Raffles Institution
2013 H2 Chemistry Preliminary Examinations Paper 2
(Suggested Solutions)

1

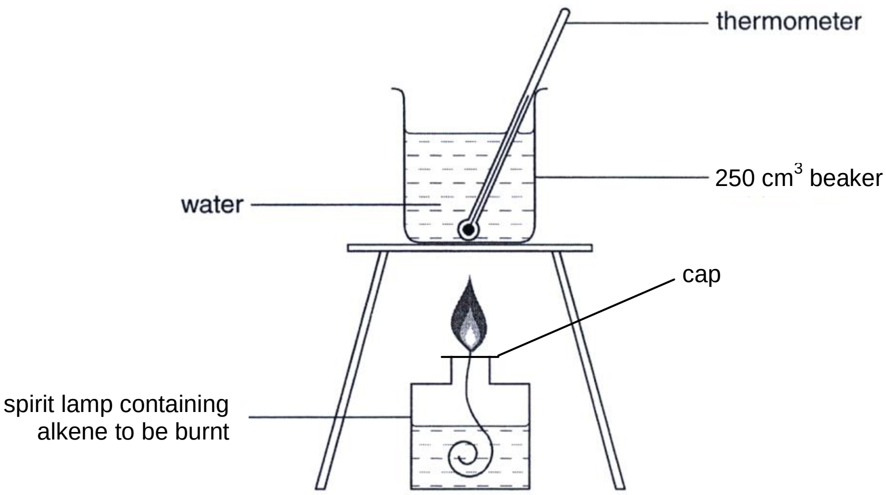
(a) $C_6H_{12}(l) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

(b)(i) Assuming no heat loss,
heat evolved from combustion = heat gained by calorimeter set-up
$-\Delta H_c^\ominus$ [*cis*–hex–3–ene] × amt of *cis*–hex–3–ene = ***C*** × temperature rise
– (–3733)(0.20 / 84.0) = ***C***(5.0)
C = 1.78 kJ K^{-1} (or kJ $^oC^{-1}$)

(b)(ii) Assuming no heat loss,
heat evolved from combustion = heat gained by calorimeter set-up
$-\Delta H_c^\ominus$ [*trans*–hex–3–ene] × amt of *trans*–hex–3–ene = ***C*** × temperature rise
$-\Delta H_c^\ominus$ [*trans*–hex–3–ene] × (0.22 / 84.0) = (1.78)(5.4)
$\Delta H_c^\ominus$ [*trans*–hex–3–ene] = –3670 kJ mol^{-1} (3 s.f.)

(b)(iii) $\Delta H_{iso}^\ominus$ = $\Delta H_c^\ominus$ [*cis*–hex–3–ene] – $\Delta H_c^\ominus$ [*trans*–hex–3–ene]
= –3733 – (–3665)
= –68.0 kJ mol^{-1}

(c)



<u>Experimental set-up</u>

1. **Fill up one spirit lamp with *cis*–hex–3–ene** (to about 80% capacity), taking care to avoid getting any *cis*–hex–3–ene on the outside surface of the lamp.
2. **Set up the apparatus as shown above**, such that the beaker is about 2-3 cm from the tip of the wick.

<u>Calibration of calorimeter set-up</u>

3. Using a 250 cm^3 measuring cylinder, **measure out 200 cm^3 of water** into a 250 cm^3 beaker.
4. Using an electronic weighing balance, weigh the mass of the spirit lamp filled with *cis*–hex–3–ene. **Record** this **mass**.
5. Using the thermometer, read the **temperature** of the water and **record** it.
6. **Use the lighter to light the lamp and place it under the beaker of water**, centering the flame under the bottom of the beaker and **ensuring the flame is at an approximately constant distance** below it.
7. Using the thermometer, carefully and gently stir the water.
8. When the temperature has risen to about **5 °C**, **blow out (extinguish)** the flame.
9. Continue to stir the water, **recording the highest temperature** reached.
10. While the lamp is cooling, clean the soot off from the bottom of the beaker.
11. **Re-weigh the spirit lamp** when it has cooled to room temperature. Record this mass.
12. Repeat **Steps 3** to **11**, using the same beaker after cleaning it. (For a more accurate estimate of the heat capacity.)

