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MARKSCHEME

May 2009

CHEMISTRY

Higher Level

Paper 2

19 pages

Subject Details: Chemistry HL Paper 2 Markscheme

Mark Allocation

Candidates are required to answer **ALL** questions in Section A **[40 marks]** and **TWO** questions in Section B **[2 × 25 marks]**. Maximum total = **[90 marks]**.

1.   A markscheme often has more marking points than the total allows. This is intentional. Do not award more than the maximum marks allowed for part of a question.

2.   Each marking point has a separate line and the end is signified by means of a semicolon (;).

3.   An alternative answer or wording is indicated in the markscheme by a slash (/) – either wording can be accepted.

4.   Words in brackets (   ) in the markscheme are not necessary to gain the mark.

5.   Words that are underlined are essential for the mark.

6.   The order of marking points does not have to be as in the markscheme, unless stated otherwise.

7.   If the candidate's answer has the same "meaning" or can be clearly interpreted as being of equivalent significance, detail and validity as that in the markscheme then award the mark. Where this point is considered to be particularly relevant in a question it is emphasized by writing ***OWTTE*** (or words to that effect).

8.   Remember that many candidates are writing in a second language. Effective communication is more important than grammatical accuracy.

9.   Occasionally, a part of a question may require an answer that is required for subsequent marking points. If an error is made in the first marking point then it should be penalized. However, if the incorrect answer is used correctly in subsequent marking points then **follow through** marks should be awarded. Indicate this with **ECF** (error carried forward).

10.   Only consider units at the end of a calculation. Unless directed otherwise in the markscheme, unit errors should only be penalized once in the paper. Indicate this by writing **–1(U)** at the first point it occurs and **U** on the cover page.

11.   Significant digits should only be considered in the final answer. Deduct **1 mark in the paper** for an **error of 2 or more digits** unless directed otherwise in the markscheme.

> *e.g.* if the answer is 1.63:
> | | |
> |---|---|
> | 2 | *reject* |
> | 1.6 | accept |
> | 1.63 | accept |
> | 1.631 | accept |
> | 1.6314 | *reject* |

Indicate the mark deduction by writing **–1(SD)** at the first point it occurs and **SD** on the cover sheet.

12.   If a question specifically asks for the name of a substance, do not award a mark for a correct formula, similarly, if the formula is specifically asked for, do not award a mark for a correct name.

13.   If a question asks for an equation for a reaction, a balanced symbol equation is usually expected, do not award a mark for a word equation or an unbalanced equation unless directed otherwise in the markscheme.

14.   Ignore missing or incorrect state symbols in an equation unless directed otherwise in the markscheme.

SECTION A

1. (a) carboxylic acid / carboxyl;
ester;
Do not allow carbonyl / acid / ethanoate / formula(–COOH).

aryl group / benzene ring / phenyl;   *[3]*

(b) (i) $M_r(C_7H_6O_3) = 138.13$;

$$n = \left(\frac{3.15}{138.13} = \right) 2.28 \times 10^{-2} \text{(mol)};$$ *[2]*

Award [2] for the correct final answer.

(ii) $M_r(C_9H_8O_4) = 180.17$;

$m = (180.17 \times 2.28 \times 10^{-2} =) 4.11 \text{(g)}$;   *[2]*
Accept range 4.10–4.14
Award [2] for the correct final answer.

(iii) (percentage yield $= \dfrac{2.50}{4.11} \times 100 =) 60.8\,\%$;   *[1]*

Accept range 60–61%.

(iv) 3;

(percentage uncertainty $= \dfrac{0.02}{2.50} \times 100 =) 0.80\,\%$;   *[2]*

Allow 0.8%.

(v) sample contaminated with ethanoic acid / aspirin not dry / impure sample;   *[1]*
Accept specific example of a systematic error.
Do not accept error in reading balance/weighing scale.
Do not accept yield greater than 100%.

(vi) hypothesis not valid/incorrect;

Accept any of the following for the second mark
C–O and C=O bond lengths will be different;
C2–O3 bond is longer than C8–O4 bond;
C8–O4 bond shorter than C2–O3 bond;
a CO single bond is longer than a CO double bond;   *[2 max]*
Accept C8–O4 is a double bond hence shorter.

(vii) *Brønsted-Lowry definition of an acid*
proton/H^+/hydrogen ion donor;

Conjugate base of CH_3COOH
CH_3COO^-/$CH_3CO_2^-$;   *[2]*
Do not accept $C_2H_3O_2^-$ /ethanoate.

