International Baccalaureate®
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MARKSCHEME

November 2013

CHEMISTRY

Higher Level

Paper 2

16 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 x 25 marks]**. Maximum total = **[90 marks]**.

1.   A markscheme often has more marking points than the total allows. This is intentional.

2.   Each marking point has a separate line and the end is shown 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 *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. When marking, indicate this by adding **ECF** (error carried forward) on the script.

10. Do **not** penalize candidates for errors in units or significant figures, **unless** it is specifically referred to in the markscheme.

11. If a question specifically asks for the name of a substance, do not award a mark for a correct formula unless directed otherwise in the markscheme. Similarly if the formula is specifically asked for, unless directed otherwise in the markscheme, do not award a mark for a correct name.

12. 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.

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

SECTION A

1. (a) KI/I⁻/potassium iodide/iodide (ion) (rapidly) reformed (in second stage of reaction);   *[1]*

    (b) amount (in mol) of H_2O_2/hydrogen peroxide >> amount (in mol) $Na_2S_2O_3$/$S_2O_3^{2-}$ /sodium thiosulfate/ thiosulfate (ion);
         Accept amount (in mol) of H_2O_2/hydrogen peroxide >> amount (in mol) KI/I⁻ /potassium iodide/iodide (ion).
         Accept "H_2O_2/hydrogen peroxide is in (large) excess/high concentration".

         (at end of reaction) $[H_2O_2]$ is only slightly decreased/virtually unchanged;   *[2]*

    (c) all $Na_2S_2O_3$/sodium thiosulfate/$S_2O_3^{2-}$/thiosulfate consumed/used up;
         Accept "iodine no longer converted to iodide".

         (free) iodine is formed / iodine reacts with starch / forms iodine-starch complex;   *[2]*

    (d) (i) $(5 \times 0.1) = (\pm)0.5\,(\text{cm}^3)$;   *[1]*

         (ii) $(\pm)0.7(\%)$;   *[1]*
               Comprises both mass of KI = ±0.5% and volume of KI = ±0.2%.

         (iii) $0.5 + 0.7 = (\pm)1.2\,\%$;   *[1]*
               Sum of (i) and (ii) (percentage uncertainty of total volume = absolute uncertainty as 100 cm³).

    (e) total volume $= 0.100\,(\text{dm}^3)/100\,(\text{cm}^3)$;

         (change in concentration $= \dfrac{1.00 \times 10^{-4}}{0.100} =)1.00 \times 10^{-3}\,(\text{mol dm}^{-3})$;

         $\left(\text{rate} = \dfrac{1.00 \times 10^{-3}}{45} = \right)2.2 \times 10^{-5}$;

         Award [3] for the correct final answer.

         $\text{mol dm}^{-3}\,\text{s}^{-1}$;   *[4]*

(f)　(i)　*x-axis:* $\dfrac{1}{\text{Temperature}}\ /\ \dfrac{1}{T}\ /\text{T}^{-1}$;

　　　　Ignore units.

　　　　y-axis: ln rate/log$_e$ rate / ln rate constant/log$_e$ rate constant / ln k/log$_e k$;　　　　*[2]*

　　(ii)　gradient $=\dfrac{-E_a}{R}$;

　　　　gradient $=\dfrac{-4.00}{(3.31\times10^{-3}-2.83\times10^{-3})}=-8333$ $/\ =\dfrac{-4.80}{(3.41\times10^{-3}-2.83\times10^{-3})}=-8276$;

　　　　$E_a=\left(\dfrac{8.31\times8333}{1000}\right)=69.3\,(\text{kJ mol}^{-1})\ /\ =\left(\dfrac{8.31\times8276}{1000}\right)=68.8\,(\text{kJ mol}^{-1})$;　　*[3]*

　　　　Award [3] for correct final answer.
　　　　Accept values from 65.0 to 73.0 kJ mol^{-1}.
　　　　Deduct [1] for final answer in J mol^{-1}.
　　　　Deduct [1] for final answer not to 3 significant figures.

