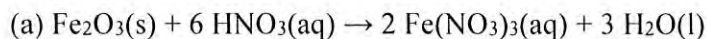


Multiple Choice Answers:

1C, 2D, 3E, 4C, 5D, 6D, 7B, 8E, 9D, 10A, 11B, 12A, 13D, 14B, 15E.

Question 16



(b) $\text{Molar mass}(\text{Fe}_2\text{O}_3) = 2 \times 55.85 + 3 \times 16.00 = 159.7 \text{ g mol}^{-1}$

(c) $n(\text{Fe}_2\text{O}_3) = 0.1292 \text{ g} / 159.7 \text{ g mol}^{-1} = 8.090 \times 10^{-4} \text{ mol}$

$[\text{Fe}_2\text{O}_3] = 8.090 \times 10^{-4} \text{ mol} / 0.2500 \text{ L} = 3.236 \text{ mmol L}^{-1}$ (or $3.236 \times 10^{-3} \text{ mol L}^{-1}$)

(d) $[\text{Fe}^{3+}] = 2 \times 3.236 \times 10^{-3} \text{ mol L}^{-1} = 6.472 \times 10^{-3} \text{ mol L}^{-1}$

(e) $[\text{Fe}^{3+}] \text{ in flask} = (0.4207 - 0.0072) / 0.1078 = 3.836 \text{ mg L}^{-1}$

$m(\text{Fe}) \text{ in flask} = 3.836 \text{ mg L}^{-1} \times 0.5 \text{ L} = 1.918 \text{ mg}$

$m(\text{Fe})_{\text{original}} = 1.918 \text{ mg L}^{-1} \times 500 / 10 = 95.90 \text{ mg}$ (or 0.09590 g)

$\%(\text{Fe}) = 0.9590 \text{ g} / 0.1082 \text{ g} \times 100 = 88.63\%$

(f) $m(\text{Fe in sample}) = 0.3647 \text{ g} \times 0.8354 = 0.3047 \text{ g}$

(g) $n(\text{Fe in sample}) = 0.3047 \text{ g} / 55.85 \text{ g mol}^{-1} = 5.455 \text{ mmol}$

$n(\text{Fe in 10.00 mL aliquot}) = 5.455 \text{ mmol} \times 10 \text{ mL} / 100 \text{ mL} = 0.5455 \text{ mmol}$

(h) $n(\text{Zn}^{2+}) = 0.02005 \text{ M} \times 20.53 \text{ mL} = 0.4116 \text{ mmol}$

(i) $n(\text{EDTA, total}) = 0.02143 \text{ M} \times 50.00 \text{ mL} = 1.072 \text{ mmol}$

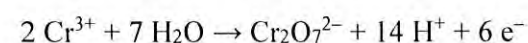
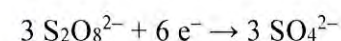
$n(\text{EDTA reacted}) = n(\text{EDTA, total}) - n(\text{EDTA, excess}) = 1.072 \text{ mmol} - 0.4116 \text{ mmol} = 0.6599 \text{ mmol}$

(j) $n(\text{Cr}^{3+}) + n(\text{Mn}^{2+})$ (both in 10.00 mL aliquot) = $n(\text{EDTA reacted with Fe}^{3+}, \text{Cr}^{3+} \text{ and Mn}^{2+}) - n(\text{Fe}^{3+})$

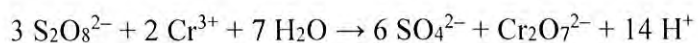
$= 0.6599 \text{ mmol} - 0.5455 \text{ mmol} = 0.1144 \text{ mmol}$

(k) $n(\text{Cr}^{3+}) + n(\text{Mn}^{2+})$ (in 0.3647 g sample) = $100.0 / 10.00 \times 0.1144 \text{ mmol} = 1.144 \text{ mmol}$

(l) Multiplying the first equation by 3 to give us 6 e^- in each equation:



