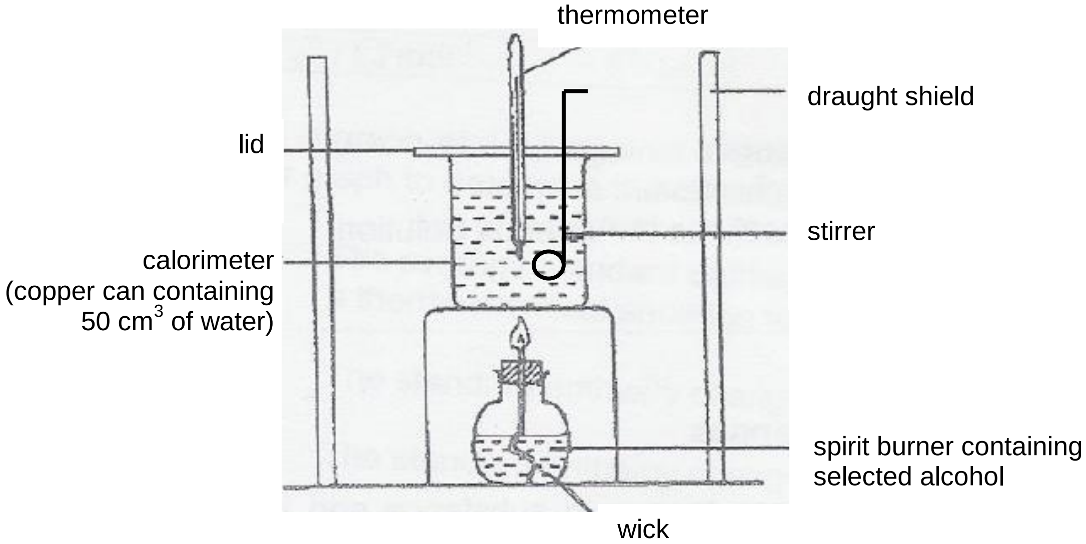
NJC Preliminary Examination
H2 Chemistry Paper 2 Solutions

1 Planning (P)

A student was provided with a spirit burner. He was asked to determine the enthalpy change of combustion under laboratory conditions, ΔH_c, for ethanol using the following setup.



Knowing that there could be significant heat loss arising from the above experimental setup, he decided to calibrate the calorimeter by burning 0.60 g of methanol (CH_3OH) to determine the calorimeter's heat capacity, $C_{calorimeter}$, which accounts for both the water and the copper can. Heat capacity is defined as the number of Joules of heat needed to raise the temperature of the calorimeter by one Kelvin or one degree Celsius. The temperature of the calorimeter rose from 25.0°C to 33.8°C.

The **same calorimeter** was then used to measure the enthalpy of combustion of ethanol.

(a) Given the enthalpy change of combustion of methanol is − 715 kJ mol^{-1}, use the information above to calculate the heat capacity of the calorimeter, $C_{calorimeter}$, stating its units.

[2]

Heat evolved from methanol = $(\frac{0.60}{32}) \times 715000$
= 13400 J

Heat gained by calorimeter = $C\Delta T$
= $C \times 8.8$

Heat evolved from methanol = Heat gained by calorimeter
13400 = (8.8)C
$C = 1520\ J\ K^{-1}$

(b) Given the enthalpy change of combustion of ethanol is approximately −1370 kJ mol^{-1}, calculate the minimum mass of ethanol required to give the same temperature change as that in the calibration.

[2]

For the combustion of ethanol to give the same temperature change as that in the calibration, it means:

Heat evolved from ethanol = Heat gained by calorimeter

$$\eta_{\text{ethanol}} \times (1370 \times 10^3) = 13400$$

$$\eta_{\text{ethanol}} = \frac{13400}{(1370 \times 10^3)}$$

$$= 9.871 \times 10^{-3} \text{ mol}$$

Minimum mass of ethanol = $(9.871 \times 10^{-3}) \times 46.0$
= 0.450 g

(c) Write a plan to determine the enthalpy change of combustion, ΔH_c, of ethanol that the student will carry out.

You may assume that you are provided with:

- a thermometer with divisions of 0.2 °C division;
- the apparatus normally found in a school or college laboratory.