<u>Determining mass and temperature changes using *trans*–hex–3–ene</u>

13. Repeat **Step 1** by filling the other spirit lamp with *trans*–hex–3–ene.
14. Repeat **Steps 3** to **11**, using this new spirit lamp, recording the relevant masses and temperatures.
15. For a more accurate estimate of the data, **Step 14** can be repeated.

The value for the standard enthalpy change of combustion of *trans*–hex–3–ene can then be found by similar calculations as shown in **(b)**.

(d) **Hexenes** are inflammable liquids and are hence a **fire hazard.**

Any of the following measures can be taken:
Containers of the hexenes should be covered and stored away, when not in use; proper disposal of hexenes; the wick should be lit away from any nearby hexenes.

Or

Hexenes are volatile and hence a **health hazard,** causing respiratory problems.
Experiment to be carried out in fume cupboard to avoid inhaling toxic vapour of hexene.

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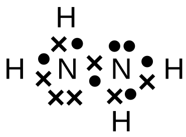
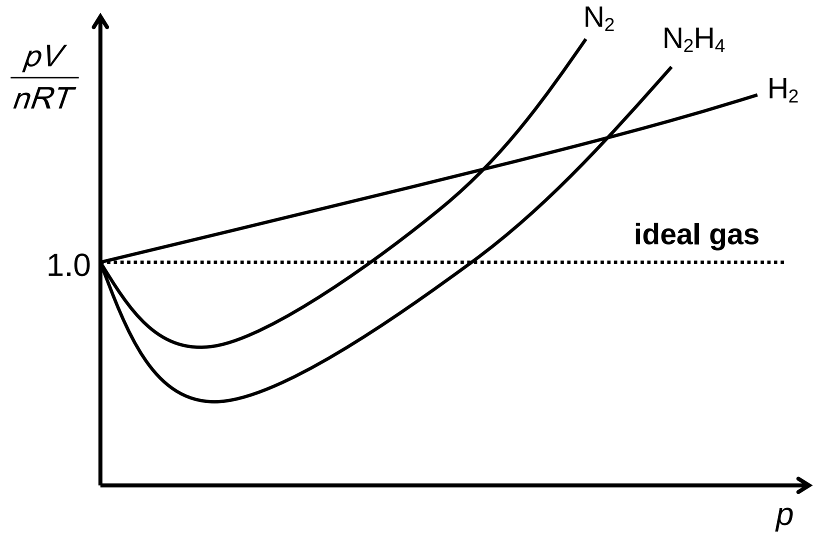
(a)



(b) sp^3 (out of syllabus);
107°

(c)



(also accepted if graph for N_2H_4 intersects graph for N_2 at very high pressures)

(d) pV = nRT = (m/M)RT
$(101 \times 10^3)(10 \times 10^{-3}) = (m / 20)(8.31)(150 + 273)$
m = 5.75 g

(e)(i) Let the initial amt of N_2H_4 be *a*.

	$N_2H_4(g)$	$\rightleftharpoons$	$N_2(g)$	+	$2H_2(g)$
initial amt / mol	x		0		0
eqm amt / mol	$x(1-\alpha)$		$x\alpha$		$2x\alpha$

Total amt of gases present at eqm
$= x(1-\alpha) + x\alpha + 2x\alpha = x(1+2\alpha)$ mol

$$\text{average } M_r = \frac{1-\alpha}{1+2\alpha} M_r(N_2H_4) + \frac{\alpha}{1+2\alpha} M_r(N_2) + \frac{2\alpha}{1+2\alpha} M_r(H_2)$$

$$20 = \frac{1-\alpha}{1+2\alpha}(32.0) + \frac{\alpha}{1+2\alpha}(28.0) + \frac{2\alpha}{1+2\alpha}(2.0)$$

$$\alpha = 0.30$$

(e)(ii)

$$p_{N_2H_4} = \chi_{N_2H_4} p_T = \frac{1-\alpha}{(1+2\alpha)} p_T = \frac{1-0.3}{(1+0.6)}(1) = 0.4375\,\text{atm} = 0.438 \text{ atm}$$

$$p_{N_2} = \chi_{N_2} p_T = \frac{\alpha}{(1+2\alpha)} p_T = \frac{0.3}{(1+0.6)}(1) = 0.1875\,\text{atm} = 0.188 \text{ atm}$$

$$p_{H_2} = \chi_{H_2} p_T = \frac{2\alpha}{(1+2\alpha)} p_T = \frac{2(0.3)}{(1+0.6)}(1) = 0.375\,\text{atm}$$

$$K_P = \frac{p_{N_2} p^2{}_{H_2}}{p_{N_2H_4}} = \frac{(0.1875)(0.375)^2}{0.4375} = 6.03 \times 10^{-2} \text{ atm}^2$$

(e)(iii) α will decrease.