(g)　acting as a catalyst / black powder reacts with thiosulfate ions / solid dissolves to give blue-black solution;
Accept any other valid suggestion which will make colour change more rapid.
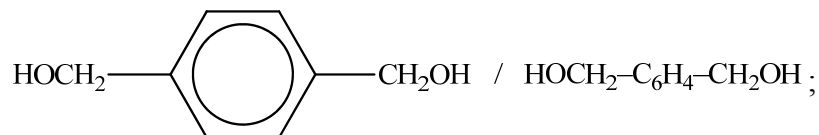
For catalyst: amount/mass of black powder remains constant / no new/different products formed / activation energy decreased;
For other suggestions: any appropriate way to test the hypothesis;　　　　*[2 max]*
Award [1] for valid hypothesis, [1] for appropriate method of testing the stated hypothesis.

2.   (a)

$HOCH_2$—⬡—CH_2OH / $HOCH_2$–C_6H_4–CH_2OH ;

[1]

Accept left hand end written as CH$_2$(OH)–.

(b)   *Reagents:* acidified/H^+ dichromate ion/$Cr_2O_7^{2-}$/potassium dichromate/$K_2Cr_2O_7$/ sodium dichromate/$Na_2Cr_2O_7$;
Accept acidified/H^+ permanganate ion/MnO_4^-/potassium permanganate/KMnO$_4$.

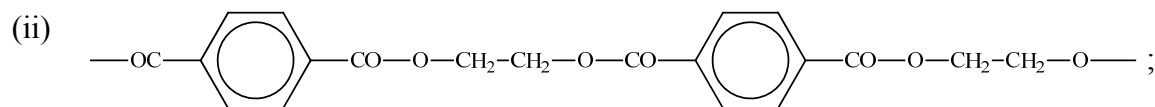*Conditions:* reflux;   *[2]*
Accept "heat" (as the intermediate aldehyde will not be volatile enough to vaporize significantly) unless distillation mentioned.

(c)   (i)   condensation;   *[1]*

(ii)

—OC—⬡—CO—O—CH_2–CH_2—O—CO—⬡—CO—O—CH_2–CH_2—O— ;

[1]

Extended bonds and two molecules of both monomers must be included.
Monomers can occur in the opposite order to that shown (glycerol part on left).
Accept repeating units starting and ending at any point in the chain.

3. (a) (i) Ca^{2+} **and** NO_3^-;
electrostatic (attraction);   *[2]*
Do not accept ionic.

(ii) nitrogen/N **and** oxygen/O;   *[1]*
Do not accept nitrate/NO_3^-.
Accept atoms in nitrate/NO_3^-.

(b) pi/π-electrons shared by more than two atoms/nuclei / a pi/π-bond/overlapping p-orbitals that extends over more than two atoms/nuclei;
all (N–O) bonds equal length/strength/bond-order / charge on all oxygen/O atoms equal / increases stability/lowers PE (of the ion);   *[2]*
Accept a diagram that clearly shows one or both points.

(c) (i) produced by high temperature combustion;   *[1]*
Accept combustion/jet/car engines / car exhaust/emissions / lightning / action of bacteria/microorganisms.
Do not accept combustion/burning, cars, planes, jets, factories, power plants etc.

(ii) nitric acid/HNO_3 / nitrous acid/nitric(III) acid/HNO_2;   *[1]*
Accept "form acidic solutions / acid rain".

(iii) acid deposition/rain / respiratory problems / corrosion problems / decomposition of ozone layer / photochemical smog / acidification/pollution of lakes / damage to plants/ trees;   *[1]*
Accept "acid rain" in either part (ii) or part (iii) but not both.
Do not accept air pollution.

4. (a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$ / $[Ar]3d^4$;   *[1]*

(b) ligand;
dative/coordinate (covalent);   *[2]*
Do not accept "covalent".