Your plan should include details of

- the procedure to determine the enthalpy change of combustion of ethanol;
- the readings recorded using appropriate table(s), including units;
- precautions taken to ensure reliability of the experiment
- an outline of how the results would be used to determine the enthalpy change of combustion of ethanol based on the plan that you have written using arbitrary values.

[7]

<u>Procedure</u>

1. Use the same calibration apparatus setup for the experiment.
2. Rinse the spirit burner with ethanol and allow the wick to dry off/ use a new wick with same length.
3. Weigh the spirit burner containing 1.0 g of ethanol using an electronic balance.
4. Measure the initial temperature of the water using a 0.2^{o}C division thermometer.
5. Light the wick of the spirit burner.
6. Monitor the temperature of water using the thermometer with constant stirring using the stirrer.
7. Extinguish the flame with a cap when the rise of temperature of the water reaches about 8.8^{o}C.
8. Measure the final temperature of the water.

9. Weigh the spirit burner with the remaining ethanol again.

10. Repeat the experiment until the % difference of $\Delta T/m < 5\%$.

Tabulation of results

Initial temperature of water / ^{o}C	T_1
Final temperature of water / ^{o}C	T_2
ΔT / ^{o}C	$T_2 – T_1 = T$
Initial mass of spirit burner with ethanol / g	x
Final mass of spirit burner with remaining ethanol / g	y
Mass of ethanol burnt, m / g	x – y = z
$\Delta T/m$	

Calculation

Heat gained by water and calorimeter = $C \times \Delta T$

$= (1520)T$ J

$= (1.52)T$ kJ

Amount of ethanol = $\frac{z}{46.0}$ mol

ΔH_c (ethanol) = $– (1.52)T/ (\frac{z}{46.0})$ kJ $mol^{–1}$

(d) Identify **one** potential safety hazard in this experiment and state how you would minimise this risk.

[1]

Methanol is toxic. Wear glove.
Methanol is toxic and volatile. Conduct the experiment in a fume hood.
Methanol and ethanol are highly flammable. Alcohols are placed away from flame when not in used in experiment.

[Total: 12]

2 The simplest chemical reactions are those that occur in the gas phase in a single step, such as the transfer of a chlorine atom from $ClNO_2$ to NO.

$$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$$

(a) **(i)** An equimolar mixture of $ClNO_2$(g) and NO(g), at total initial pressure of 3 atm, is allowed to react in a closed vessel at 1000 K. When equilibrium is attained at the 5th minute, the partial pressure of $ClNO_2$ is found to be 0.57 atm.

Calculate the value for the equilibrium constant, K_p, of this system.

	$ClNO_2(g)$ +	$NO(g)$ ⇌	$NO_2(g)$ +	$ClNO(g)$
Initial/ atm	1.5	1.5	0	0
Change/ atm	–0.93	–0.93	+0.93	+0.93
Eqm/ atm	0.57	0.57	0.93	0.93

$$K_p = \frac{P(NO_2)P(ClNO)}{P(ClNO_2)P(NO)}$$

$$K_p = \frac{(0.93)^2}{(0.57)^2}$$

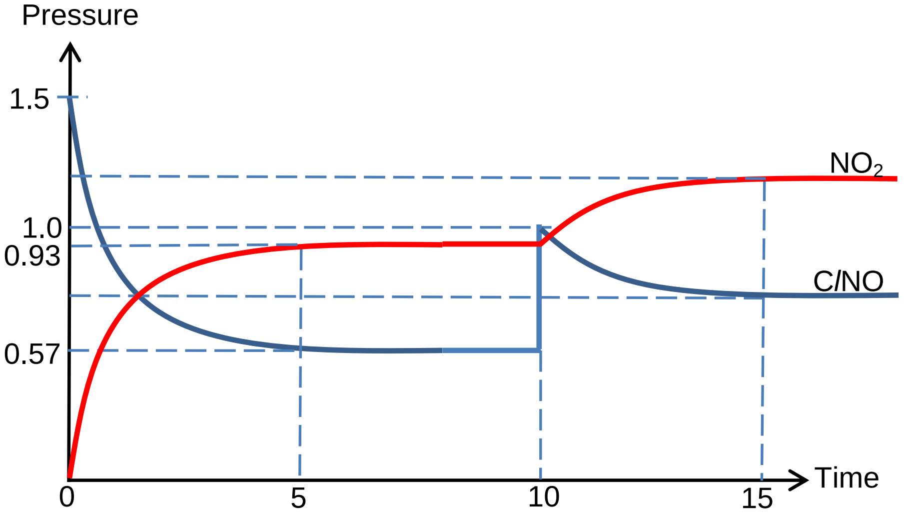
K_p = 2.67 (no units)

(ii) At the 10th minute, more $ClNO_2$ gas was pumped into the vessel at 1000 K, increasing the partial pressure of $ClNO_2$ to 1 atm.
Suggest how the position of the equilibrium would change.