2. (a) (i) $K_a = 6.310 \times 10^{-5} / 6.31 \times 10^{-5}$;   **[1]**
             Accept 6.3×10^{-5}.

     (ii) weak (acid);
          $K_a \ll 1$ / small K_a;   **[2]**

     (iii) $[H_3O^+]/[H^+] = \sqrt{K_a \times 0.010}$;
           $[H_3O^+]/[H^+] = 7.9 \times 10^{-4} (\text{mol dm}^{-3})$;
           $pH = 3.10 / 3.1 / 3.12$;
           Award [3] for correct final answer of pH.

           assume $x \ll 0.010 \,(\text{mol dm}^{-3})$ / ionization of water is insignificant /
           $[C_6H_5COOH]_{\text{initial}} = [C_6H_5COOH]_{\text{eq.}}$ / temperature $25\,^{\circ}C / 298$ K;   **[4]**

   (b) Na, Mg: basic;
       Al: amphoteric;
       Do not accept amphiprotic.

       Si to Cl: acidic;   **[3]**
       Award [1] for stating oxides become more basic towards left/Na and more acidic
       towards right/Cl.
       Do not penalize incorrect formulas of oxides.

   (c) NO$_2$/nitrogen dioxide / N$_2$O$_4$/dinitrogen tetroxide / SO$_2$/sulfur dioxide / SO$_3$/sulfur
       trioxide;   **[1]**
       Do not accept NO/NOx/CO$_2$/CO.

3. (a) (i) dumbbell-shaped representation along the *z*-axis:
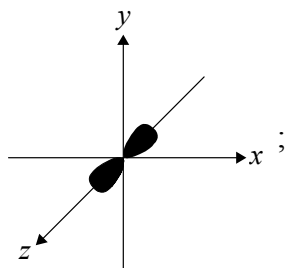
Sign of wave function not required. **[1]**

(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ / $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$ / $[Ar]4s^0 3d^5$ / $[Ar]3d^5$; **[1]**
Do not allow 2, 8, 13.

(iii) Lewis base / (species/ion/molecule) with lone pair **and** dative
covalent/coordinate bond (to metal) / bonds with metal (ion)/complex ion; **[1]**

(iv) has partially filled d subshell/sublevel/orbitals;
d orbitals are split (into two sets of different energies);
colour due to electron transition between (split) d orbitals;
frequencies of visible light absorbed by electrons moving from lower to higher
d levels, colour due to remaining frequencies; **[3 max]**
Allow wavelength as well as frequency.

(v) **[1]**

$4s^2$ $3d^{10}$ $4p^4$

Accept half-arrows or full arrows.
Do not penalize if additional sublevels are shown, if sublevels are not labelled
or if no boxes are drawn (providing system of arrows correct).
Do not award mark if sublevels are incorrectly labelled.
Orbital diagram may also be represented with sublevels shown at different
relative energy positions.

4. (a) $\Delta H^{\ominus}_{\text{reaction}} = \Sigma \Delta H_{\text{f}}^{\ominus}(\text{products}) - \Sigma \Delta H_{\text{f}}^{\ominus}(\text{reactants})$
$= [(1)(-85) + (2)(-242)] - [(2)(-201)];$
$= -167 \,(\text{kJ/kJ mol}^{-1});$ **[2]**
Award [1] for (+) 167.

(b) $\Delta S^{\ominus}_{\text{reaction}} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$
$= [(1)(230) + (2)(189)] - [(2)(238) + (1)(131)];$
$= 1 \,(\text{J K}^{-1}/\text{J K}^{-1} \text{mol}^{-1});$ **[2]**

(c) $\Delta G^{\ominus}_{\text{reaction}} = (\Delta H^{\ominus} - T\Delta S^{\ominus}) = (-167) - (298)(0.001);$
Award [1] for correct substitution of values.

$= -167 \,\text{kJ} / -167000 \,\text{J};$
Units needed for mark in (c) only.
Accept –167 kJ mol^{-1} or –167000 J mol^{-1}.

spontaneous;   **[3]**

*Award marks for final correct answers throughout in each of (a), (b) and (c).*

SECTION B

5.   (a)   (i)   *Group*: number of valence/outer energy level electrons same;

Ⅰ   *Period*: electrons are in same valence/outer energy level;   **[2]**
Accept number of energy levels containing electrons occupied.

