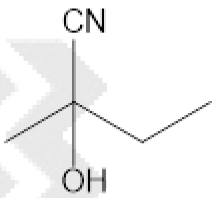
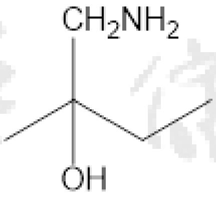
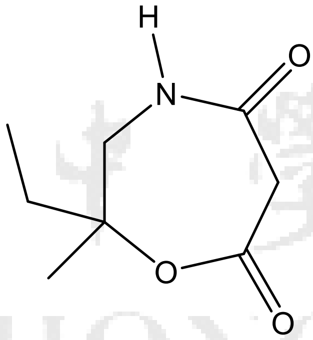
HWA CHONG INSTITUTION
2019 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS

Paper 2

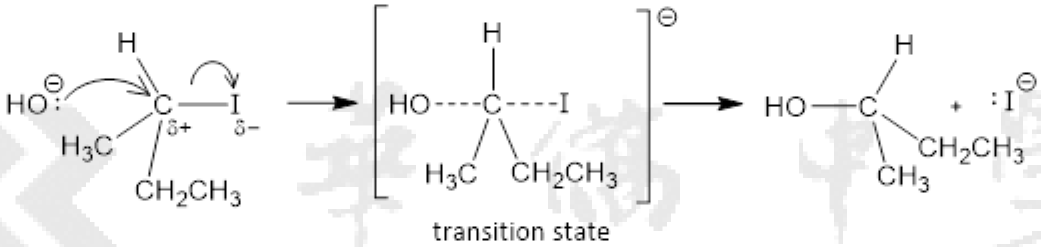
1 (a) (i) HCN with trace amount of KCN (or NaOH(aq)), cold **[1]**

(ii)

 **A**	 **B**	 **C**

[1] for each correct structure

(b) (i) Mechanism: **Bimolecular** Nucleophilic Substitution (**S$_N$2**) **[1]**

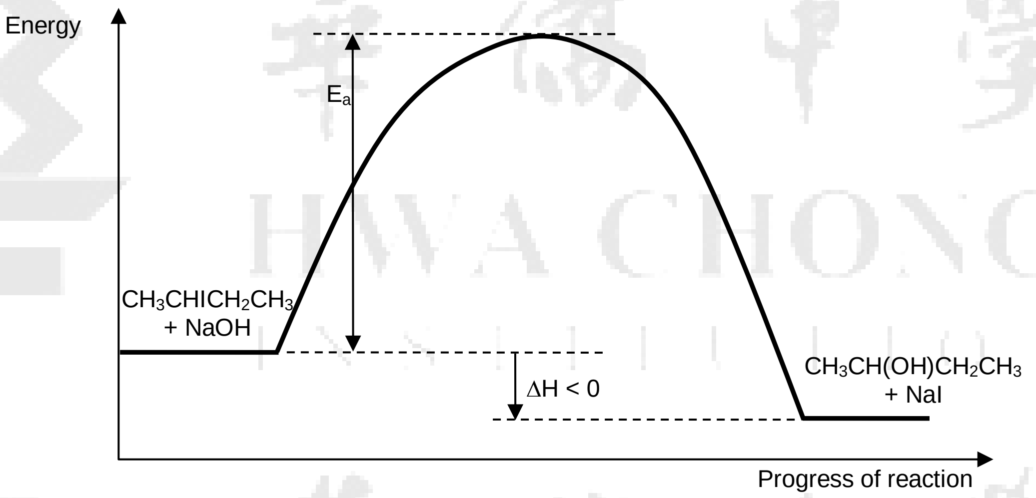


[1] for:
- ✓ OH$^-$ is the nucleophile that attacks C$^{\delta+}$ of C–I (attack from the side that's opposite to the I)
- ✓ partial charges: C$^{\delta+}$–C/$^{\delta-}$
- ✓ curly arrow going from lone pair of OH$^-$ to C$^{\delta+}$ of C–I
- ✓ curly arrow going from C–I bond, to I

[1] for:
- ✓ transition state negatively charged (need not label "transition state")
- ✓ I$^-$ is produced at the end of the reaction
- ✓ no slow or fast step

−½m for every mistake

(ii)



[1] shape of graph
[1] labelling graph
✓ label E_a
✓ label ΔH
✓ label "reactants" and "products"
✓ label axes
−½m for every mistake

(c) The halogens Cl_2, Br_2 and I_2 exist as simple non-polar covalent molecules. From Cl_2 to Br_2 to I_2, the <u>size of the electron cloud</u> and hence, the polarisability of the halogen molecule <u>increases</u> [1]. More energy is needed to overcome the <u>stronger dispersion forces</u> between the molecules. Hence, the <u>volatility of the halogens decreases</u> [1] from chlorine to iodine.