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(a) When pH increases, the **concentration of H^+ decreases**.
By Le Chatelier's Principle, the **position of equilibrium shifts to the right** to increase the concentration of H^+, causing the fraction of HF to decrease.

(b) Since $R_{HF} = R_{F^-} = 0.5$,
$\Rightarrow [HF]_{eqm} = [F^-]_{eqm}$
$\Rightarrow$ buffer solution at maximum buffering capacity.

$$pH = pK_a + \lg\frac{[F^-]}{[HF]}$$
$\Rightarrow 3.2 = pK_a + \lg 1$
$\Rightarrow K_a = 10^{-3.2} = 6.31 \times 10^{-4}$ mol dm^{-3}

(c)(i) $a = ½$

(c)(ii) The addition of H^+ causes the position of the equilibrium (2) to shift right, reducing $[F^-]$ in solution.

This, in turn, causes the position of equilibrium (1) to shift right, increasing $[Ca^{2+}]$ in solution.

(c)(iii) From the graph, at pH 3.0,
fraction of HF = 0.61 and fraction of F^- = 0.39

$$\frac{[F^-(aq)]}{[HF(aq)]} = \frac{0.39}{0.61} = 0.639$$
At pH 3.0, $[F^-] = (0.639)(4.63 \times 10^{-4}) = 2.96 \times 10^{-4}$ mol dm^{-3}

(c)(iv) $[Ca^{2+}] = ½ ([HF] + [F^-])$

(c)(v) From **(iii)** and **(iv)**,
$[Ca^{2+}] = ½ \times (4.63 + 2.96) \times 10^{-4} = 3.795 \times 10^{-4}$ mol dm^{-3}

$K_{sp} = [Ca^{2+}][F^-]^2 = (3.795 \times 10^{-4})(2.96 \times 10^{-4})^2 = 3.33 \times 10^{-11}$ mol^3 dm^{-9}

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(a) $Ca(OH)_2(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$

(b)(i) $MgCO_3$

(b)(ii) As shown by plot (II), **$MgCO_3$ decomposes more readily** than $BaCO_3$.

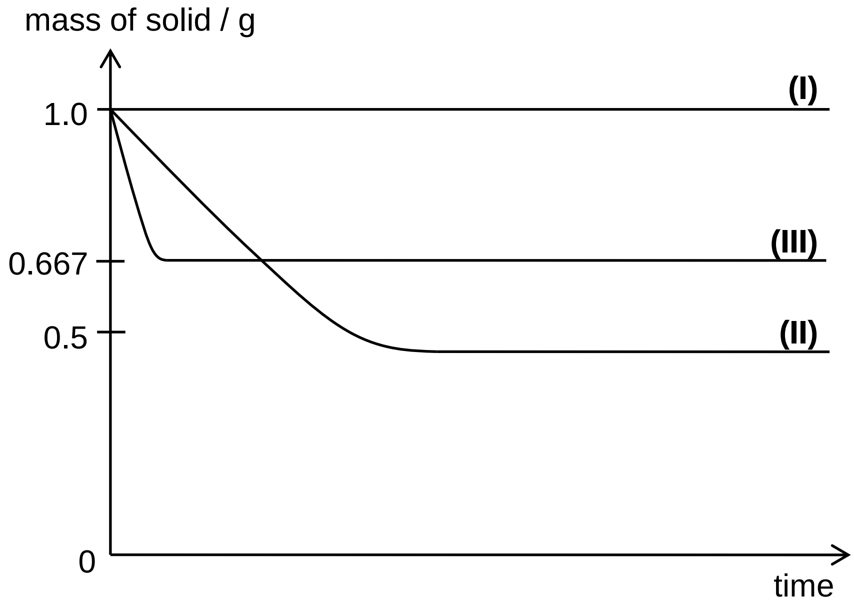
Mg^{2+} is **smaller** than Ba^{2+} and has a **higher charge density** and **polarising power**.