By LCP, the position of the equilibrium will shift **forward** to **consume some of the extra $ClNO_2$** in the reaction to **partially decrease its partial pressure**.

(iii) Hence illustrate clearly, in a pressure–time graph below, the changes in the partial pressures of $ClNO_2$ and NO_2 when

(I) the above gaseous system first reaches equilibrium at the 5th minute,
(II) more $ClNO_2$ gas was added into the vessel at the 10th minute and a new equilibrium is attained at the 15th minute.



(iv) Suggest whether the addition of an inert gas into the vessel would affect the position of the equilibrium.

The position of the equilibrium is **not affected** by the addition of the inert gas as the partial pressure of all gaseous reactants and products remained unchanged

[7]

(b) $\mathrm{C}l\mathrm{NO}_2$ can behave as an *ideal gas* under certain experimental conditions.

(i) State the two assumptions of kinetic theory of ideal gas.

There are **no/ negligible intermolecular forces of attraction or repulsion** between the **gaseous particles**.

A gas is composed of tiny **gaseous particles** that have a **negligible volume** compared to the **volume of the gas container**.

(ii) Predict whether $\mathrm{C}l\mathrm{NO}_2$ behaves ideally under high pressure.

Under high pressure, the gaseous **particles** are **very close together** in a small volume.

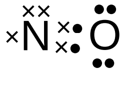
- They experience **significant intermolecular forces of repulsions/ attractions** between them.
  OR
- The **volume of the gas particles is no longer negligible compared to the volume of the container**.

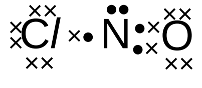
So it is **not behaving ideally** under high pressure.

[4]

(c) **(i)** Draw the dot-and-cross diagrams of NO and $\mathrm{C}l\mathrm{NO}$. Hence, suggest the shape and bond angle of $\mathrm{C}l\mathrm{NO}$.

Shape : **bent**
Bond angle : Stating a value that is within the range –
$110^\circ \le x < 120^\circ$





(ii) Hence, suggest why the formation of $\mathrm{C}l\mathrm{NO}$ from NO is favoured.

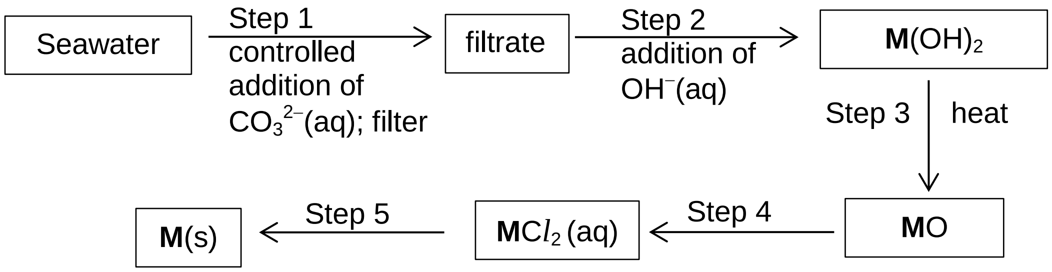
NO contains a single unpaired electron. **Formation of N-Cl bond** allows N to achieve **noble gas/ octet configuration** drives the formation of $\mathrm{C}l\mathrm{NO}$.

[5]
[Total: 16]

3 The four most abundant salts in sea water are given in the table below.

salt	**kg m^{-3}**
Sodium chloride	27.5
Magnesium chloride	6.75
Magnesium sulfate	5.63
Calcium sulfate	1.80

The following flow scheme shows the series of reactions that involve seawater.



(a) Seawater contains chloride and sulfate ions. To verify the presence of chloride and sulfate ions instead of bromide and sulfite ions in sea water, the following chemicals can be used:

HNO_3(aq), $AgNO_3$(aq), $BaCl_2$(aq), NH_3(aq)

(i) Explain the importance of adding HNO_3(aq) before other chemicals during this verification process.

