Australian Science Olympiads

## 2015 AUSTRALIAN SCIENCE OLYMPIAD EXAM <br> CHEMISTRY - SECTIONS A \& B <br> TO BE COMPLETED BY THE STUDENT. USE CAPITAL LETTERS

Student Name: $\qquad$
Home Address:
Post Code: $\qquad$
Telephone: $\qquad$ ). $\qquad$ Mobile: $\qquad$
E-Mail: ............................................................. Date of Birth: ....../............. $\square$ Male Female Year 10 $\qquad$ Year $11 \square$ Other: $\qquad$

Name of School: State: $\qquad$

To be eligible for selection for the Australian Science Olympiad Summer School, students must be able to hold an Australian passport by the time of team selection (March 2016).

The Australian Olympiad teams in Biology, Chemistry, Earth and Environmental Sciences and Physics will be selected from students participating in the Australian Science Olympiad Science Summer School.

Please note - students in Yr12 in 2015 are not eligible to attend the 2016 Australian Science Olympiad Science Summer School

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Page 1 of 29

## Time Allowed:

## Reading Time: 10 minutes

## Examination Time: 120 minutes

## INSTRUCTIONS

- Attempt ALL questions in ALL sections of this paper.
- Permitted materials: Non-programmable non-graphical calculator, pens, pencils, erasers and a ruler.
- Answer SECTION A on the Multiple Choice Answer Sheet provided. Use a pencil.
- Answer SECTION B in the spaces provided in this paper. Write in pen and use a pencil only for graphs.
- Ensure that your diagrams are clear and labelled.
- All numerical answers must have correct units.
- Marks will not be deducted for incorrect answers.
- Rough working must be done only on pages 27 to 28 of this booklet.
- Relevant data that may be required for a question will be found on page 3 .
- Do not staple the multiple choice answer sheet to this booklet.


## MARKS

| SECTION A | 15 multiple choice questions | 30 marks |
| :--- | :--- | :--- |
| SECTION B | 3 short answer questions | 90 marks |
|  | Total marks for the paper | 120 marks |


| Avogadro constant (N) $\quad 6.022 \times 10^{23} \mathrm{~mol}^{-1}$ | Velocity of light (c) $\quad 2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$ |
| :---: | :---: |
| 1 faraday 96,486 coulombs | Density of water at $25^{\circ} \mathrm{C} \quad 0.9971 \mathrm{~g} \mathrm{~cm}^{-3}$ |
| 1 coulomb $1 \mathrm{~A} \mathrm{~s}^{-1}$ | Acceleration due to gravity $\quad 9.81 \mathrm{~m} \mathrm{~s}^{-2}$ |
| Universal gas constant (R) $8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-}$ $8.206 \times 10^{-2} \mathrm{~L} \mathrm{~atm} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ | 1 newton ( N ) $1 \mathrm{~kg} \mathrm{~m} \mathrm{~s}^{-2}$ |
| Planck's constant (h) $\quad 6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$ | 1 pascal ( Pa ) $1 \mathrm{~N} \mathrm{~m}^{-2}$ |
| ```Standard temperature and pressure (STP) 273 K and 100 kPa \(0^{\circ} \mathrm{C}\) and 100 kPa \(0^{\circ} \mathrm{C}\) and 1 bar \(0^{\circ} \mathrm{C}\) and 750 mm Hg``` | $\begin{aligned} & \mathrm{p} H=-\log _{10}\left[\mathrm{H}^{+}\right] \\ & \mathrm{p} H+\mathrm{p} O H=14.00 \text { at } 25^{\circ} \mathrm{C} \\ & K_{\mathrm{a}}=\left\{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]\right\} /[\mathrm{HA}] \\ & \mathrm{p} H=\mathrm{p} K_{\mathrm{a}}+\log _{10}\left\{\left[\mathrm{~A}^{-}\right] /[\mathrm{HA}]\right\} \\ & \mathrm{PV}=\mathrm{nRT} \\ & \mathrm{E}=\mathrm{h} v \\ & \mathrm{c}=v \lambda \\ & \text { Surface area of sphere } \mathrm{A}=4 \pi \mathrm{r}^{2} \\ & \hline \end{aligned}$ |
| Molar volume of ideal gas at STP $\quad 22.71 \mathrm{~L}$ |  |
| $1 \mathrm{bar}=100 \mathrm{kPa}$ |  |