Accept shell for energy level.

(ii)   4;   **[1]**
Allow the mark if the correct individual orbitals (e.g. 2s etc.) are listed.

(b)   (i)

;

octahedral/octahedron/square bipyramidal;
90° / 90° **and** 180°;   **[3]**

(ii)

;

linear;
180°;   **[3]**

Allow dots, crosses or lines in Lewis structures.
Penalize missing charge, missing bracket once only in (i) and (ii).
Lone pairs required for BOTH (i) and (ii).

(c)   boiling points increase going down the group (from PH_3 to AsH_3 to SbH_3);
M_r/number of electrons/molecular size increases down the group;
Accept electron cloud increases down the group.

greater dispersion/London/van der Waal's forces;

NH_3/ammonia has a higher boiling point than expected due to <u>hydrogen bonding
between</u> the molecules;   **[4]**
Do not accept hydrogen bonding alone.

(d) NO_2 :
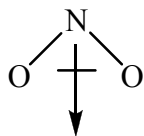
*Award [1] for correct representation of the bent shape **and** [1] for showing the net dipole moment, or explaining it in words (unsymmetrical distribution of charge).*

CO_2 :
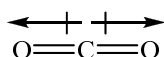
*Award [1] for correct representation of the linear shape **and** for showing the two equal but opposite dipoles or explaining it in words (symmetrical distribution of charge).* **[3]**

For both species, allow either arrow or arrow with bar for representation of dipole moment.
Allow correct partial charges instead of the representation of the vector dipole moment.
Ignore incorrect bonds.
Lone pairs not needed.

(e) *Structure:*
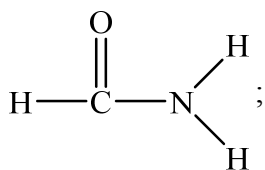network/giant lattice / macromolecular / repeating tetrahedral units;
Bonding:
(single) covalent (bonds); **[2]**
It is not necessary to identify which part refers to structure and bonding specifically.

(f) (i) methanamide;

; **[2]**

(ii) mixing/joining together/combining/merging of atomic orbitals to form molecular /new orbitals / orbitals of equal energy; **[1]**

(iii)   σ *bond*:
end-on/axial overlap with electron density between the two atoms/nuclei;
π *bond*:
sideways/parallel overlap with electron density above **and** below internuclear
axis/σ bond;   **[2]**
Marks can be scored from a suitable diagram.
*Award **[1 max]** for stating end-on/axial overlap for σ and sideways/parallel*
overlap for π only i.e. without mentioning electron density OR stating electron
density between the two atoms/nuclei for σ above and below internuclear axis/σ
bond for π i.e. without mentioning overlap.

(iv)

sp^2; sp^2/sp^3;

                                                                                     [2]
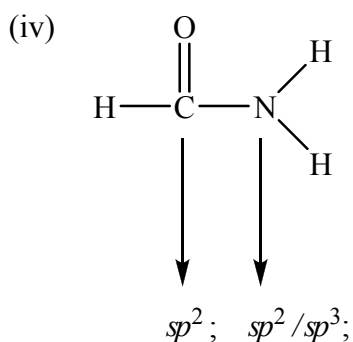
Correct answer is actually sp^2 *for nitrogen because of delocalization/planar*
geometry.
Accept sp^3.

6. (a) (i) $(K_c =) [SO_3]^2 / [O_2][SO_2]^2$; **[1]**

(ii) yield (of SO_3) increases / equilibrium moves to right / more SO_3 formed;
3 <u>gaseous</u> molecules $\rightarrow$ 2 <u>gaseous</u> molecules / decrease in volume of <u>gaseous</u> molecules / fewer <u>gaseous</u> molecules on right hand side; **[2]**
Do not allow ECF.

(iii) yield (of SO_3) decreases;
forward reaction is exothermic / reverse/backwards reaction is endothermic / equilibrium shifts to absorb (some of) the heat; **[2]**
Do not accept exothermic reaction or Le Châtelier's Principle.
Do not allow ECF.