(d) **(i)** $2HX \rightarrow H_2 + X_2$ **[1]**

(ii) Down the group, <u>as atomic radius increases</u> from C*l* to I, the <u>bond length of the H–X bond increases</u> / <u>bond strength decreases</u> **[1].**
Hence, <u>less energy is needed to break the H–X bond</u>. Thus, the thermal stability of the hydrogen halides <u>decreases</u> down the group **[1].**

Remarks: can also justify by quoting the bond energy data, H–Cl = +431, H–Br = +366, H–I = +299 kJ mol^{-1}*. Weaker H–X bond needs less energy to break during thermal decomposition*

(e) From *Data Booklet*,

	$E^\ominus$/V
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

Bromine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$, which will be further oxidised to SO_2 and subsequently SO_4^{2-}.
$E^\ominus_{cell} = +1.07 - (+0.09) = +0.98$ V > 0 (spontaneous)
$E^\ominus_{cell} = +1.07 - (+0.51) = +0.56$ V > 0 (spontaneous)
$E^\ominus_{cell} = +1.07 - (+0.17) = +0.90$ V > 0 (spontaneous)

Iodine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$ but there is no further oxidation of $S_4O_6^{2-}$ to SO_2.
$E^\ominus_{cell} = +0.54 - (+0.09) = +0.45$ V > 0 (spontaneous)
$E^\ominus_{cell} = +0.54 - (+0.51) = +0.03$ V > 0 (spontaneous but extent of reaction is too small)

[1] $E^{\ominus}_{cell}$ for reaction with bromine or showing that the $E^{\ominus}_{(Br2/Br-)}$ > all the 3 $E^{\ominus}$
[1] $E^{\ominus}_{cell}$ for reaction with iodine or showing that $E^{\ominus}_{(I2/I-)}$ > +0.09 V but only slightly larger than +0.51 V
[½] spontaneous since $E^{\ominus}_{cell} > 0$
[½] spontaneous but extent of reaction too small

2 (a) (i) $K_a = [H^+][A^–] / [HA]$
$K_a = (10^{–5.5})(1) / 4$
$K_a = 7.91 \times 10^{–7}$ mol dm$^{–3}$
pK_a = – lg(7.91 × $10^{–7}$) = 6.10 **[1]**

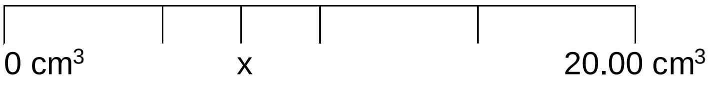
OR

pH = pKa + lg[$A^–$]/[HA]
5.5 = pKa + lg(1/4)
pK_a = 6.10 **[1]**

(ii) 1:1 **[1]**

(iii) Let x be the volume of NaOH required to achieve maximum buffer capacity

For visualization:



Since the ratio of the [$A^–$]:[HA] in the buffer is 1:4, a titre value of 20.00 cm^3 must correspond to 4 units. Hence, maximum buffer capacity must occur when there are 2.5 units of [$A^–$] and 2.5 units of [HA]. **[1]**

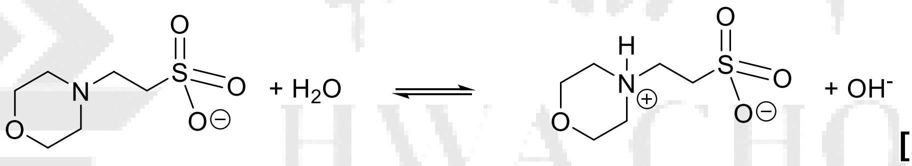
Therefore, the volume of NaOH required, x, corresponds to 1.5 units.