Adding these together and cancelling the electrons on both sides gives the following:



$$(m) \ n(\text{Fe}^{2+}) = 0.05683 \text{ M} \times 34.70 \text{ mL} = 1.972 \text{ mmol}$$

$$(n) \text{ From part (m), } n(\text{Fe}^{2+} \text{ required for total sample}) = 1.972 \text{ mmol}$$

$$n(\text{Fe}^{2+})_{\text{total}} = n(\text{Fe}^{2+} \text{ that reacted with } \text{MnO}_4^-) + n(\text{Fe}^{2+} \text{ that reacted with } \text{Cr}_2\text{O}_7^{2-})$$

$$\text{From the equations above, } n(\text{Fe}^{2+})_{\text{total}} = 5 \times n(\text{Mn}^{2+}) + 3 \times n(\text{Cr}^{3+})$$

$$\text{So } 5 \times n(\text{Mn}^{2+}) + 3 \times n(\text{Cr}^{3+}) \text{ (in 0.1848 g sample)} = 1.972 \text{ mmol}$$

$$\text{From part (k), } n(\text{Cr}^{3+}) + n(\text{Mn}^{2+}) \text{ (in 0.3647 g sample)} = 1.144 \text{ mmol}$$

Scaling this to a sample mass of 0.1848 g:

$$n(\text{Cr}^{3+}) + n(\text{Mn}^{2+}) \text{ (in 0.1848 g sample)} = 1.144 \text{ mmol} \times 0.1848 \text{ g} / 0.3647 \text{ g} = 0.5795 \text{ mmol}$$

$$\text{So } 5 \times n(\text{Cr}^{3+}) + 5 \times n(\text{Mn}^{2+}) = 5 \times 0.5795 \text{ mmol} = 2.897 \text{ mmol}$$

$$\text{But we saw above that } 5 \times n(\text{Mn}^{2+}) + 3 \times n(\text{Cr}^{3+}) = 1.972 \text{ mmol}$$

$$\text{So } 2 \times n(\text{Cr}^{3+}) = 2.897 \text{ mmol} - 1.972 \text{ mmol} = 0.925 \text{ mmol}$$

$$n(\text{Cr}^{3+}) = 0.925 \text{ mmol} / 2 = 0.463 \text{ mmol}$$

$$m(\text{Cr}) = 0.463 \text{ mmol} / 1000 \times 52.00 \text{ g mol}^{-1} = 0.0241 \text{ g}$$

$$\%(\text{Cr}) = 0.0241 \text{ g} / 0.1848 \text{ g} \times 100 = 13.0\%(\text{w/w})$$

Question 17

Polymers are an extremely important class of molecules, which comprise of small repeating units called monomers. There are a wide variety of polymers and polymerisation methods, however two of the most important are radical polymerisation and condensation polymerisation.

In organic chemistry, we use skeletal structures to represent organic molecules. We do not draw the carbon atoms or hydrogen atoms which are attached to carbon atoms.