(iv) rates of both forward and reverse reactions increase <u>equally</u>;
no effect on position of equilibrium;
no effect on value of K_c; **[3]**

(b) $2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$

	NO(g)	**H$_2$(g)**	**N$_2$(g)**	**H$_2$O(g)**
Initial/mol dm^{-3}	0.100	0.051	0.000	0.100
Change/mol dm^{-3}	−0.038	−0.038	+0.019	+0.038
Equilibrium/mol dm^{-3}	0.062	0.013	0.019	0.138

$[H_2]$ at equilibrium $= 0.013\,(mol\,dm^{-3})$;
$[N_2]$ at equilibrium $= 0.019\,(mol\,dm^{-3})$;
$[H_2O]$ at equilibrium $= 0.138\,(mol\,dm^{-3})$;
$K_c = [N_2][H_2O]^2 / [NO]^2[H_2]^2 = (0.019)(0.138)^2 / (0.062)^2(0.013)^2 = 5.6 \times 10^2$; **[4]**
Award [4] for final correct answer .
Accept any value also in range 557–560.
Do not penalize significant figures.

(c) (i) electrolytic cell converts electrical energy to chemical energy **and** voltaic cell converts chemical energy to electrical energy / electrolytic cell uses electricity to carry out a (redox) chemical reaction **and** voltaic cell uses a (redox) chemical reaction to produce electricity / electrolytic cell requires a power supply **and** voltaic cell does not;

electrolytic cell involves a non-spontaneous (redox) reaction **and** voltaic cell involves a spontaneous (redox) reaction;

in an electrolytic cell, cathode is negative and anode is positive **and** *vice-versa* for a voltaic cell / electrolytic cell, anode is positive and voltaic cell, anode is negative / electrolytic cell, cathode is negative and voltaic cell, cathode is positive;

voltaic cell has two separate solutions **and** electrolytic cell has one solution / voltaic cell has salt bridge and electrolytic cell has no salt bridge;

electrolytic cell, oxidation occurs at the positive electrode/anode **and** voltaic cell, oxidation occurs at the negative electrode/anode and *vice-versa*;   *[2 max]*

(ii) (solid) ions in a lattice / ions cannot move;
(molten) ions mobile / ions free to move;   *[2]*

(iii) reduction occurs at the cathode/negative electrode **and** oxidation occurs at the anode/positive electrode;
Cathode/negative electrode: $Na^+ + e^- \rightarrow Na$;

Anode/positive electrode: $2Cl^- \rightarrow Cl_2 + 2e^- / Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$;
Award [1 max] if the two electrodes are not labelled/labelled incorrectly for the two half-equations.

Overall cell reaction: $Na^+(1) + Cl^-(1) \rightarrow Na(1) + \frac{1}{2}Cl_2(g)$ *[5]*
Award [1] for correct equation and [1] for correct state symbols.
Allow NaCl (l) instead of Na⁺(l) and Cl⁻(l).

(iv) Al does not corrode/rust / Al is less dense/better conductor/more malleable;   *[1]*
Accept Al is lighter (metal compared to Fe).
Accept converse argument.

(v) *Cathode/negative electrode*:
object to be plated;
Allow a specific example here e.g. spoon.
Accept inert metal/graphite.
Do not accept silver halides or their formulae.

Anode/positive electrode:
Silver/Ag;
Electrolyte:
$[Ag(CN)_2]^-$;   *[3]*
Allow silver nitrate/AgNO₃ / silver cyanide/any other suitable silver salt/solution.
Do not accept AgCl.

7.   (a)   (i)   decrease in concentration/mass/amount/volume of reactant with time / increase in concentration/mass/amount/volume of product with time / change in concentration/mass/amount/volume of reactant/product with time;   *[1]*

(ii) $MgCO_3(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + CO_2(g) + H_2O(l)$;   *[1]*
Ignore state symbols.

(iii)