(c) variable oxidation state/number;
catalytic properties;   *[2]*

(d) d sublevel/orbitals split (into two levels by ligands);
electrons absorb light/photons and move to the higher energy orbital;
frequency of light/photons absorbed in the visible region;   *[3]*

SECTION B

5. (a) $\underline{(1)}\,N(NO_2)_3\,(g) + \underline{2}\,CH_3OH\,(l) \rightarrow \underline{2}\,N_2\,(g) + \underline{2}\,CO_2\,(g) + \underline{4}\,H_2O\,(l)$; *[1]*

(b) products from the reaction are non-toxic / normal components of the atmosphere / nitrogen is a product rather than oxides of nitrogen; *[1]*
Accept "no chlorine produced".
*Do **not** accept "non-polluting".*

(c) *bonds broken:* $(6 \times 305) + (3 \times 158) = 1830 + 474 = 2304\,(kJ\,mol^{-1})$;
bonds made: $(2 \times 945) + (3 \times 498) = 1890 + 1494 = 3384\,(kJ\,mol^{-1})$;
enthalpy change: $2304 - 3384 = -1080\,(kJ\,mol^{-1})$; *[3]*
Award [3] for correct final answer.
Award [2 max] for +1080 (kJ mol^{-1}).

Accept –234 kJ mol^{-1} which arise from students assuming that 305 kJ mol^{-1} refers to the strength of a single N–O bond. Students may then take N=O from the data book value (587 kJ mol^{-1}).
bonds broken: $(3 \times 305) + (3 \times 587) + (3 \times 158) = 915 + 1761 + 474 = 3150\,(kJ\,mol^{-1})$
bonds made: $(2 \times 945) + (3 \times 498) = 1890 + 1494 = 3384\,(kJ\,mol^{-1})$
enthalpy change: $3150 - 3384 = -234\,(kJ\,mol^{-1})$.

Award [2 max] for correct calculation of the enthalpy change of reaction for the equation in part (a), which gives –2160 (kJ mol^{-1}).
Award [1] if the final answer is not –2160 but the candidate has correctly calculated the bonds broken in trinitramide as 2304 (kJ mol^{-1}).

(d) increase in the number of moles of gas;
gases have a greater entropy/degree of randomness (than liquids or solids); *[2]*
Award [1 max] for answers stating that positive value indicates an increase in disorder/randomness.

(e) $\Delta G = \Delta H - T \times \Delta S$;
$= -1080 - 300 \times \dfrac{700}{1000}$;
$-1290\,(kJ\,mol^{-1})$; *[3]*
Award [3] for correct final answer.
Award [2 max] for incorrect conversions of units.
If no answer to part (c), using $\Delta H = -1000\,kJ\,mol^{-1}$, gives $-1020\,(kJ\,mol^{-1})$.

(f) no change in spontaneity / temp has no effect on spontaneity / spontaneous at all temperatures;
ΔG negative at all temperatures / exothermic/ΔH negative **and** involves an increase in entropy/ΔS positive; *[2]*

(g) (N–N bond in) trinitramide is longer/nitrogen (gas) is shorter / 0.145 nm in trinitramide versus 0.110 nm in nitrogen;
trinitramide has single (N–N) bond **and** nitrogen (gas) has triple bond; *[2]*

(h) $106° - 108°$;
       Accept $< 109°$.

       Any two for [2 max].
       4 (negative) charge centres/electron pairs/electron domains around central nitrogen;
       <u>central</u> nitrogen has a lone/non-bonding pair;
       lone/non-bonding pairs repel more than bonding pairs;
       molecule will be (trigonal/triangular) pyramidal;
       (negative) charge centres/electron pairs/electron domains will be tetrahedrally arranged/orientated/ have tetrahedral geometry;   **[3 max]**
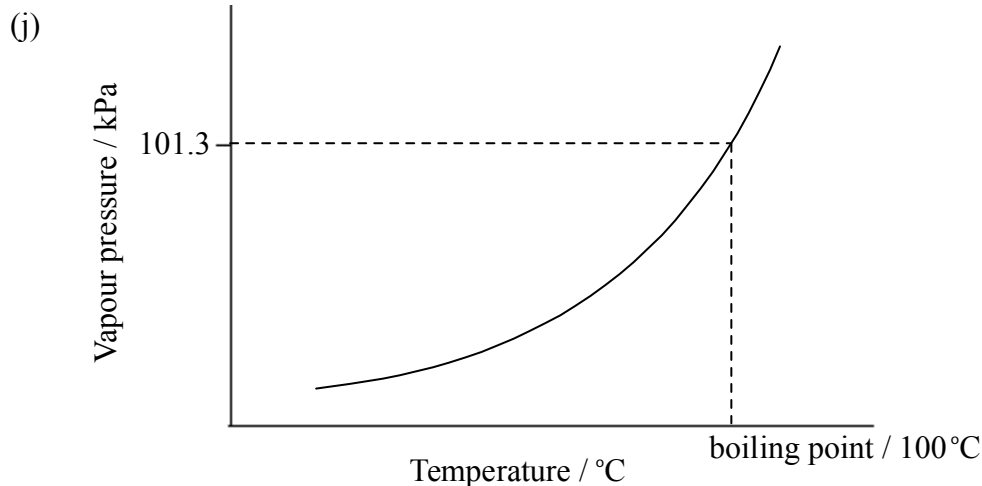   *Do not apply ECF.*