It is to react the sulfite ion away. This is so that when $BaCl_2$ is added, the white precipitate is due to $BaSO_4$ instead of $BaSO_3$.

(ii) Suggest a sequence of chemical tests that can be used to verify the presence of chloride and sulfate ions in sea water after acidification.

Step 1: divide acidified sea water into two portions
Step 2: add $BaCl_2$ to one portion, precipitation verifies presence sulfate ion.
Step 3: add $AgNO_3$ to the second portion.
Step 4: Add NH_3(aq) to mixture obtained in step 3 until in excess. If white precipitate obtained is soluble in excess NH_3(aq), presence of chloride ions are verified.

Flowchart is also acceptable.

[3]

(b) **(i)** Calculate the concentration of magnesium and calcium ions in 1 dm^3 of seawater.

$[MgCl_2]$ = 67.5 kg in 1 m^3
= 67500g in 1000 dm^3
= 67.5 g in 1 dm^3
$[CaSO_4]$ = 1.8 g in 1 dm^3
$[MgSO_4]$ = 5.625 g in 1 dm^3

$[Ca^{2+}] = \dfrac{1.8}{(40.1+32.1+64.0)}$ = 0.0132 mol dm^{-3}

$[Mg^{2+}]_{MgCl_2} = \dfrac{6.75}{(24.3+71.0)}$ = 0.07029 mol dm^{-3}

$[Mg^{2+}]_{MgSO_4} = \dfrac{5.63}{(24.3+32.1+64.0)}$ = 0.046761 mol dm^{-3}

$[Mg^{2+}]_{total}$ = 0.07029 + 0.046761 = 0.117 mol dm^{-3} (3sf)

Answers in kg dm^{-3} or g dm^{-3} are also accepted.

(ii) Write an expression for the solubility product of magnesium carbonate.

$K_{sp} = [Mg^{2+}][CO_3^{2-}]$

(iii) Determine the range of concentrations of CO_3^{2-}(aq) required to cause selective precipitation of only one cation in seawater given the following data.

compound	**solubility product**
Magnesium carbonate	1.0×10^{-5}
Calcium carbonate	5.0×10^{-9}

$CaCO_3$ will precipitate first.
In order for $CaCO_3$ to ppt, ionic product $[Ca^{2+}][CO_3^{2-}] > K_{sp}$.
$\therefore$ min $[CO_3^{2-}] = \dfrac{5.0\times10^{-9}}{0.013216}$ = 3.79×10^{-7} mol dm^{-3}
To prevent precipitation of $MgCO_3$, ionic product $[Mg^{2+}][CO_3^{2-}] < K_{sp}$
$\therefore$ max $[CO_3^{2-}] = \dfrac{1.0\times10^{-5}}{0.01175}$ = 8.51×10^{-4} mol dm^{-3}

(iv) Hence deduce the identity of **M** in the above flow scheme.
Mg

[6]

(c) **(i)** Write an equation with state symbols for Step 3 using **M** to represent your cation.
$Mg(OH)_2 (s) \rightarrow MO (s) + H_2O (g)$

(ii) Suggest and explain why magnesium hydroxide has a lower thermal stability than calcium hydroxide.

Mg(II) ion has higher charge over size ratio than Ca(II) ion, hence it polarises (distorts) the electron cloud of hydroxide ion to greater extent, covalent bond in hydroxide ion is weakened to greater extent therefore lower energy needed to cause decomposition. Thus it has lower thermal stability.

[3]

(d) **(i)** If the mass of **M**O isolated in Step 3 is 0.05 g, calculate the volume of 0.1 mol dm^{-3} of HC*l* required to convert all **M**O to **M**Cl_2.

$$\eta_{MO} = \frac{0.05}{(24.3+16.0)} = 1.241\times10^{-3} mol$$

MO + 2HC*l* → MCl_2 + H_2O

$$\eta_{HCl} = 2\times1.241\times10^{-3} = 2.48\times10^{-3} mol$$

Vol of HC*l* = $\frac{2.48\times10^{-3}}{0.1}\times1000 = 24.8cm^3$

(ii) Suggest how Step 5 can be carried out.

Evaporate MgCl_2 solution to dryness, to obtain MgCl_2 salt. Carry out electrolysis of MgCl_2 at molten state.