## Periodic table of the Elements



[^0]Page 3 of 29

## SECTION A: MULTIPLE CHOICE USE THE ANSWER SHEET PROVIDED

1. What is the concentration (in $\mathrm{mol} \mathrm{L}^{-1}$ ) of $\mathrm{Na}^{+}$ions in a solution prepared by diluting 250.0 mL of $0.550 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{Na}_{2} \mathrm{SO}_{4}$ to 1250 mL ?
(a) $0.110 \mathrm{~mol} \mathrm{~L}^{-1}$
(b) $0.138 \mathrm{~mol} \mathrm{~L}^{-1}$
(c) $0.220 \mathrm{~mol} \mathrm{~L}^{-1}$
(d) $0.275 \mathrm{~mol} \mathrm{~L}^{-1}$
(e) $\quad 0.550 \mathrm{~mol} \mathrm{~L}^{-1}$
2. Which compound contains the highest percentage by mass of magnesium $(\mathrm{Mg})$ ?
(a) $\mathrm{MgNH}_{4} \mathrm{PO}_{4}$
(b) $\quad \mathrm{Mg}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}$
(c) $\quad \mathrm{Mg}_{2} \mathrm{P}_{4} \mathrm{O}_{7}$
(d) $\quad \mathrm{Mg}_{3}\left(\mathrm{PO}_{4}\right)_{2}$
(e) $\mathrm{MgHPO}_{4}$
3. Which one of the following is not assumed by the kinetic theory of gases?
(a) Gases are composed of particles in random motion.
(b) Gas particles do not attract or repel each other.
(c) Gas particles constantly collide with each other.
(d) The size of gas particles is negligible compared to the size of the container.
(e) When gas particles collide, kinetic energy is lost.
4. The formula for terbium phosphate is $\mathrm{TbPO}_{4}$. What is the formula for terbium sulfate?
(a) $\quad \mathrm{Tb}_{2} \mathrm{SO}_{4}$
(b) $\quad \mathrm{TbSO}_{4}$
(c) $\quad \mathrm{Tb}_{2}\left(\mathrm{SO}_{4}\right)_{3}$
(d) $\quad \mathrm{Tb}\left(\mathrm{SO}_{4}\right)_{2}$
(e) $\quad \mathrm{Tb}_{3}\left(\mathrm{SO}_{4}\right)_{2}$
5. The molecular compound $\mathrm{BH}_{3}$ has three bonding pairs of electrons and no lone pairs of electrons around the central boron atom. What is the shape of $\mathrm{BH}_{3}$ ?
(a) bent
(b) linear
(c) tetrahedral
(d) triangular (trigonal) planar
(e) triangular (trigonal) pyramidal

6 A student dissolves solid calcium carbonate in an excess of $0.01 \mathrm{~mol} \mathrm{~L}^{-1}$ nitric acid while stirring, and is looking for ways to make this reaction faster. Which of the following actions would increase the rate of reaction?
(a) Adding distilled water to the solution while stirring.
(b) Cooling the nitric acid before adding the calcium carbonate.
(c) Decreasing the concentration of nitric acid.
(d) Heating the nitric acid before adding the calcium carbonate.
(e) Increasing the volume of nitric acid.
7. Which list below gives non-metals that can be found in their elemental form in nature?
(a) neon, phosphorus, fluorine
(b) helium, hydrogen, iodine
(c) helium, carbon, fluorine
(d) nitrogen, chlorine, sulfur
(e) oxygen, chlorine, phosphorus
8. Solid silver was added to a solution of copper(II) nitrate at standard conditions. Given that silver is a less reactive metal than copper, which of the following observations would be most likely?
(a) A blue precipitate forms on the silvery solid and the solution turns colourless.
(b) The blue solid dissolves in the colourless solution and a silvery precipitate is formed.
(c) The silvery solid dissolves and a blue precipitate forms; the blue colour of the solution fades.
(d) The silvery solid dissolves into the blue solution, and an odourless gas is evolved.
(e) No visible reaction.
9. $\quad 25.00 \mathrm{~mL}$ of each of the following solutions is added to 20 g of solid $\mathrm{MgCO}_{3}$. After the reactions are complete, which of the solutions will produce the largest volume of $\mathrm{CO}_{2}$ at room temperature and pressure?
(a) $1 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{H}_{2} \mathrm{SO}_{4}$
(b) $2 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HC} \ell$
(c) $2 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HNO}_{3}$
(d) $2 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{H}_{2} \mathrm{SO}_{4}$
(e) $3 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HC} \ell$
10. Which of the following compounds contains polar covalent bonds, but has no net dipole moment?
(a) $\mathrm{CO}_{2}$
(b) $\mathrm{H}_{2} \mathrm{O}$
(c) HCN
(d) $\mathrm{N}_{2}$
(e) $\mathrm{NaC} \ell$
11. What is the correct Lewis (electron dot) structure for $\mathrm{N}_{2} \mathrm{O}$ ?
(a)