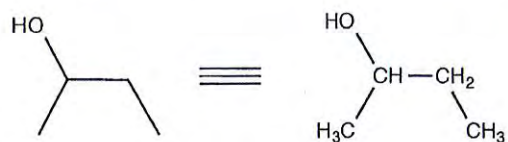


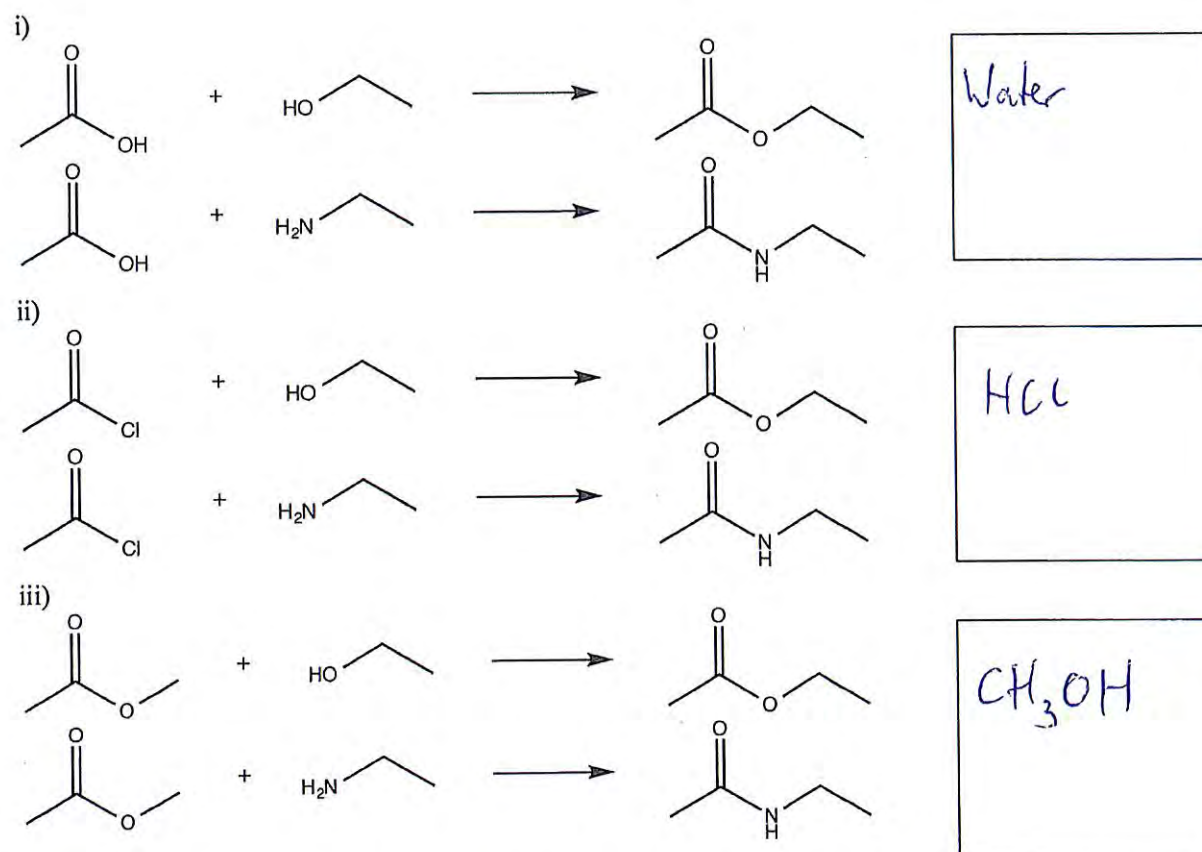
Table 1: Common functional groups

Functional Group Name	Name	Structure
Carboxylic acid	-oic acid	
Acid chloride	-oyl chloride	
Ester	-yl -oate	
Amide	-yl -amide	
Aldehyde	-al	
Ketone	-one	
Alcohol	-ol	
Amine	-amine	
Alkene	-ene	
Alkyne	-yne	

Note that R here can be a hydrogen or a carbon chain, except where when R being a hydrogen would change the name of the group, e.g. aldehydes and ketones. For alkenes and alkynes only, R can be another type of atom.

Before we start examining polymers, let us start by looking at some smaller molecules with the same functional groups. We are mostly interested in esters and amides for condensation polymerisation. We can use a wide variety of functional groups to make esters and amides, but the reaction is similar.

(a) What is the other product for these esterification and amidation reactions?

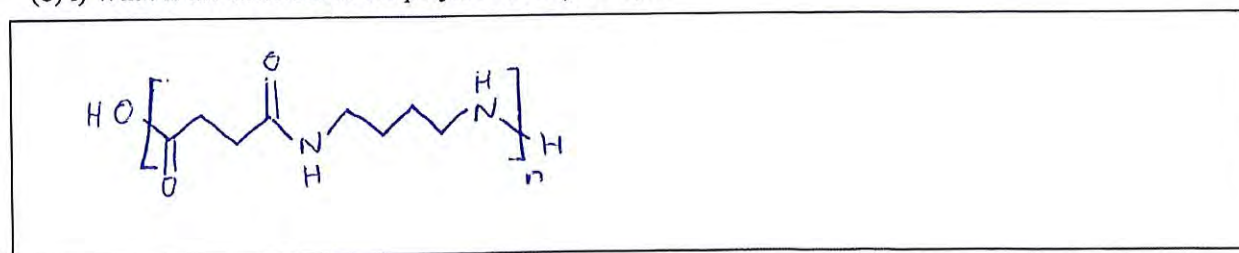


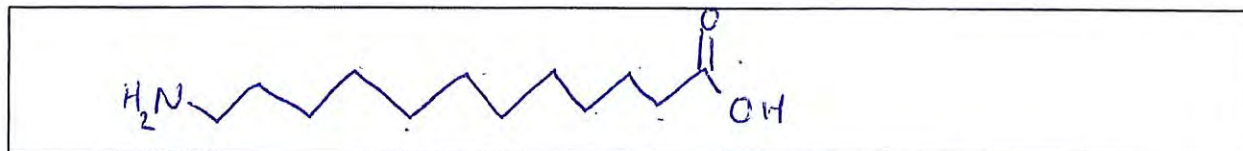
The nylons are a familiar group of polymers to many people as they are used widely in clothing.