;
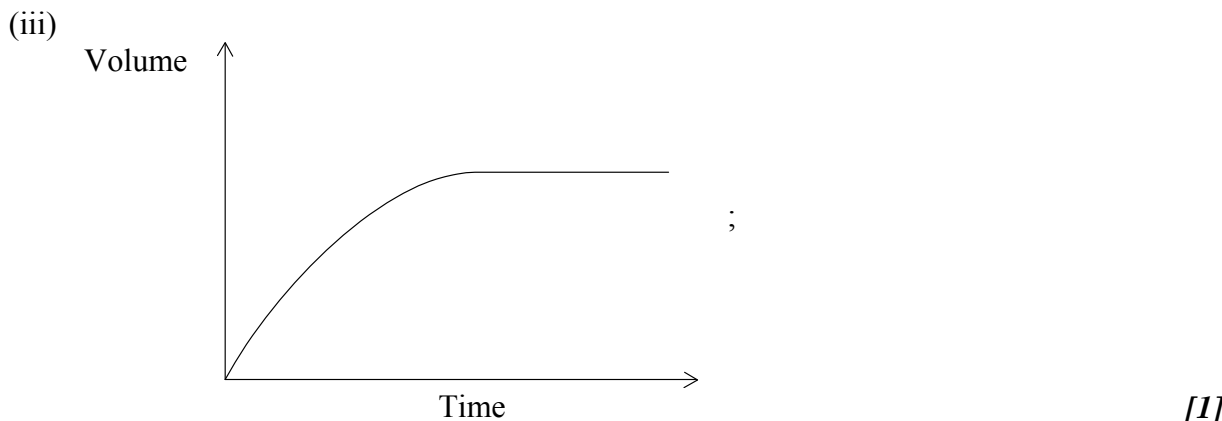
Plot starts at the origin and levels off.
No mark awarded if axes are not labelled.   *[1]*

(iv)   new curve reaches same height as original curve;
new curve less steep than original curve;
volume of gas produced is the same because the same amount of acid is used;
reaction is slower because concentration is decreased;   *[4]*

(b)   (i)   (from experiments 1 and 2 at constant $[H_2]$), [NO] doubles, rate quadruples;
hence, second order with respect to NO;
(from experiments 2 and 3 at constant [NO]), $[H_2]$ doubles, rate doubles;
first order with respect to H_2;   *[4]*
Allow alternative mathematical deductions also.
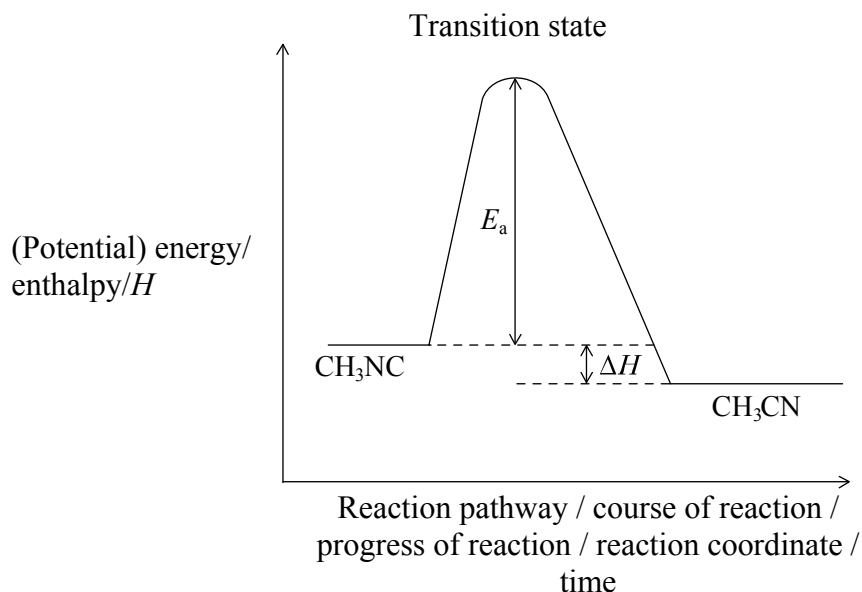
(ii)   rate $= k\,[NO]^2\,[H_2]$;   *[1]*

(iii) $k\left(= (10.00 \times 10^{-5})/(10.00 \times 10^{-3})^2(4.00 \times 10^{-3})\right) = 2.50 \times 10^2$;
Do not penalize if Experiments 1 or 2 are used to determine k.
$mol^{-2}\,dm^6\,s^{-1}$;   *[2]*

(c)   (i)   step 1 / equation showing step 1;   *[1]*

(ii)   O (atom) / oxygen atom;   *[1]*
Do not allow oxygen or O_2.

(d)　(i)　(minimum) energy needed for a reaction to occur / difference in energy between the reactants and transition state;　*[1]*

　　(ii)

Transition state

(Potential) energy/ enthalpy/H

E_a

CH_3NC　　　ΔH

CH_3CN

Reaction pathway / course of reaction / progress of reaction / reaction coordinate / time

correct position of activation energy;
correct position of ΔH **and** $H(CH_3NC)$/reactant line above $H(CH_3CN)$/ product line;
Accept ΔE instead of ΔH on diagram if y-axis is labelled as energy.
Do not penalize if CH₃NC and CH₃CN are not labelled on diagram.

correct position of transition state;　*[3]*
Allow [2 max] if axes are not labelled on diagram.