(b)

(c)

(d)

(e)

12. Which one of the following responses is the correct name for the structure below?

(a) hex-2-yne
(b) hex-4-yne
(c) hept-2-yne
(d) hept-4-yne
(e) hex-2-ene
13. Which of the following is true of elements as one moves from left to right across a period of the periodic table?
(a) electronegativity increases, atomic radius increases
(b) electronegativity decreases, atomic radius increases
(c) electronegativity increases, atomic radius does not change
(d) electronegativity increases, atomic radius decreases
(e) electronegativity decreases, atomic radius decreases
14. How is the structure and bonding in diamond best described?
(a) covalent molecular
(b) covalent network
(c) metallic
(d) molecular
(e) polymeric
15. Which of these pairs of compounds could be separated on the basis of their solubility in water?
(a) $\mathrm{AgNO}_{3} \quad \mathrm{CaBr}_{2}$
(b) $\quad \mathrm{CC}_{4} \quad \mathrm{C}_{6} \mathrm{H}_{14}$
(c) $\quad \mathrm{PbCO}_{3} \quad \mathrm{CaCO}_{3}$
(d) $\quad \mathrm{SiO}_{2} \quad \mathrm{BaSO}_{4}$
(e) $\mathrm{ZnSO}_{4} \quad \mathrm{AgC} \ell$

## ANSWER IN THE SPACES PROVIDED

## Question 16

Atomic absorption spectrophotometry (AAS) is a simple and rapid method for the quantitative determination of metals in solution. In this technique, the solution is sprayed into a flame; the metal atoms then absorb light from a beam passing through the flame. The measured absorbance is directly proportional to the concentration of the metal in the solution.

Before a sample containing an unknown concentration of metal can be determined, a standard curve needs to be generated by measuring the absorbance of known concentrations of metal. In this question we will examine the analysis of steel for iron and other elements. For our standard, iron(III) oxide will be dissolved in nitric acid.
(a) Write a balanced equation for the reaction of iron(III) oxide with nitric acid.
(b) Calculate the molar mass of iron(III) oxide $\left(\mathrm{Fe}_{2} \mathrm{O}_{3}\right)$.
0.1292 g iron(III) oxide is dissolved in nitric acid and made up to 250.0 mL in a volumetric flask.
(c) Calculate the chemical amount (in mol or mmol ) of iron(III) oxide dissolved per litre of solution.
$\square$

It is normal in AAS to express solution concentrations in terms of the concentration of metal ions present.
(d) Calculate the concentration of iron(III) ions in the solution (in $\mathrm{mol} \mathrm{L}^{-1}$ ).

The concentration range used in iron AAS is typically $2-10 \mathrm{mg}$ of iron per litre. Dilutions were performed as necessary to generate a standard curve. The linear fit was good and the equation of the line of best fit was $y=0.1078 x+0.0072$, with $y$ representing absorbance and $x$ representing $m g$ of iron per litre.


A steel sample of mass 0.1082 g was digested in concentrated nitric acid, cooled, filtered and made up to 500.0 mL volumetric flask (this procedure converts all iron in the steel sample to $\mathrm{Fe}^{3+}$ ). A 10.00 mL sample of this solution were taken and made up to 500.0 mL in a volumetric flask. The solution was analysed on the same AAS machine as the standard curve, with the absorbance measured to be 0.4207.
(e) Calculate the percentage by mass of iron in the steel.