Some can be synthesised by using a diamine and a dicarboxylic acid. For example, Nylon 6,6 is synthesised as below. The 6,6 indicates the number of carbons in the diamine and the number of carbons in the dicarboxylic acid respectively.

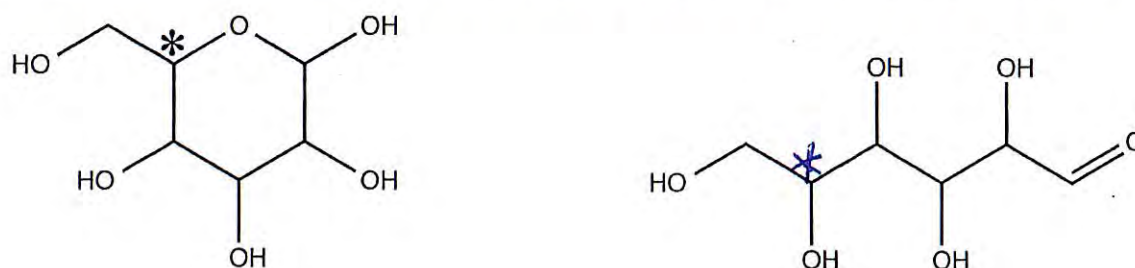


(b) i) What is the structure of the polymer for Nylon 4,4?

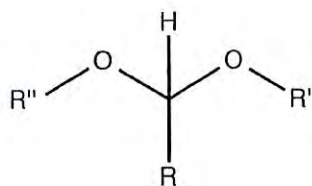


$$\text{H} - \left[\begin{array}{c} \text{H} \\ | \\ \text{N} - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O}) \\ | \\ \text{OH} \end{array} \right]_n$$


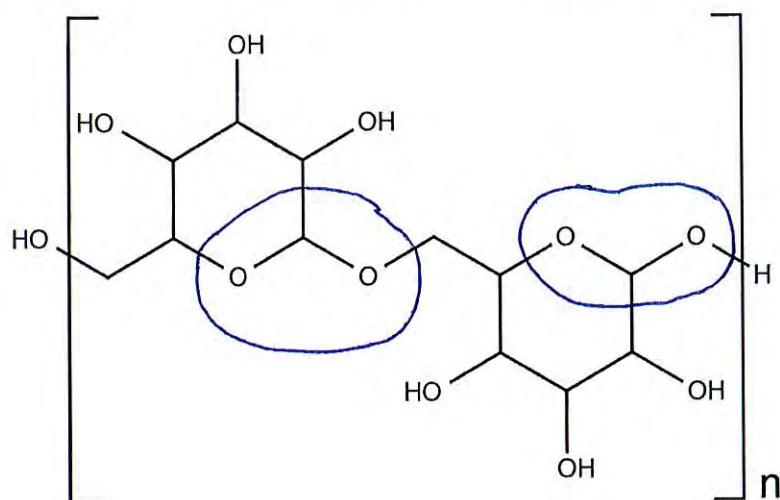
(c) i) Label which carbon atom of the open-chain form is the starred (*) carbon atom of the cyclic form.


$$\begin{array}{c} \text{H} \\ | \\ \text{HO} - \text{C} - \text{O} - \text{R}' \\ | \\ \text{R} \end{array} \quad \text{hemiacetal functional group}$$
OCC1(O)C(O)C(O)C(O)C1O

In starch, units are linked by acetal groups, condensing out water. The acetal group is shown below.



iii) Circle the acetal groups in the segment of starch drawn below.



