ sign must be present) (1)
m/z for molecular ion: 145 (Allow ecf from molecular formula) (1)
number of ^{13}C signals: 3 (Allow ecf from formula if structure given) (1) [3]

(iii)



Also allow



Ignore charge unless it's negative, in which case the mark is lost. [1]

(c) (i) Amount = 4×10^{-18} dm^3 × 5×10^{-4} mol dm^{-3} = 2×10^{-21} mol [1]

(ii) Number of molecules = 2×10^{-21} mol × 6.02×10^{23} mol^{-1} = 1204
Allow use of 6×10^{23} mol^{-1} and 1200 as an answer.
Allow 1×10^3 molecules.
Allow ecf from **(c)(i)**. [1]

[Total: 11]

7 **(a)** alkane → ester → alcohol [1]

(b) **(i)** $C_3H_6O_2 + 7/2\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O$ or equation multiplied through by 2.
Accept a structural or displayed formula for the ester but not a skeletal formula. [1]

(ii) Enthalpy change when **1 mol** of substance is formed **from its elements**.
1 mark for each of the points in bold
Mention of standard states or under standard conditions or 1 bar pressure. (1) [3]

(iii) $\Delta_fH^{\ominus}(C_3H_6O_2) = 3\ \Delta_cH^{\ominus}$**(c)** $+ 3\ \Delta_cH^{\ominus}(H_2) - \Delta_cH^{\ominus}(C_3H_6O_2) =$
$= ((3\times-393.5) + (3\times-285.8) - (-1592.1))$ kJ mol^{-1} = –445.8 kJ mol^{-1}
Correctly multiplying carbon and hydrogen values by 3 or a 3:3:1 ratio of $C:H_2:C_3H_6O_2$ (1)
Correct signs, i.e. $-\Delta_cH^{\ominus}$(ester) $+ \Delta_cH^{\ominus}$(elements) (1)
Correct final answer to 1 d.p. (1)
Allow ecf from an earlier penalised error if it has been worked through correctly. [3]

(c) **(i)** Use a measuring cylinder to add 300 cm^3 of water to the copper can. (1)
Measure initial mass of spirit burner (+ester) on mass balance. (1)
Measure initial temperature of water in copper can using thermometer. (1)
Light the wick on the spirit burner. (Not 'burn the ester') (1)
Extinguish the spirit burner when the temperature of the water has risen by 10 degrees. (1)
Reweigh the spirit burner. (1)
Subtract the final mass from the initial mass to determine mass of ester burnt. (1)
[Max: 6]

(ii) Thermal energy added to water = 4.18 J K^{-1} g^{-1} × 10.0 K × 300 g = 12540 J (1)
Thermal energy added to copper = 0.384 J K^{-1} g^{-1} × 10.0 K × 250 g = 960 J (1)
Total energy = 13.5 kJ (3 s.f. required) (1)
Answer must be in kJ, not Joules, but no penalty for omitting to write kJ. [3]

(iii) Amount of ester = 0.980 g / 74.0 g mol^{-1} = 0.0132 mol (1)
Theoretical energy released = 0.0132 mol × 1592.1 kJ mol^{-1} = 21.1 kJ (1)
Allow ecf with amount of ester.
3 s.f. required in final answer, but don't penalise if penalty already sustained in previous part. [2]

(iv) Find thermal capacity of apparatus using: thermal capacity = theoretical energy released / observed temperature change

Thermal capacity = 21.1 kJ / 10 K = 2.11 kJ K^{-1}. (1)
Theoretical heat produced from combustion of ethyl ethanoate = 2.11 kJ K^{-1} × 11.5 K = 24.3 kJ (1)

[ALTERNATIVE METHOD: 13.5 kJ / 21.1 kJ => 64% of energy detected. ∴Divide measured energy change by 0.64] (1)
[Correct calculation of measured energy change with this method as 15.5 kJ (1)
[No credit for 14.4 kJ (omitting Cu)]

i.e. 24.3 kJ of heat produced earns 2 marks
No credit for a simple additative correction for the heat loss (since there was a different temperature change)

Amount of ethyl ethanoate = 0.948 g / 88 g mol^{-1} = 0.010773 mol (1)
Standard enthalpy change of combustion of ethyl ethanoate = −24.3 kJ / 0.010773 mol = −2250 kJ mol^{-1}. (1)
This mark is lost if the final answer isn't negative.
3 s.f. required in final answer, but don't penalise if penalty already sustained
Allow ecf from earlier parts. Give two marks for use of ratio 11.5/10 rather than explicitly calculating thermal capacity. [4]

(d) Put a lid on the calorimeter (1)
Add insulation around the side and/or top of the calorimeter (1)
Stir the water in the copper pot (1)
Draw hot vapour from the flame through a calorimeter using suction (1)
Do repeats and **take an average** (1)
Put a cap on the spirit burner when it isn't lit to avoid evaporative losses (1)
Other sensible refinement (1)
A mark for any of the above up to a maximum of four
Marks not awarded for: improving the thermometer
comments about height of the can above the burner
use of a different burner or different material for the can
draft excluders [max 4]

(e) The methyl ethanoate will be easier to light (more volatile) (1)
The flame will be less yellow/smoky from the methyl ethanoate (less oxygen required for complete combustion) (1) [2]

[Total: 29]