[4]

[Total: 16]

4 Methanol is the simplest alcohol, and is a volatile, colourless and flammable liquid. Methanol is mainly used as an antifreeze, solvent or fuel.

(a) Define the *standard enthalpy change of combustion of methanol* in words.

Standard enthalpy change of combustion of methanol is the heat evolved when 1 mole of methanol is burnt in excess oxygen under standard conditions (298K, 1 atm).

[1]

(b) **(i)** Using appropriate data from the *Data Booklet*, calculate the ΔH_r of the following reaction.

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l) \qquad \Delta H_r$$

ΔHr = 2[3BE(C-H) + BE(C-O) + BE(O-H)] + 3BE(O=O) – 4BE(C=O) – 8BE(O–H)
= 2 [3(410) + 360 + 460)] + 3(496) – 4(740) – 8(460)
= –1052 kJ mol^{-1}

(ii) Hence determine the standard enthalpy change of combustion of methanol.

$\boldsymbol{\Delta Hc = \frac{1}{2} \times (-1052) = -526\ kJ\ mol^{-1}}$

[3]

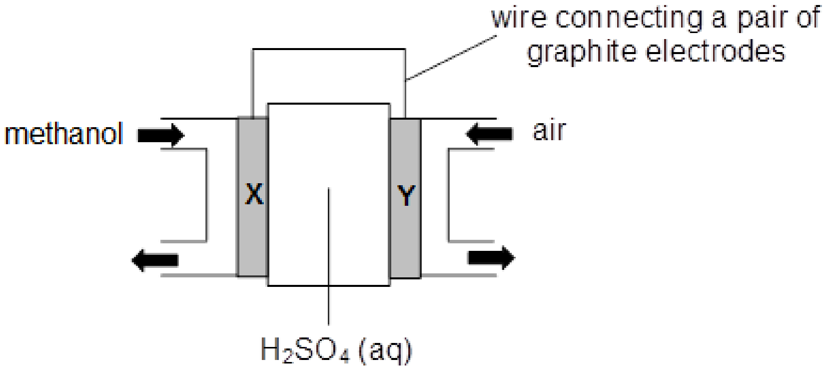
(c) The theoretical standard enthalpy change of combustion of methanol is −715 kJ mol^{-1}. Give two reasons to explain the discrepancy between this value and your answer in **(b)(ii)**.

The bond energy values from the Data Booklet are average values of a particular bond.

Methanol and water are in liquid states. Bond energy values are used for gaseous molecules.

[2]

(d) Other than direct burning of methanol to generate energy, methanol can also be used in a fuel cell. Methanol fuel cells are *more practical* than hydrogen fuel cells. Carbon dioxide and water are the products of the methanol fuel cell.



(i) For each electrode **X** and **Y**, name the type of electrode and state its polarity.

Electrode **X**
Type of electrode: **anode**

Polarity: **negative**

Electrode **Y**
Type of electrode: **cathode**

Polarity: **positive**

(ii) On the diagram above, indicate the direction of electron flow in the wire with an arrow.
Arrow is drawn from anode to cathode

(iii) Write the half-equation of the reaction taking place at each electrode.

X: $\mathbf{CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e}$

Y: $\mathbf{O_2 + 4H^+ + 4e \rightarrow 2H_2O}$

(iv) Explain why methanol fuel cells are *more practical* than hydrogen fuel cells.

Methanol is in liquid state and it is more compact to be transported/
Methanol gives out more energy when burnt compared to hydrogen as it released more electron per mole or methanol.

(v) Use appropriate data from the *Data Booklet* to explain why an acidic electrolyte is often preferred to an alkaline or neutral electrolyte.

In neutral or alkaline medium, $O_2 + 2H_2O + 4e \rightarrow 4OH^- \ E^o = +0.40\ V$

In acidic medium, $O_2 + 4H^+ + 4e \rightarrow 2H_2O \ E^o = +1.23\ V$

Since the E^o *value in acidic medium is more positive,* O_2 *is more easily reduced in acidic medium/ reduction is more feasible.*

[8]

(e) In a laboratory, methanol can also be oxidised to other organic compounds using suitable chemicals.

Give the appropriate reagents and conditions required for the following conversion.