Volume of NaOH required = 20.00/4 × 1.5 = 7.5 cm^3 **[1]**

OR

Let x be the volume of NaOH required to achieve maximum buffer capacity
Since the ratio of the [$A^–$]/[HA] in the buffer is 1:4,
(20 – 2x) / (20) = 1/4 **[1]**
2(10 – x) = 20/4
x = 7.5 cm^3 **[1]**

(iv)



[1]

(v) Given that the **region of rapid pH change will be at about pH 9.4,** I would use an indicator with a **working range that coincides with that pH range [1]**, which would be **cresolphthalein**. **[1]**

(b) (i) Initially, the graph is a straight line/increases steadily. This is because the reaction is **first order wrt to [sugar]/ rate is directly proportional to [sugar]/ more enzyme-substrate complex can be formed by increasing [sugar]. [1]** Thus, the rate of reaction increase.

The graph plateaus/becomes horizontal/becomes zero order wrt [sugar] **because the enzyme is now saturated/all active sites are occupied [1],** thus, the rate of reaction cannot be increased by increasing [sugar].

(ii)

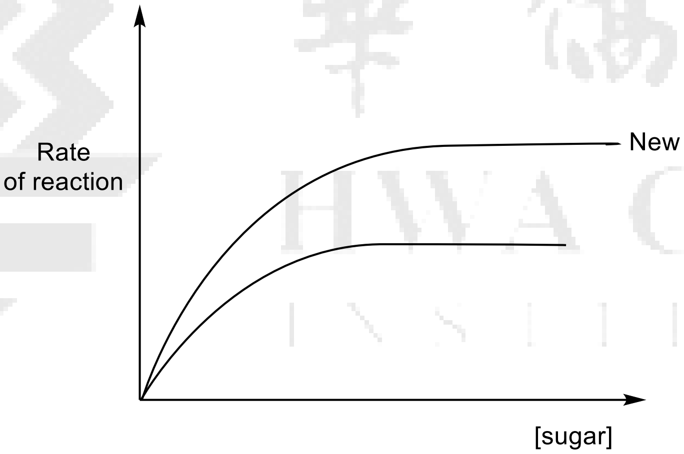


Fig. 2.1

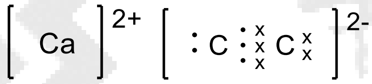
[1]
Key points

- Initial rate increases more quickly
- Plateau occurs at a higher concentration of sugar
- Plateau occurs at a higher rate

(iii) Order wrt to [sugar]:
Comparing experiment 1 and 2,
When [sugar] is doubled from 0.20 mol dm^{-3} to 0.40 mol dm^{-3}, the relative rate of reaction doubled.
Thus, [sugar] is directly proportional to the rate of reaction, and is first order.
[1] for explanation

Order wrt to [zymase]:
Comparing experiment 1 and 3,
When [sugar] is halved from 0.20 mol dm^{-3} to 0.10 mol dm^{-3}, the relative rate of reaction is expected to halve.
When [zymase] is doubled from 0.010 mol dm^{-3} to 0.020 mol dm^{-3}, the relative rate is doubled from ½ to 1
Thus, [zymase] is directly proportional to the rate of reaction, and is first order.
[1] for explanation
[½] x 2 for each correctly identified order

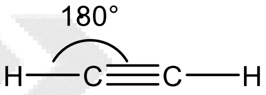
3 (a) (i)



Anion:
additional electrons of opposite symbol were accepted
additional electrons of third symbol were accepted
dative bonds were rejected
[½] for each ion

(ii) $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + C_2H_2(g)$ [1]
[1] balanced equation with correct state symbols

(b) (i)



[1] for correct bond angle (only one needs to be labelled on the diagram itself), and correct Lewis structure which must show linear shape.

Type of hybridisation: sp **[1]**

(ii) Two characteristics of ethyne, and explanation:

1. Ethyne has a small molecular size, which means the volume of the particles of ethyne is small compared to the volume of the container, and so can be considered negligible just as for ideal gases; and
2. Ethyne is a non-polar molecule, so it has relatively weak intermolecular dispersion forces, which could therefore be considered negligible, just as for ideal gases.