(i)   polar;
       net dipole moment present in molecule / unsymmetrical distribution of charge / polar bonds do not cancel out / centre of negatively charged oxygen atoms does not coincide with positively charged nitrogen atom;   **[2]**
       Marks may also be awarded for a suitably presented diagram showing net dipole moment.
       Do not accept "unsymmetrical molecule".
       Apply ECF from part (h).

(j)

       (smooth) upward sloping curve;
       *Do **not** award mark for straight line.*
       boiling point $= 100 °C$;   **[2]**

(k)   atm P reduced/lower atm P so vp = atm pressure occurs at a lower temperature;   **[1]**
       Mark can be gained by suitable lines on graph.
       *Do **not** award mark for "boiling point reduced".*

(l)   rate at which molecules escape into vapour equal to rate at which they return to liquid;
(at higher temperature) molecules have greater (kinetic) energy;
(at higher temperature) more/greater proportion of molecules have required escape energy/speed/velocity / more/greater proportion of molecules are able to evaporate/break free from surface;
greater pressure required for return rate to equal greater escape rate;   *[3 max]*
Award [1 max] for correct explanations in terms of applying Le Chatelier to an endothermic change.

6. (a) potential of the half-cell / reduction half-reaction under standard conditions measured relative to standard hydrogen electrode/SHE; **[1]**
Allow instead of standard conditions, solute concentration of 1 mol dm^{-3} or 1 bar/1 atm (pressure) for gases.

(b) (i)

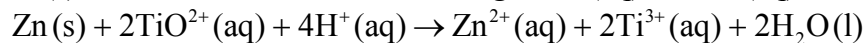| Initial oxidation number		Final oxidation number	Oxidized / reduced
IV/+4	**and**	III/+3;	reduced;

[2]

+ sign must be present. Do not award mark for incorrect notation 4, 4+, 3, 3+ etc.
Do not award M2 if inconsistent with M1.

(ii) increases / makes it stronger;
(more H$^+$ would) drive/shift equilibrium to the right/towards products (accepting more electrons); **[2]**

(c) *KI (aq) is added to a solution containing Ti^{3+}(aq) ions:*
no reaction;

Zn (s) is added to a solution containing TiO^{2+}(aq) and H$^+$(aq) ions:
$Zn(s) + 2TiO^{2+}(aq) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + 2Ti^{3+}(aq) + 2H_2O(l)$
correct reactants **and** products;
balanced equation; **[3]**
Ignore state symbols.

(d) (i) $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$;
Ignore state symbols.
Accept equilibrium arrow.

reduction; **[2]**
Do not apply ECF.

(ii) $(+0.77 - (-0.06)) = (+)0.83(V)$; **[1]**
Do not accept –0.83 V.

(iii) wire and salt bridge **both** have arrows from B to A; **[1]**
Accept arrows above or below each provided it is obvious which they refer to.
Apply ECF from part (i).

(e) (i)

	Na₂O		**SiO₂**		**SO₂**	
Bonding type	ionic	**and**	(giant/network) covalent	**and**	(molecular) covalent	;
State	solid	**and**	solid	**and**	gas	;
Effect on pH	increase *Accept basic/ alkaline.*	**and**	no effect *Accept small decrease.* *Accept neutral.*	**and**	decrease *Accept acidic.*	;

[3]

For any parts (properties) where mark not awarded, award [1] for every three correct responses.