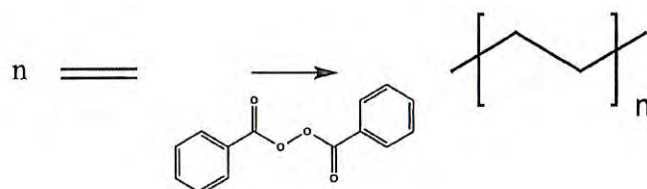
iv) Name two functional groups that react to form a hemiacetal.

aldehyde & alcohol

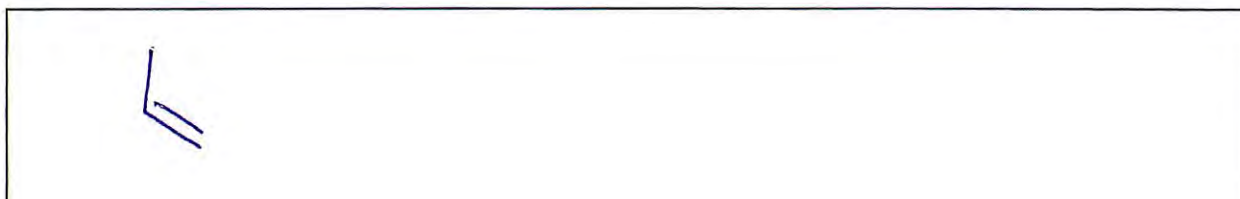
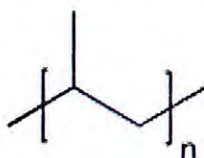
v) Name two functional groups that react to form an acetal.

hemiacetal & alcohol

Condensation polymerisation is not the only method we have of making polymers. In radical polymerisations, we break a weaker double bond to form a stronger single bond. We also require an initiator, like potassium persulfate or benzoyl peroxide to start the reaction. One example shown below of this shown below is the polymerisation of ethene to polyethylene using benzoyl peroxide as the initiator. Behaviour at the end of the polymer chains is complicated and we need not consider the ends of the chains.



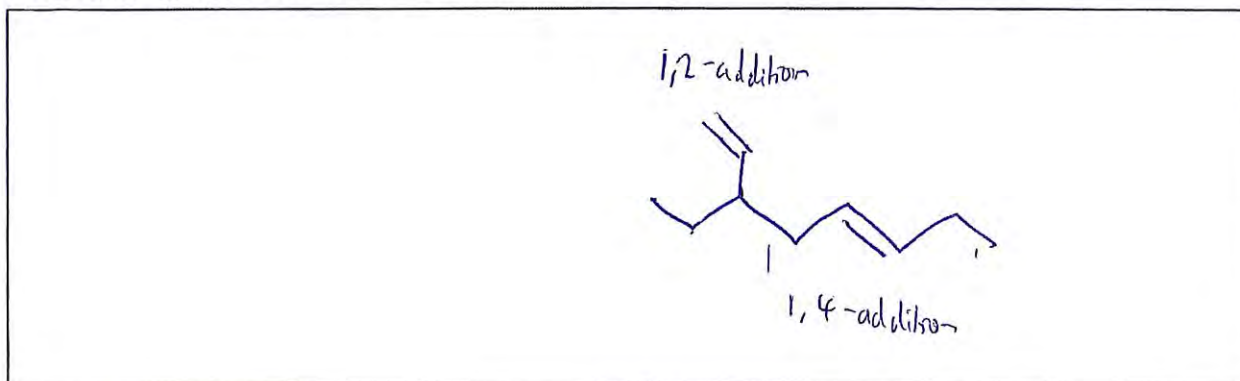
d) i) A similar polymer can also be formed and a segment is shown below. What is the monomer?



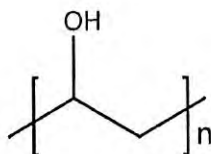
Another polymer polybutadiene is formed by the radical polymerisation of butadiene, shown below.



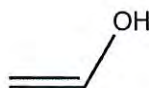
ii) As butadiene has two double bonds, there are two possible ways that it can polymerise. Draw a segment of polymer showing both the ways butadiene can polymerise.



Polyvinyl alcohol is a water-soluble polymer and is used in emulsion polymerisations, which are another method of polymerisation.



You are tasked with synthesising a sample and are provided with a number of jars of chemicals. One jar is labelled “ethenol (vinyl alcohol)” and the structure of ethenol is shown below. You however know that this label is incorrect, as ethenol, like glucose, tautomerises almost completely to another structure.



iii) What is the actual structure of the contents of the jar?



On the bench, there are jars labelled “acetic acid”, “potassium persulfate”, “ethanol”, “ethenol” “butanal” and “vinyl acetate”.