I: Methanol → Methanal

Reagents and conditions: **$K_2Cr_2O_7$, dil. H_2SO_4, distill**

II: Methanol → Methanoic acid

Reagents and conditions: **$K_2Cr_2O_7$, dil. H_2SO_4, reflux**

III: Methanol → Carbon dioxide

Reagents and conditions: **$KMnO_4$, dil. H_2SO_4, reflux or Burn in excess oxygen**

[3]

[Total:17]

5 Lactic acid is a carboxylic acid with the formula $CH_3CH(OH)CO_2H$.

(a) State the type of stereoisomerism exhibited by lactic acid. Draw appropriate structures to illustrate your answer.

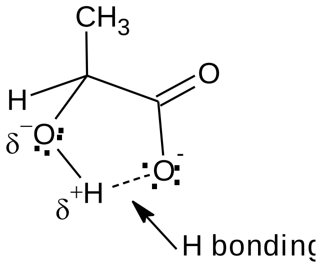
Optical isomerism

[2]

(b) In solution, lactic acid can lose a proton from the carboxyl group, producing the lactate ion $CH_3CH(OH)CO_2^-$. Compared to ethanoic acid, lactic acid is more acidic as it deprotonates ten times more easily than ethanoic acid.

Other than the electron withdrawing effect of –OH group, suggest **another** factor which explains the additional stability of the lactate ion. Illustrate your answer with a diagram.

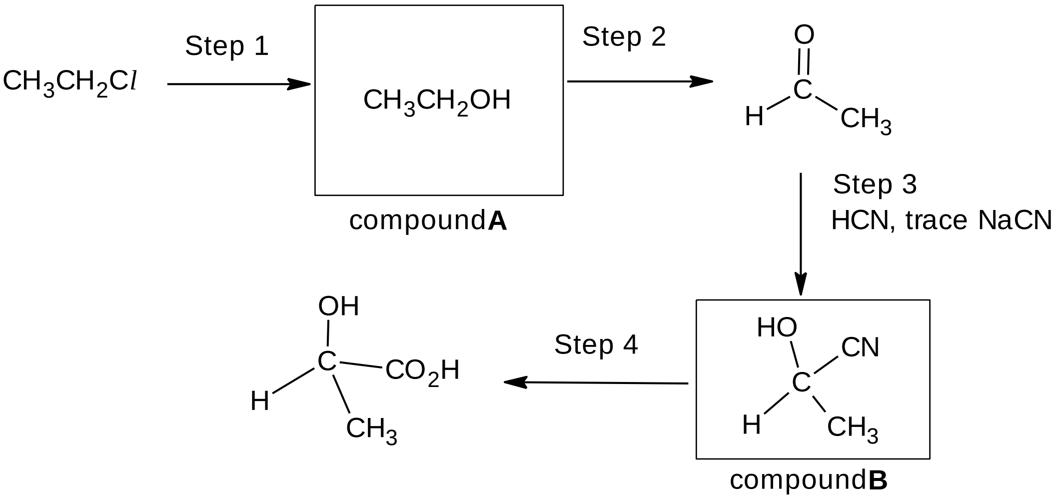
Intramolecular hydrogen bond is possible in lactate ion between the carboxylate ion and the protonic H in –OH.



[2]

(c) A student tries to synthesise lactic acid from chloroethane using a series of reactions as shown.

(i) Fill in the intermediate organic compounds **A** and **B** in the following flow scheme.



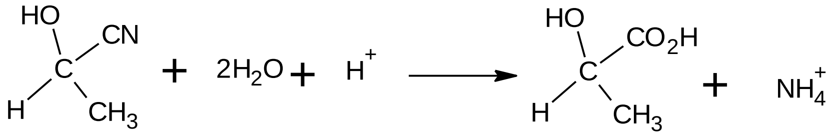
(ii) State the reagents and conditions for Step 1.

Reagents and conditions: *NaOH(aq), heat*

(iii) State the type of reaction for Step 4 and write a balanced equation for this step.

Type of reaction: **Hydrolysis**

Balanced equation:



(iv) Lactic acid formed in the above flow scheme is a racemic mixture while lactic acid formed via bacteria fermentation contains only one optical isomer. Explain.

Carbonyl carbon is trigonal planar and the CN^- nucleophile can attack the carbonyl carbon from top and bottom of the plane with equal propability, forming equal amount of each optical isomers, resulting in a racemic mixture. In bacteria fermentation, the attack can only take place from one side since enzyme has specific reaction site, thus only 1 optical isomer is formed.

[7]
[Total: 11]