[1] x 2 for each characteristic

(c) (i) Total initial pressure $= x + y$
$= 760$ mm Hg **[1]**

(ii) Since p mm Hg is the change in partial pressure of ethyne during the combustion:

	$C_2H_2(g)$	+	$5/2\ O_2(g)$	→	$2CO_2(g)$	+	$H_2O(l)$
Initial partial pressure / mm Hg	x		y		0		-
Change / mm Hg	$-p$		$-5/2p$		$+2p$		-
Final partial pressure / mm Hg	$x - p$		$y - 5/2p$		$2p$		-

Total pressure after combustion $= (x - p) + (y - \frac{5}{2}p) + 2p$
$= [(x + y) - \frac{3}{2}p]$ mm Hg

[1] Correct expression of total pressure after combustion in terms of *x*, *y* and *p*

(iii) Total initial pressure = $(x + y)$ mm Hg
Total pressure after combustion = $(x + y) - \frac{3}{2}p$ mm Hg

Since a reaction occurs, p must be > 0

$$\text{so } (x + y) - \tfrac{3}{2}p < (x + y),$$
i.e. (final pressure) < (initial pressure)

and ∴ the term "$-\frac{3}{2}p$" represents a fall in pressure from the original $(x + y)$ mm Hg (shown)

[1] Convincing argument in which there is a comparison of initial and final pressures in terms of *x*, *y* and *p*.

(iv) From **(ii)** and **(iii)**, we know that the fall in pressure inside the flask corresponds to difference in height (atmospheric pressure remains unchanged):

$\frac{3}{2}p = 65$
$p = 65 \div (3/2)$
$\quad = \underline{\underline{43.3}}$ (to 1 d.p.) (in mm Hg)

[1] Answer must be to 1 d.p. to get the full credit.

(v) **(I)** Since final partial pressure of CO_2 is $2p$
∴ $P_{CO2} = 2p = \underline{86.7 \text{ mm Hg}}$ **[1]** (to 3 s.f.)

(II) If all oxygen was used up, then $y - 5/2p = 0$
∴ $y = 5/2p$
$y = 5/2\ (65 \div 3/2) = 108.3$ mm Hg (1 d.p.)
$= \underline{\underline{108}}$ mm Hg (3 s.f.) **[½]**

And $x = 760 - 108.3 = 651.7$ mm Hg (1 d.p.)
$= \underline{\underline{652}}$ mm Hg (3 s.f.) **[½]**

(d) **(i)** pV = nRT
From graph, $\eta_{H2} = \underline{1.06}$ mol (accepted 1.04 – 1.06)
[1] for correct reading of no. of moles of H_2 from graph

$P_{H2} = nRT/V = (1.06)(8.31)(1250 + 273) / (0.100)$
$= 134{,}155$ Pa
$= \underline{1.34 \times 10^5 \text{ Pa}}$
$= \underline{134 \text{ kPa}}$ (to 3 s.f.)
[1] for correct use of ideal gas equation, and answer

ALTERNATIVE:
From graph, $\eta_{(total)} = (1.06 + 0.30 + 0.26)$
$= 1.62$ mol

$$P_{(total)} = n_{(total)}RT/V = (1.62)(8.31)(1250 + 273) / (0.100)$$
$$= 205{,}029 \text{ Pa}$$

$$P_{H2} = (\text{mole fraction of } H_2) \times P_{(total)}$$
$$= (1.06/1.62) \times 205{,}029$$
$$= 134{,}155 \text{ Pa} = \underline{\underline{1.34 \times 10^5 \text{ Pa}}} = \underline{\underline{134 \text{ kPa}}} \text{ (to 3 s.f.)}$$

(ii)

$$\left.\begin{aligned} K_p &= \frac{(P_{H2})^3(P_{C2H2})}{(P_{CH4})^2} \\ &= \frac{(\frac{n_{H2}RT}{V})^3(\frac{n_{C2H2}RT}{V})}{(\frac{n_{CH4}RT}{V})^2} \\ &= \frac{(n_{H2})^3(n_{C2H2})}{(n_{CH4})^2} \times \left(\frac{RT}{V}\right)^{4-2} \\ &= \frac{(n_{H2})^3(n_{C2H2})}{(n_{CH4})^2} \times \left(\frac{RT}{V}\right)^{2} \end{aligned}\right\}$$

[1] for <u>convincing</u> proof and use of pV = nRT

$$= \frac{1.06^3 \times 0.30}{0.26^2} \times \left(\frac{8.31 \times 1523}{0.100}\right)^2$$