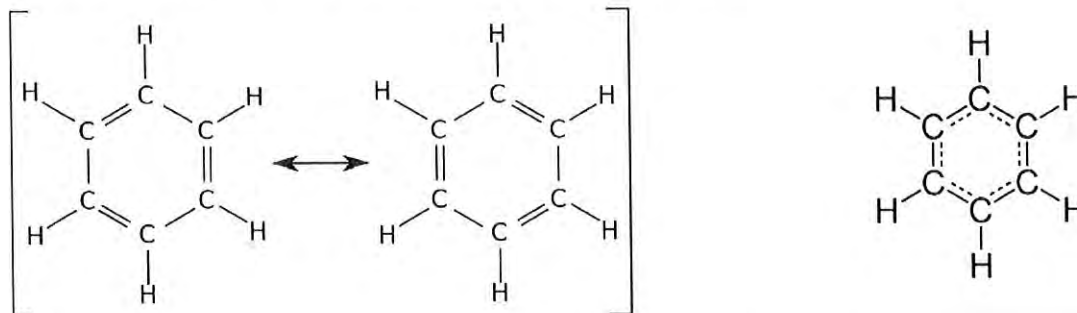
Acetic acid	Potassium persulfate	Ethanol	Ethenol	Butanal	Vinyl acetate

Question 17 continues on the next page.

iv) Propose the steps of a synthesis of PVA using the provided chemicals. You may like to review the reactions in part (a).

1. Polymerise vinyl acetate with $K_2S_2O_8$ as initiator to form poly(vinyl acetate)
2. React the formed poly(vinyl acetate) with ethanol in ~~a~~ as in (a)iii) to form poly(vinyl alcohol) and ethyl acetate.

Many students have the mistaken belief that chemical structures were correctly worked out only after modern instrumentation and analytical tools became available. It may come as a surprise that by 1910, structures were formulated for more than 200,000 unique organic compounds! One of the compounds with an interesting history is benzene (C_6H_6), whose structure is shown below. Benzene is a cyclic aromatic hydrocarbon in which all the carbon-carbon bonds are equal.



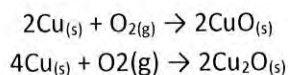
What is the empirical formula of benzene?

CH

The pivotal moment in the history of benzene was the announcement of its discovery by Michael Faraday to the Royal Society of Chemistry on June 16, 1825. He isolated what he then called “bicarburet of hydrogen” from a byproduct formed when producing “illuminating gas” for lights. After purifying this compound by fractional distillation and crystallisation, he performed a number of experiments to identify it.

To determine the empirical formula, Faraday analysed the products of combustion by weight by passing the vapour of benzene over heated copper(II) oxide. Copper(II) oxide can be made by heating elemental copper in pure oxygen, but this method produces some copper(I) oxide as well.

Write equations for the synthesis of copper(I) oxide and copper(II) oxide from their elements.



The following is a paraphrased extract from Faraday's paper, in which he reacted the unknown substance with copper(II) oxide completely to produce only carbon dioxide and water:

"The following is a result obtained when it was passed in vapour over heated copper(II) oxide. 0.776 grain of the unknown substance produced 5.6 cubic inches of carbonic gas (at a temperature of 60° and a pressure of 29.98 inches); and 0.57 grain of water were collected."

Carbonic gas is an old name for carbon dioxide, because it dissolves in water to produce carbonic acid. The grain is an old unit of weight, and its conversion to SI units is not required in this problem.

What percentage of water by weight is hydrogen?

$$\begin{aligned}\text{MW}(\text{H}_2\text{O}) &= 18.016 \\ \% &= 2 \times 1.0008 / 18.016 \times 100 = 11.19\%\end{aligned}$$

How many grains of hydrogen did the substance contain originally?

$$0.57 \text{ grain H}_2\text{O} \times 11.19\% = 0.064 \text{ grain hydrogen}$$

The 5.6 cubic inches of gas produced in this experiment are equivalent to 0.761704 grain of carbon.

What is the ratio of mass of carbon to mass of hydrogen in this sample of benzene.

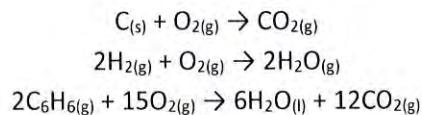
$$0.761704 \text{ grain} / 0.064 \text{ grain} = 11.9$$

What is the empirical formula of benzene when determined by this method?