　　(iii)　as temperature/T increases rate constant/k increases (exponentially);　*[1]*

　　(iv)　from graph gradient $m = -\dfrac{E_a}{R}$;

measurement of gradient from chosen points on graph;
Units of m are K. Do not penalize if not given, but do not award mark for incorrect units.
Value of m is based on any two suitable points well separated on the plot.

correct answer for E_a;
correct units corresponding to answer;　*[4]*
Note: *A typical answer for $E_a = 1.6 \times 10^2 kJ$ / kJ mol^{-1}.*

8. (a) (i) energy required to break (1 mol of) a bond in a <u>gaseous</u> molecule/state;
Accept energy released when (1 mol of) a bond is formed in a gaseous molecule/state / enthalpy change when (1 mol of) bonds are made or broken in the gaseous molecule/state.

average values obtained from a number of <u>similar</u> bonds/compounds / *OWTTE*;   *[2]*

(ii) *Bonds broken*
(1)(C–C) + (1)(O–H) + (5)(C–H) + (1)(C–O) + (3)(O=O)
= (1)(347) + (1)(464) + (5)(413) + (1)(358) + (3)(498) = 4728 (kJ);
Bonds formed
(2×2) (C=O) + (3×2) (O–H)
= (4)(746) + (6)(464) = 5768 (kJ);
$\Delta H = 4728 - 5768 = -1040$ kJ mol^{-1} / -1040 kJ;   *[3]*
Units needed for last mark.
Award [3] for final correct answer.
Award [2] for +1040 kJ.

(iii) $M_r(C_2H_5OH) = 46.08 / 46.1$ **and** $M_r(C_8H_{18}) = 114.26 / 114.3$;
1 g ethanol produces 22.57 kJ **and** 1 g octane produces 47.88 kJ;   *[2]*
Accept values ranges of 22.5–23 and 47.8–48 kJ respectively.
No penalty for use of $M_r = 46$ and $M_r = 114$.

(iv) **A**: CH_3CHO;

B: CH_3COOH/CH_3CO_2H;

Accept either full or condensed structural formulas but not the names or molecular formulas.

A: distillation;
B: reflux;   *[4]*

(v) (concentrated) H_3PO_4/(concentrated) phosphoric acid / H_2SO_4/sulfuric acid;

dyes / drugs / cosmetics / solvent / (used to make) esters / (used in) esterification / disinfectant;   *[2]*

(b) (i) $CH_3CH_2OH \xrightarrow[H^+]{K_2Cr_2O_7} CH_3COOH \xrightarrow[H_2SO_4]{CH_3CH_2OH} CH_3CO_2CH_2CH_3 + H_2O$

Structural formulas of reactants and products
CH_3CH_2OH **and** CH_3COOH/CH_3CO_2H **and** $CH_3CO_2CH_2CH_3$ (+ H_2O);

Conditions/reagents used
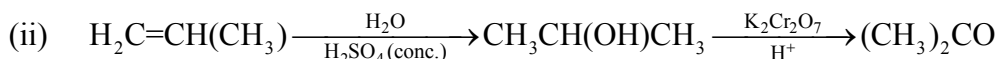reflux with named suitable acidified oxidising agent **and** then heat with alcohol and sulfuric acid;   *[2]*
Suitable oxidising agents are potassium dichromate/$K_2Cr_2O_7$ / sodium dichromate/$Na_2Cr_2O_7$ / dichromate/$Cr_2O_7^{2-}$ / potassium manganate(VII)/potassium permanganate/$KMnO_4$ / permanganate/manganate (VII)/MnO_4^-.
Accept H^+/H_2SO_4 instead of sulfuric acid and acidified.
Award [1] for structural formulas of reactants and products and [1] for the correct conditions/reagents used.