[1] for substitution of correct terms from graph

$$= \underline{\underline{8.47 \times 10^{10} \text{ Pa}^2}} \text{ (3 s.f.)}$$

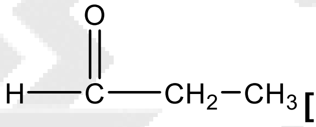
[1] for correct answer and units

Other accepted units of K_p: ($J^2\ m^{-6}$)

$\equiv Pa^2$

(iii) When the temperature is changed from 1250 °C to 1000 °C, the value of K_p would <u>decrease / be smaller</u> **[1]**.

(e) **(i)**



$H-C(=O)-CH_2-CH_3$ **[1]**

Propanal **[1]** (must be spelt clearly and correctly, no benefit of doubt)

(ii) To each separate samples of propyne and propanal, (any of the following):

	Chemical test	**Observations**	
		propyne	**propanal**
1	Add 2,4-DNPH	No orange ppt	Orange ppt formed
2	warm with Tollen's reagent	No silver mirror	Silver mirror produced
3	warm with Fehling's solution	No brick-red ppt	Brick-red ppt formed
4	add aqueous bromine	Yellow-orange aqueous bromine decolourised	Yellow-orange colour remains
5	Add $Br_2(l)$ (at r.t., no UV) or Br_2 in CCl_4 (at r.t., no UV)	Reddish-brown liquid bromine decolourised Orange-red Br_2 in CCl_4 decolourised	Reddish-brown colour remains Orange-red colour remains

6	Heat with acidified potassium dichromate	Orange colour remains	Orange solution turns green

Careful! hot acidified or alkaline $KMnO_4$ is not ideal here as both propyne and propanal can undergo oxidation (propyne undergoes oxidative cleavage, while propanal will be oxidsed to propanoic acid). However, students who added hot *acidifed* $KMnO_4$ to both compounds and used the effervescence of CO_2 to identify propyne (effervescence not seen for propanal) were awarded the mark.

Careful! Cold $KMnO_4$ to form the diol for propyne is a dubious choice, as propanal may still get oxidized in cold conditions, so decolourisation might happen for both compounds.

[1] correct choice of test
[1] correct distinguishing observation (incorrect colours of ppts or solutions were penalized)

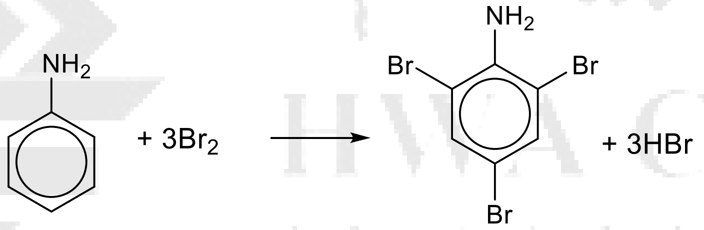
Ecf was only awarded if product drawn in (e)(i) was an aldehyde or ketone

4 **(a)** The π cloud has high electron density/ is electron-rich that will attract electron-deficient electrophiles but will repel electron-rich nucleophiles. **[1]**

(b) Electrophilic addition destroys the delocalisation in the π electron cloud/disrupts aromaticity which requires a significant amount of energy, whereas electrophilic substitution retains aromaticity. **[1]**

(c) **(i)** Step 1: Conc. HNO_3, conc. H_2SO_4, maintained at 55 ^oC **[1]**
Step 2: 1. Sn, (excess) conc. HC*l*, heat 2. NaOH(aq) **[1]**

(ii)



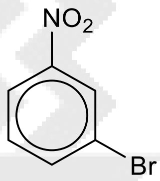
X

[1] for X
[1] for equation (ecf for equation if X is monosubstituted)

(iii) Nitrobenzene < benzene < phenylamine.**[½]**

The nitro group is electron withdrawing and withdraws electron density from the π electron cloud on the benzene ring **[½]**, reducing the susceptibility of the benzene ring towards electrophiles/deactivating the ring towards electrophiles **[½]**. The NH_2 group on phenylamine is electron-donating as it can donate its lone pair of electrons to the ring and increases electron density of the π electron cloud in the benzene ring. **[½]**
(only need to mention susceptibility towards electrophiles/activating or deactivating towards electrophiles once)