Since $\text{MW}(\text{C}) : \text{MW}(\text{H}) = 12 \text{ approx} = 11.9$, the empirical formula is CH

Faraday also confirmed his results by detonating the benzene vapour in pure oxygen.

Write the formula for complete combustion of carbon, hydrogen, and benzene vapour in oxygen.



Faraday gives us an account of his experimental detonation of a mixture of 1 part benzene vapour with 19.6 parts oxygen gas. Not all the oxygen is used up, since the 19.6 parts of oxygen is in excess. Again, the paraphrased extract is shown below:

7 volumes of this mixture were detonated in a tube by an electric spark, and the total volume decreased as a result to 6.13 volumes; The resulting gas mixture was acted upon by potash to further decrease the gas volume to 4 volumes. These remaining 4 volumes were pure oxygen.

Liquid water is formed from this reaction and not counted as gaseous volume. Potash is an old name for potassium hydroxide which reacts with carbon dioxide to form solid potassium carbonate.

How many volumes of carbon dioxide were produced in the combustion process?

Potash absorbs CO_2 from 6.13 to 4 volumes
Therefore 2.13 volumes were CO_2

How many volumes of oxygen were consumed in the combustion process?

$7 - 4 = 3$ volumes of gas were consumed in this combustion
 $V(\text{"benzene"}) = 1/20.6 \times 7 = 0.34$ volumes to begin with
Therefore $V(\text{O}_2) = 3 - 0.34 = 2.66$ volumes consumed

The volume of a gaseous substance is directly proportional to molar amount of the substance.

What is the ratio of mass of carbon to mass of hydrogen in the unknown substance, as determined by this combustion experiment? From this ratio, what is the empirical formula of benzene?

2.13 volumes CO_2 produced. Therefore (from combustion equation), 2.13 volumes O_2 consumed in the reaction with carbon.

$$\text{Then } n(\text{C}) = k \times 2.13$$

Therefore $2.66 - 2.13 = 0.53$ volumes of oxygen reacted with hydrogen.

$$\text{From combustion equation, } V(\text{H}_2) = 2 \times 0.53 = 1.06 \text{ volumes}$$

$$\text{So } n(\text{H}) = k \times 2 \times 1.06 = k \times 2.12$$

$$n(\text{C}):n(\text{H}) = 1.00 \text{ so empirical formula} = \text{CH}$$

At the time of Faraday's experiments, hydrogen was not yet known as a diatomic gas, but thought of as monoatomic. This meant that carbon was assigned a molar mass of 6.00 and oxygen had a molar mass of 8.00, relative to hydrogen, which weighed 1.00.

***What did Faraday calculate as the molar mass of benzene, using only the data from this combustion experiment?**

0.34 volumes of this compound react to produce the equivalent of 2.13 volumes of C and 1.06 volumes of H.

Therefore 1 volume of the compound forms 6.26 volumes of C and 3.12 volumes of H.

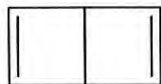
$$\text{So } k \times \text{MW}(\text{benzene}) = k \times 6.26 \times 6.00 + k \times 3.12 \times 1.00 = k \times 81.52$$

$$\text{Therefore } \text{MW}(\text{benzene}) = 40.68 \text{ g mol}^{-1}$$

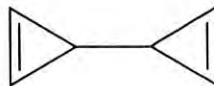
Having determined the molar mass of benzene, the next challenge for chemists was to understand the structure of benzene. Because of its highly unsaturated structure and unusual reactivity, there was a lot of debate as to the true chemical nature of benzene. Several structures were proposed for benzene, shown below, all of which satisfy the valency rules for carbon.



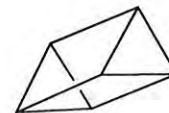
Kekulé



Dewar



Bicyclo-propenyl



Prismane

Draw one other structure for C_6H_6 that satisfies the valency rules for carbon.