(ii) (combustion of) coal / diesel;   **[1]**
Accept "burning of fossil fuels", "industrial processes" or "combustion/car engines".
Do not accept "Contact process".

(iii) $^-|\overline{\underline{O}}\!—\!\overline{\underline{O}}|^{\,-}$
e-pairs correct;
charges in correct positions;   **[2]**
Accept lines, or pairs of dots or crosses, for electron pairs.

Accept $\left[|\overline{\underline{O}}\!—\!\overline{\underline{O}}|\right]^{2-}$.

(f) (i) C is sp hybridized **and** Si is sp³ hybridized;
C–O bond in CO_2 has one σ-bond and one π-bond;
Si–O bond in SiO_2 has one σ-bond only;   **[3]**
Award [1 max] for last two marking points for "C–O double bond and Si–O single bond".

(ii) silicon-oxygen bonds will have a tetrahedral distribution;
xenon-oxygen bonds will have a square planar distribution;
xenon dioxide has **two** non-bonding/lone pairs of electrons;   **[3]**
Award any of the above marks if clearly indicated in suitable diagrams.

(g) $SiCl_4(l) + 3H_2O(l) \rightarrow SiO(OH)_2(s) + 4HCl(aq)$;   **[1]**
Accept balanced equations (such as $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$)
with SiO₂ and Si(OH)₄ as products.
Ignore state symbols.

7. (a) arsenic/As; *[1]*
Accept bismuth/Bi.

(b) (i) SbF_5 accepts an electron pair (from F^-) / SbF_6^- donates an electron pair (to H_2F^+);
SbF_5 acts as a Lewis acid / SbF_6^- acts as a Lewis base; *[2]*

(ii) one HF donates a H^+/proton and the other accepts a H^+/proton;
HF acts as both a Brønsted–Lowry acid **and** a Brønsted–Lowry base; *[2]*
Award [1 max] for correct description of HF acting as a Brønsted–Lowry acid or base.

(c) (i) H–F bond stronger than H–Cl bond / H–Cl bond weaker than H–F bond; *[1]*

(ii) H–F can hydrogen bond to water **and** H–Cl cannot; *[1]*

(d) (i) not a good choice / poor choice;
requires same volume of base / the amount/volume to react/for neutralization does not depend on the acid strength; *[2]*

(ii) phenolphthalein / phenol red;
pH at equivalence point 7 or above; *[2]*
Accept pH range for colour change/end-point corresponds to rapid change in pH.

(iii) sulfuric acid is diprotic/dibasic/liberates two protons/H^+; *[1]*
Accept "reacts with 2 moles of alkali/base".

(iv) weak;
strong $0.100 \, mol \, dm^{-3}$ acid has a pH of 1/lower than that observed; *[2]*
Accept "pH value of 3.7 means that it produces only $10^{-3.7}/2.0 \times 10^{-4}$ [H^+] in water".

(e) (i) when volume of alkali is half equivalence volume/volume required for neutralization;
pK_a is equal to the pH; *[2]*

(ii) $[H^+] = 10^{-3.7} = 2.00 \times 10^{-4} \, (mol \, dm^{-3})$;
$$K_a = \frac{[H^+][Q^-]}{[HQ]} = \frac{(2.00 \times 10^{-4})^2}{0.100};$$
$= 3.98 \times 10^{-7}$;
$pK_a = 6.4$; *[4]*
Award [4] for correct final answer.

(f)   amount NaQ = amount $NaOH = 0.001\,(mol)$;
       excess $HQ = 0.004 - 0.001 = 0.003\,(mol)$;

$$[Q^-] = 0.001 \times \frac{1000}{50} = 0.02\,(mol\,dm^{-3})\ \textbf{and}\ [HQ] = 0.003 \times \frac{1000}{50} = 0.06\,(mol\,dm^{-3});$$

$$[H^+] = K_a\frac{[HQ]}{[Q^-]} = 1.8 \times 10^{-5}\frac{0.06}{0.02} = 5.4 \times 10^{-5}\,(mol\,dm^{-3});$$

$$pH = -\log(5.4 \times 10^{-5}) = 4.268;$$ **[5]**

Accept other methods of reaching the answer.
*Award **[3 max]** if final answer given without working.*

8.   *Penalise missing hydrogens once only in Q8.*

(a)   water/H_2O;
Accept steam.