A stainless steel sample is known to contain iron ( $83.54 \%$ by mass, determined by AAS as described previously) as well as chromium, manganese, carbon, silicon and oxygen. A 0.3647 g sample of this stainless steel was digested in concentrated nitric acid, cooled, filtered and made up to 100.0 mL in a volumetric flask. This procedure converts all iron in the stainless steel sample to $\mathrm{Fe}^{3+}$, chromium to $\mathrm{Cr}^{3+}$ and manganese to $\mathrm{Mn}^{2+}$.
(f) Calculate the mass of iron present in the 0.3647 g sample.
$\square$
(g) Calculate the chemical amount (in mol or mmol) of $\mathrm{Fe}^{3+}$ present in a 10.00 mL sample of the digested stainless steel solution.

EDTA is a complexing agent that reacts in a $1: 1$ mole ratio with many metal ions including $\mathrm{Fe}^{3+}, \mathrm{Cr}^{3+}, \mathrm{Mn}^{2+}$ and $\mathrm{Zn}^{2+}$. For example $\mathrm{Zn}^{2+}$ reacts as follows:

$$
\mathrm{Zn}^{2+}+\mathrm{EDTA}^{4-} \rightarrow[\mathrm{Zn}(\mathrm{EDTA})]^{2-}
$$

50.00 mL of 0.02143 M EDTA was added to a 10.00 mL sample of the digested stainless steel solution and the resulting solution heated for 15 minutes. The excess EDTA required on average 20.53 mL of 0.02005 M $\mathrm{Zn}^{2+}$ for complete reaction.
(h) Calculate the chemical amount (in mol or mmol ) of $\mathrm{Zn}^{2+}$ required for reaction with the excess EDTA.
(i) Calculate the chemical amount (in mol or mmol) of EDTA that reacted with the $\mathrm{Fe}^{3+}, \mathrm{Cr}^{3+}$ and $\mathrm{Mn}^{2+}$ ions present in the 10.00 mL sample of the digested stainless steel solution.
(j) Calculate the sum of the chemical amounts of $\mathrm{Cr}^{3+}$ and $\mathrm{Mn}^{2+}$ ions (in mol or mmol) present in the 10.00 mL sample of the digested stainless steel solution.
(k) Calculate the sum of the chemical amounts of $\mathrm{Cr}^{3+}$ and $\mathrm{Mn}^{2+}$ (in mol or mmol) present in the original 0.3647 g stainless steel sample (n.b. if you do not get an answer to this part of the question you may use $\mathbf{n}\left(\mathbf{C r}^{\mathbf{3 +}}\right)+\mathbf{n}\left(\mathrm{Mn}^{2+}\right)$ in the $\mathbf{0 . 3 6 4 7} \mathrm{g}$ sample $\left.=1.200 \times 10^{-3} \mathbf{~ m o l ~ f o r ~ s u b s e q u e n t ~ p a r t s ~ o f ~ t h e ~ q u e s t i o n ~}\right)$.

In a separate experiment, 0.1848 g of the same stainless steel dissolved in $\mathrm{HNO}_{3}$ and heated. The resulting solution is treated with potassium peroxydisulfate $\left(\mathrm{K}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}\right)$, which oxidises $\mathrm{Cr}^{3+}$ to $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$ and $\mathrm{Mn}^{2+}$ to $\mathrm{MnO}_{4}{ }^{-}$.
(1) Write a balanced equation for the oxidation of $\mathrm{Cr}^{3+}$ to $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ by peroxydisulfate, given the following half equations:

$$
\begin{gathered}
\mathrm{S}_{2} \mathrm{O}_{8}^{2-}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{SO}_{4}{ }^{2-} \\
2 \mathrm{Cr}^{3+}+7 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+14 \mathrm{H}^{+}+6 \mathrm{e}^{-}
\end{gathered}
$$

Following boiling (to decompose any excess peroxydisulfate), cooling and filtration, the solution required 34.70 mL of standard $0.05683 \mathrm{M} \mathrm{Fe}^{2+}$ to completely react with all of the $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$ and $\mathrm{MnO}_{4}^{-}$present.
(m) Calculate the chemical amount (in mol or mmol ) of $\mathrm{Fe}^{2+}$ required in this reaction.