Hence it **distorts the electron cloud of the CO_3^{2-} anion**, and **weakens** the carbon-oxygen **bond within the anion to a greater extent**, resulting in $MgCO_3$ requiring less energy for thermal decomposition and thus it decomposes more readily.

(b)(iii) Mg^{2+}: $1s^2\ 2s^2\ 2p^6$

Mg^{2+} has **one less** occupied **principal quantum shell** than that of its parent atom Mg.

(c)



(d) Let the A_r of **Z** be a.

$3\mathbf{Z}CO_3 \equiv \mathbf{Z}_3O_4$ (i.e. 3 moles of $\mathbf{Z}CO_3$ decomposes to give 1 mole of $\mathbf{Z}_3O_4$)
amount of $\mathbf{Z}CO_3$ = 3 × amount of $\mathbf{Z}_3O_4$
$1.0 / (a + 12.0 + 3 \times 16.0) = 3 \times 0.667 / (3a + 4 \times 16.0)$
$1 / (a + 60) = 2.001 / (3a + 64)$
$3a + 64 = 2.001a + 120.06$
$a = 56.1$

Comparing to periodic table, value is closest to 55.8
Therefore, **Z** is Fe.

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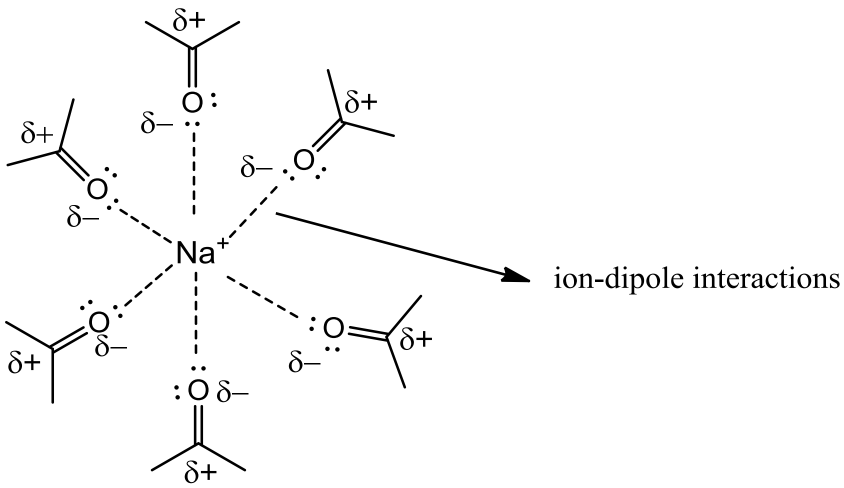
(a) BE(C–C*l*) = +**340** kJ mol^{-1}
BE(C–I) = +**240** kJ mol^{-1}

The energy given out by the C–I bond formed is insufficient to compensate for the energy needed to break the C–C*l* bond, hence **ΔH is endothermic**.
OR
The C–I bond formed is weaker than the C–C*l* bond broken, hence **ΔH is endothermic**.

Since **$\Delta G \approx \Delta H > 0$**, the reaction is not energetically feasible / does not go to completion.

(b)(i)

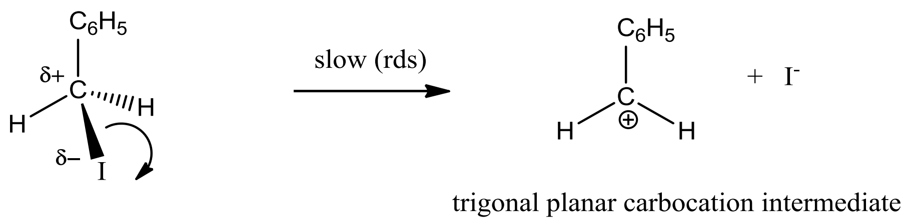


Note:
The above diagram shows what it actually looks like in 3-dimensional space i.e. Na^+ is surrounded by six propanone molecules.
Only one Na^+ with one propanone molecule needs to be shown for this answer.