(concentrated) sulfuric acid/H_2SO_4 (catalyst);   *[2]*
Accept phosphoric acid/H_3PO_4.
Award [2] for HBr and NaOH (two-stage process via the halogenoalkane).

(b)   not react;
tertiary alcohol (not easily oxidized);   *[2]*

(c)   (i)   rotates the plane (of polarization) of plane polarized light;   *[1]*
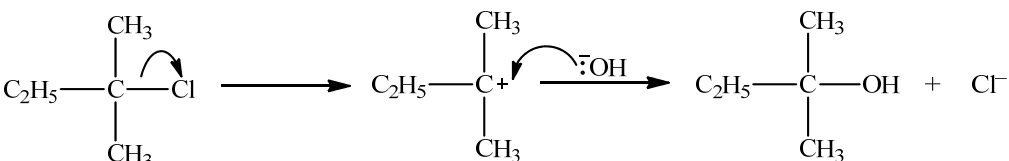*Accept answers in which **one** of the "plane"s is missing.*

(ii)   two isomers that are enantiomers/chiral/non-superimposable mirror images;   *[1]*
*Accept "contains an asymmetric/chiral carbon" or "contains a carbon
bonded to four <u>different</u> groups".*

(iii)   polarizes light / polarized light source;
light passed through sample;
analyser / second polarizer detects whether plane of polarization rotated;   *[3]*

(iv)

$(CH_3)_2CH\text{—}CH(OH)\text{—}CH_3$ /

H₃C—C—C—CH₃ with CH₃ and H on top carbon positions, H and OH on bottom ;   *[1]*

Accept C_3H_7–CH(OH)–CH_3, but not CH_3–CH_2–CH_2–CH(OH)–CH_3.

(d)   2-methylbutan-2-ol has hydroxyl/OH group;
Do not accept "hydroxide group".
Allow 2-methylbutan-2-ol is an alcohol.

2-methylbutan-2-ol can form <u>H-bonds</u> (to water) / 2-methylbut-2-ene cannot form
<u>H-bonds</u> (to water);   *[2]*

(e)   (i)

curly arrow showing Cl^- leaving;
representation of tertiary carbocation;
curly arrow going from lone pair/negative charge on O in HO^- to C^+;
Do not allow arrow originating on H in HO^-.

formation of organic product $CH_3CH_2C(CH_3)_2OH$ **and** Cl^-/NaCl
(somewhere in mechanism);   *[4]*
Award [3 max] if a candidate gives a fully correct S_N2 mechanism.

(ii) rate $= k \times$ [2-chloro-2-methylbutane]/[$CH_3CH_2C(CH_3)_2Cl$]/[halogenoalkane]
/[R–Cl];
s^{-1};   *[2]*

(iii) hydroxide ion/OH^- is a better nucleophile than water / hydroxide ion/OH^-
has negative charge;
undergo S_N2 hydrolysis / RDS depends on attack of OH^-/hydroxide ion
(nucleophile);   *[1 max]*
Accept other suggestions that are chemically valid.

(f) (i) chlorine can be ^{35}Cl/Cl–35 or ^{37}Cl/Cl–37;   *[1]*
Accept "chlorine can exist as two isotopes".
Answer must refer to chlorine rather than isotopes in general.

(ii) same rate as (isotopes have) same chemical properties;   *[1]*
*Accept different rate if reference is made to molecules having different
speeds/collision rate.*

(g) (i)

$$H_3C-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C\equiv N \quad ;$$ *[1]*

Do not accept condensed formulas such as CH₃CH₂C(CH₃)₂CN.
Accept the cyanide group as –CN without showing the triple bond.

(ii) *Formation of Y:*
cyanide ion/CN^- / potassium cyanide/KCN;
Accept hydrogen cyanide/HCN.

Conversion of Y into Z:
hydrogen/H_2;
nickel/Ni / platinum/Pt / palladium/Pd (catalyst);   *[3]*