The equations for the reduction of $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ and $\mathrm{MnO}_{4}^{-}$by $\mathrm{Fe}^{2+}$ are as follows:

$$
\begin{aligned}
\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+14 \mathrm{H}^{+}+6 \mathrm{Fe}^{2+} & \rightarrow 2 \mathrm{Cr}^{3+}+7 \mathrm{H}_{2} \mathrm{O}+6 \mathrm{Fe}^{3+} \\
\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+5 \mathrm{Fe}^{2+} & \rightarrow \mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}+5 \mathrm{Fe}^{3+}
\end{aligned}
$$

(n) Calculate the percentage by mass of chromium in the stainless steel sample.

## 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 | -oic acid |
| :--- | :--- | :--- |
| Carboxylic acid | -oyl chloride |  |
| Acid chloride | -yl -oate |  |
| Ester | -yl -amide |  |
| Amide | -yne |  |
| Aldehyde | -al |  |
| Alkyne | -amine |  |
| Alkene | -one |  |

Page 13 of 29
2015 Australian Science Olympiad Exam - Chemistry
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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?
i)

$\square$
ii)



iii)




The nylons are a familiar group of polymers to many people as they are used widely in clothing.
Some can 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 ?
ii) Nylon 12 is produced using a different monomer than that used in Nylon 4,4 or 6,6 . What is the structure of the monomer given the polymer?


A biologically important class of polymers are the starches, which are familiar from food. We first examine glucose, which is the monomer of starch. It can exist in open-chain and cyclic isomers (compounds with the same formula). This process of interconversion between the open-chain and cyclic forms is called tautomerism, as there is an equilibrium between two isomers. Glucose, however, is almost completely found in the cyclic form.
(c) i) Label which carbon atom of the open-chain form is the starred $\left(^{*}\right)$ carbon atom of the cyclic form.



Another functional group, the hemiacetal, which is shown below, is formed in the cyclic form.

hemiacetal functional group
ii) Circle the hemiacetal group in the cyclic form shown below.


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

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 |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |

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

## Question 18

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 $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)$, whose structure is shown below. Benzene is a cyclic aromatic hydrocarbon in which all the carbon-carbon bonds are equal.

(a) What is the empirical formula of benzene?

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.
(b) Write an equation for the synthesis of copper(I) oxide and an equation for the synthesis of copper(II) oxide both 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 $60^{\circ}$ 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.
(c) What percentage of water by weight is hydrogen?

(d) How many grains of hydrogen did the substance contain originally?


The 5.6 cubic inches of gas produced in this experiment are equivalent to 0.761704 grain of carbon.
(e) What is the ratio of mass of carbon to mass of hydrogen in this sample of benzene?
$\square$
(f) What is the empirical formula of benzene when determined by this method?

Faraday also confirmed his results by detonating the benzene vapour in pure oxygen.
(g) Write an equation for complete combustion of (i) carbon, (ii) hydrogen, and (iii) benzene vapour in excess 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.
(h) How many volumes of carbon dioxide were produced in the combustion process?
(i) How many volumes of oxygen were consumed in the combustion process?

The volume of a gaseous substance is directly proportional to molar amount of the substance.
(j) 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?

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 .
(k) What did Faraday calculate as the molar mass of benzene, using only the data from this combustion experiment?

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 (A Triangular Prism)
(l) Draw one other structure for $\mathrm{C}_{6} \mathrm{H}_{6}$ that satisfies the valency rules for carbon.


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.
(m) Which of the structures above would produce only one monosubstituted product?

Question 18 continues on the next page.

Substitution of two of the hydrogen atoms with two chlorine atoms ('disubstitution') results in three different products. This observation meant that only the Kekule and prismane structures could potentially be the correct structure.
(n) 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.
(o) Which of the isomers you have drawn above is optically active?

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Page 27 of 29
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Page 28 of 29
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## Integrity of Competition

If there is evidence of collusion or other academic dishonesty, students will be disqualified. Markers' decisions are final.


[^0]:    Atomic mass values given here are to four significant figures. A value given in parentheses denotes the mass of the longest-lived isotope.