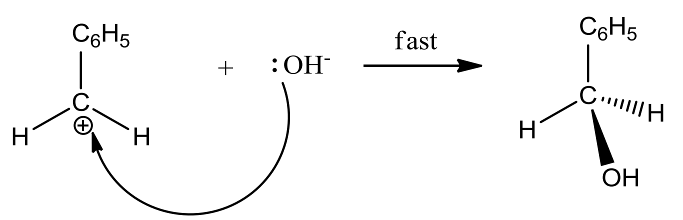
(b)(ii) NaC*l* is **precipitated out** as a solid.
By Le Chatelier's Principle, [NaCl(aq)] is low and position of equilibrium shifts to the right towards completion.

(c)(i) Mechanism: Nucleophilic Substitution (S_N1)

Step 1: Formation of carbocation



Step 2: Attack of OH^- nucleophile



(Part (c)(ii) hints that the mechanism is S_N1)

(c)(ii) The **$C_6H_5CH_2^+$ carbocation** is **resonance stabilised** as the **π electron cloud of the benzene ring can overlap with the empty *p* orbital of the carbocation**.
For $C_6H_5CH_2CH_2I$, the carbocation is not resonance-stabilised. Hence, the reaction proceeds by S_N2 mechanism instead.

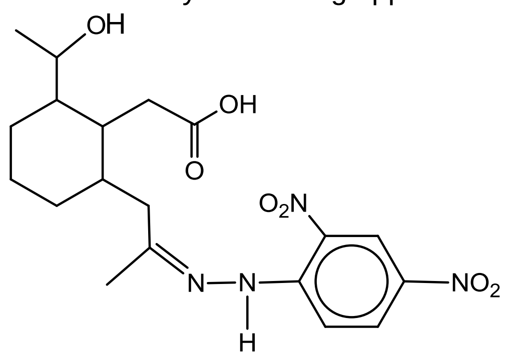
(d)(i) Secondary alcohol; alkene

(d)(ii) As a **base / proton acceptor** to react with R–OH group.

(d)(iii) Step **III**: $KMnO_4$(aq), NaOH(aq), heat under reflux
Step **IV**: I_2, NaOH(aq), warm

(d)(iv) Secondary **alcohol**
The secondary alcohol will **undergo oxidation in reaction III** to form a methyl ketone, which **subsequently loses 1 carbon in the iodoform reaction in reaction IV**.

(d)(v) Test: Use 2,4-dintrophenylhydrazine
Observations: yellow/orange ppt formed for **U** and no orange ppt for **T**



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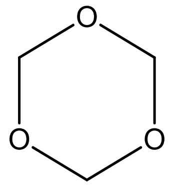
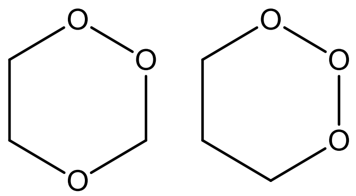
(a)(i)



(a)(ii)

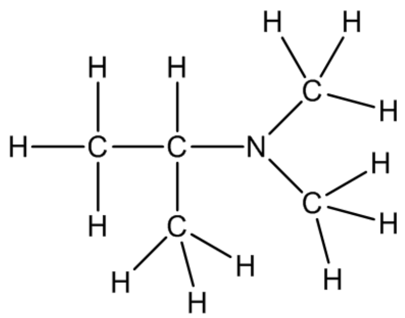


(a)(iii) Weak O–O bond due to
repulsion of lone pairs of electrons on adjacent O atoms
OR
repulsion of two δ– charges on adjacent O atoms.

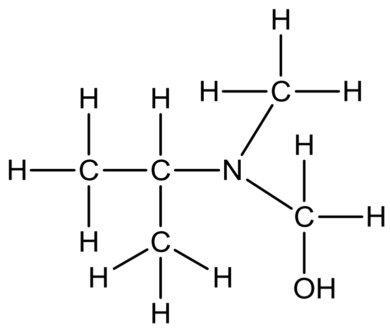
(b)(i) any value < 3.3

The additional **methyl group** is **electron-donating**. Hence it **increases the availability of the lone pair of electrons on N atom** for protonation.

(b)(ii)



or



(b)(iii) For phenylamine, **lone pair on N is delocalised into** the π electron cloud of **the benzene ring**. Hence, the lone pair is less available for donation, and phenylamine acts as a **weak nucleophile**.