(ii) $H_2C{=}CH(CH_3) \xrightarrow[H_2SO_4\,(conc.)]{H_2O} CH_3CH(OH)CH_3 \xrightarrow[H^+]{K_2Cr_2O_7} (CH_3)_2CO$

Structural formulas of reactants and products
$H_2C{=}CH(CH_3)$ **and** $CH_3CH(OH)CH_3$ **and** $(CH_3)_2CO$;

Conditions/reagents used
water/H_2O and sulfuric acid/H_2SO_4 / dilute acid medium **and** heat/reflux with suitable acidified oxidising agent;   *[2]*
Suitable oxidising agents are potassium dichromate/$K_2Cr_2O_7$ / sodium dichromate/$Na_2Cr_2O_7$ / dichromate/$Cr_2O_7^{2-}$ / potassium manganate(VII)/potassium permanganate/$KMnO_4$ / permanganate/manganate (VII)/MnO_4^-.
Accept H^+/H_2SO_4 instead of acidified.
Note: If primary alcohol is given as product of first step, and everything else correct, award [1 max].
Accept either full or condensed structural formulas throughout (b).

(c)
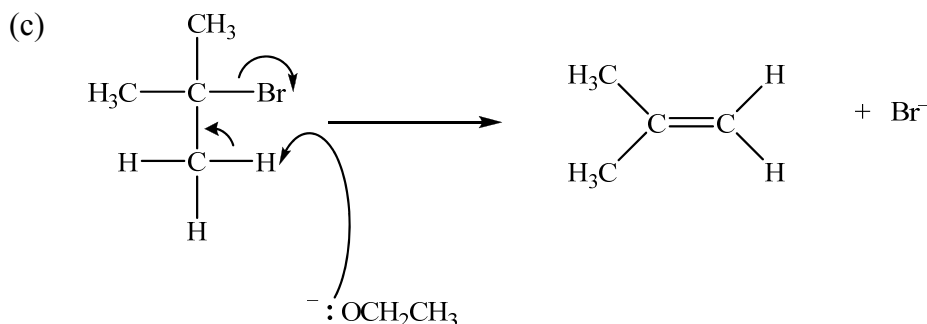
curly arrow going from O of $^-OCH_2CH_3$ attacking hydrogen;

Allow the curly arrow to originate from either the lone pair or O of $^-OCH_2CH_3$ but not from H of $^-OCH_2CH_3$.

Do not award first mark if curly arrow originates from O of $NaOCH_2CH_3$.

curly arrow going from the C–H bond on the β carbon to the bond joining the α carbon to the β carbon **and** curly arrow showing Br acting as leaving group;
formation of $(CH_3)_2C=CH_2$ **and** Br^-;   *[3]*

Allow formation of NaBr for third marking point, if $NaOCH_2CH_3$ was used (incorrectly) in the mechanism. Use of $NaOCH_2CH_3$ with curly arrow originating on O of $NaOCH_2CH_3$ is penalized already in the first marking point.

Accept alternative E1 type mechanism
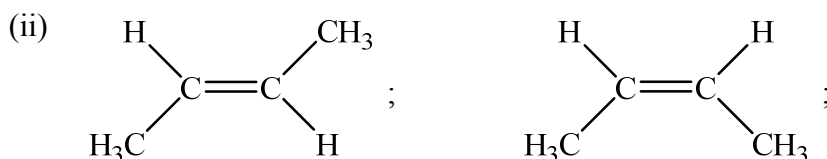curly arrow showing Br acting as leaving group to form carbocation;
curly arrow going from O of $^-OCH_2CH_3$ attacking hydrogen;
formation of $(CH_3)_2C=CH_2$ **and** Br^-;
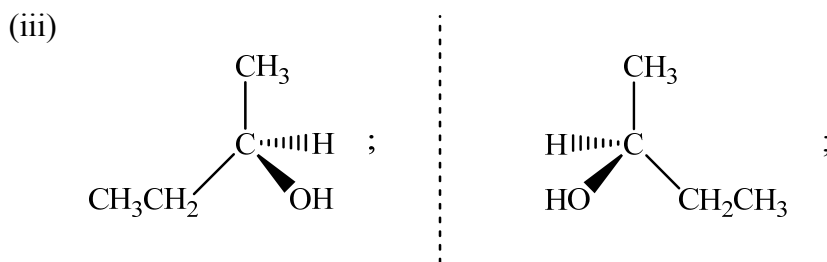*No marks awarded if a substitution mechanism is given.*

(d) (i) compounds with the same (molecular formula and) structural formula but different arrangements of atoms in space / *OWTTE*;   *[1]*

(ii)

Allow [1 max] if structures are correct but arrangement of groups in space does not clearly show the cis/ trans isomerism.

(iii)

Allow [1 max] if the structures are correct but it is not clear that they are mirror images.