Any valid structure (There are roughly 217 possibilities, over 300 if stereoisomers are included in the count)

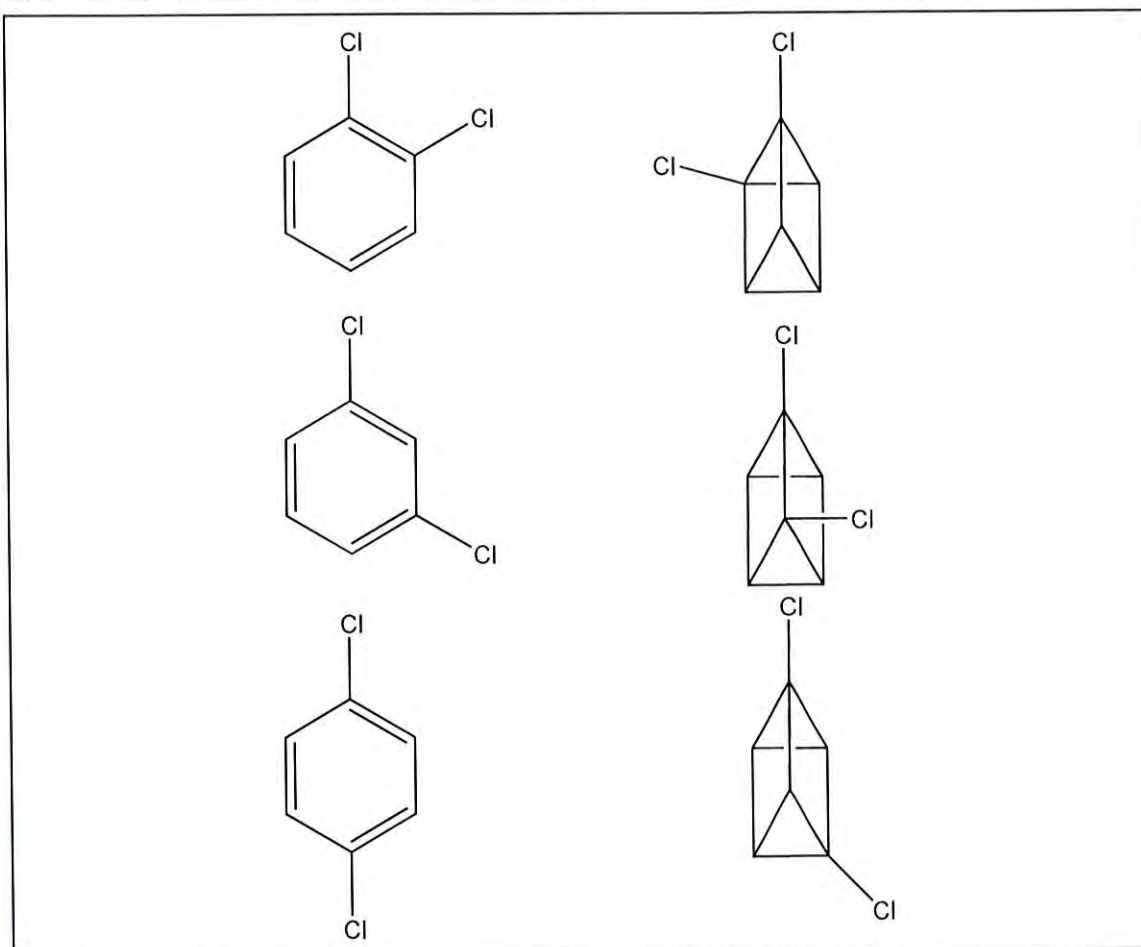
One of the arguments for the correct structure was the number of isomers (chemically different molecules) that were produced when substituting hydrogens for chlorine atoms. It was found that substituting one of the hydrogens for chlorine in the benzene molecule produced only one new molecule. This means all hydrogen atoms in the benzene molecule are equivalent.

Which of the structures above would produce only one monosubstituted product?

Only the Kekulé and prismane structures.

Substitution of two of the hydrogen atoms with two chlorine atoms ('disubstitution') results in three different products. This observation meant that only the Kekulé and prismane structures could potentially be the correct structure.

Draw the different three disubstituted isomers for each of the Kekulé and prismane structures.



The correct structure that we know today, the Kekulé structure, was identified because Van't Hoff realised that one of the structures you have drawn above is optically active, and substitution of benzene does not produce optically active compounds. One way to tell an optically active compound is that it contains a carbon atom with four single bonds, each bond attached to something different.

***Which of the isomers you have drawn above is optically active, and explain why?**