(iv)



[1]

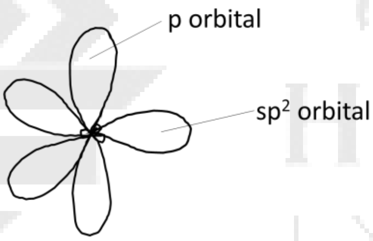
(d) **D** has only 4 π electrons in the ring, so it doesn't satisfy criteria 4. **[1]**

F has two carbon atoms in the ring that are sp^3 hybridised, so those carbons do not have available p orbitals, so it doesn't satisfy criteria 2

OR

F does not satisfy criteria 3, since the p orbitals are not overlapped in a continuous fashion/ since the structure is not planar at the carbons that are sp^3. **[1]**

(e) **(i)**



[1] for correct shape, arrangement and label for p orbital
[1] for correct shapes, arrangement and label for sp^2 orbitals

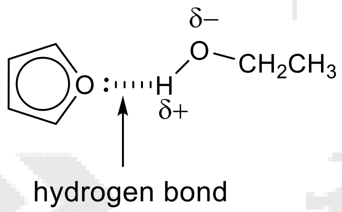
(ii) <u>2</u> **[1]**

(iii) p orbital. **[1]**

(iv) The <u>lone pair</u> on N of pyrrole is <u>delocalised</u> into the π cloud and is <u>less/not available</u> for donation to a H$^+$. **[1]**

(f) **(i)** Furan has very low resonance energy of <u>80 kJ mol^{-1}</u> **[1]**, so disrupting its aromaticity requires very little energy OR formation of strong σ bonds in an addition can compensate for the loss in its small resonance energy **[1]**.

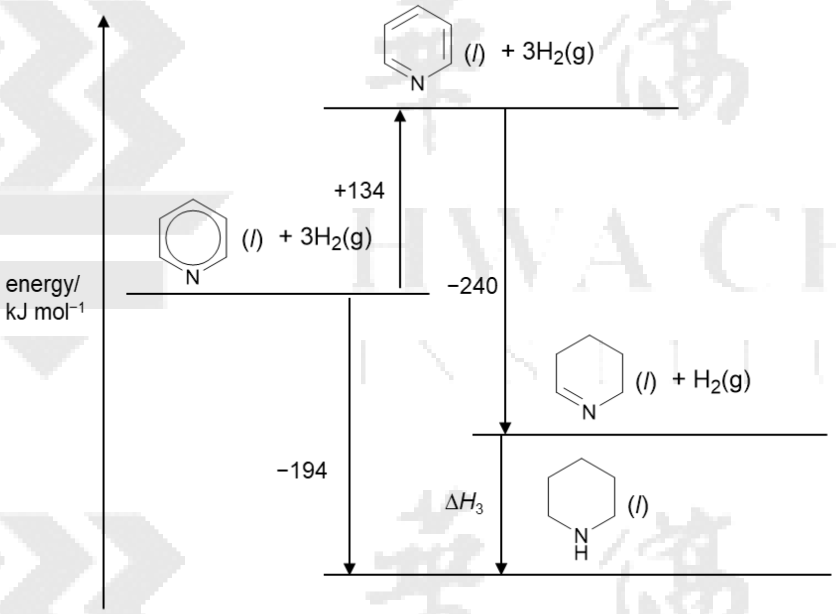
(ii)



[1] (correct bond, lone pair, partial charges and label) (-1/2 per mistake)

The <u>hydrogen</u> atom <u>bonded to the</u> highly <u>electronegative O</u> on ethanol has a very significant <u>δ+ charge</u> and the electron density in the covalent bond is highly polarised towards the oxygen atom. As a result, the H can form a very strong <u>attraction to the lone pair of electrons</u> on the highly electronegative <u>oxygen atom on furan</u>. This is a hydrogen bond. **[1]**

(g)



Cycle: **[2]**

–[½]m per mistake (max ½ m for cycle if students put the diene on the highest energy level, the ½ m can only be awarded if they put in -194 at the correct position)

By Hess' Law,

$\Delta H_3 = -(-120 - 120) - 134 + (-194) = -88$ kJ mol^{-1} **[1] ecf for correct use of Hess' Law.**