GAS COMBUSTION FOR LABORATORY ANALYSIS

A

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INTRODUCTION
Gas analysis is carried on by any one of several methods, which are suggested by the nature of the gases themselves. The gases may be separated:—

1. By successive absorption of the different constituents and the volumetric determination of each.
2. By absorption and subsequent determination by titration or weighing.
3. By combustion and volumetric or gravimetric determination of the products.

Of these, this paper shall treat of the last named. The combustion of the gas may be accomplished as a slow burning process as the gas enters the combustion chamber, or else an explosion after the gas has been mixed with the essential oxygen, which may, in turn, come from a tank of commercial oxygen, or from atmospheric oxygen. The explosion method is limited by the size and strength of equipment, and further, if water is the confining liquid, certain authors say that CO₂ is forced into solution by the sudden pressure of the explosion and that this gas in the water is given up only with difficulty.

Slow combustion consists of passing the gas into a combustion chamber that has been filled previously to the desired quantity with some source of the essential oxygen, which is a calculated excess, and allowing the combustion to take place just as the combustible gas enters the chamber. The ignition for either the explosion or the slow burning process may be accomplished by either an electrically heated
spiral of metallic wire, or by a spark from a source of high potential as a 15,000 volt spark coil.

These two and the copper oxide methods of slow combustion are to be treated. A study is made of the errors of determination by each, technical difficulties of each, and with the view of developing the equipment and methods of actual procedure for analysis. So important and critical are some of these, that for specific parts of the set up, months were put in on concentrated effort and study of reproducible results.

In no field of science is the need for a clear conception of the meaning of certain terms more necessary than that under discussion. Such terms as fire, flame and combustion for centuries have been household expressions, and as such they have been used frequently to denote phenomena, which to the popular mind may appear alike, but which in reality are separated widely from each other. By combustion it is now usual to imply some form of chemical change accompanied by either, or both, heat and light. Thus heating a platinum wire to redness, or the electrical discharge in a Geissler tube are not examples of combustion, since they are not accompanied by chemical change. Examples of true combustion are found in the entire absence of oxygen, however. In 1912, Egerton showed that the hydrocarbon, coal gas, burned in chlorine to form soot and the yellowish green chlorine was replaced by the steamy clouds.

of hydrochloric acid fumes. Similarly, yellow phosphorus in bromine vapor, or powdered arsenic in liquid bromine produces true combustion. Copper foil burns brilliantly in sulfur vapor, and a red hot iron rod pressed into a lump of sulfur burns with the sulfur vapor thus produced to produce scintillating globules of molten ferrous sulfide.

Slow combustion may be in the absence of light, but accompanied by heat as the oxidation of food matter in the animal body which is merely slow in action. The temperature at which rapid combustion becomes independent of external supplies of heat is known as the ignition temperature. A mass of gas raised to incandescence by heat is termed a flame, this is produced only in those cases of combustion in which gases or vapors are present; of course there is such a thing as rapid surface combustion on a catalyzing surface as hydrogen or coal gas on platinized asbestos or porous fire brick in air. When a chemical reaction proceeds with a rise in temperature and an ever increasing velocity until a high maximum velocity is attained, an explosion or detonation results.
PART I

GENERAL METHODS OF COMBUSTION FOR ANALYSIS
This is a study of the analysis of gas mixtures, a part of the components of which may be separated by ordinary absorption and a part by combustion methods. Such mixtures may include all or part of the following gases:

- CO₂ - Carbon dioxide
- H₂ - Hydrogen
- I₂ - Iodine
- CH₄ - Methane
- O₂ - Oxygen
- C₂H₆ - Ethane
- C₆O - Carbon monoxide
- N₂ - Nitrogen

Other gases such as cyanogen, hydrogen-sulphide, etc., may be present but are determined by other methods in separate samples.

**Measuring The Sample**

Under all circumstances the first operation is the measuring of the gas. From the very nature of the gas it is clear that its quantity can be determined generally by measuring its volume more easily than by ascertaining its weight, thus this is one of the most important operations in gas analysis. It is well known that the volume of a gas is influenced by pressure, temperature, and the vapor tension of the liquid present.

By Boyle’s law, the density and the pressure of a gas are proportional to each other. The vapor tension of the confining or absorbing liquid causes an increase in volume. This increase is dependent upon temperature, independent of the pressure, and varies with the chemical nature of the liquid in question. Since all the experiments reported herein are of constant temperature, constant pressure, and varying volume, the comparison of volumes alone are used with no attempt
to reduce to standard conditions (except in the case of copper oxide combustion and a subsequent weighing), and the relations are given in per cent by volume, which reduce to the same value at standard conditions.

Professor Hempel, for whom the hot filament method of slow combustion analysis is named, shows that a moist gas of volume \( V \), temperature \( t \)°C., barometric pressure \( b \), and maximum tension of aqueous vapor at this temperature, \( e \), would have a volume \( V_0 \) at standard conditions according to the following equation:

\[
V_0 = V \frac{b - e}{760(1 - 0.00674t)}
\]

Procedure In Brief

Essentially the procedure consists of first confining a measured quantity of the gas in a graduated glass cylindrical burette, wherefrom the various components are successively removed by combustion, absorption, etc. After the gas mixture is treated in any of these steps, it is drawn back into the burette and measured again. The decrease in volume, if any, is determined and the percentage of the particular component under consideration calculated in terms of per cent by volume of the original mixture.

Apparatus

Gas analysis equipment is ordinarily divided into two general classes, namely, laboratory and portable models,
the former for accuracy and the latter for greater tolerance and portability. At the same time several types of burettes are used; the one approved by the U.S. Bureau of Mines is of 100 milliliter capacity graduated over the entire length in ml and 1/10 ml divisions, each ml being numbered, with zero at the top stopcock. Sometimes a pressure compensator is used with these burettes to insure constant volume-pressure relations when mercury is the confining fluid,—if water is used then no compensator is necessary.

Until short years ago it was difficult to obtain glass stopcocks which were perfectly tight, but the manufacture of glass apparatus has been so greatly improved of late that satisfactory instruments can now be procured easily. Dennis recommends reasonable certainty of absolute air-tightness can be obtained only with a minimum of stopcocks and fusing the glass tubes together which would otherwise be joined by rubber hose. Careful regrinding of straight bore stopcocks with short interval strokes and frequent renewals of very fine dry emery powder gives good joints when clean and lubricated with a preparation that does not deteriorate, work out the ends of the key, nor give off hydrocarbon vapors. Dennis recommends a superior design after Greiner and Friedrichs to prevent the channeling of the barrel of the stopcock.

1. Dennis, Hempel's Gas Analysis (1912) 50.
2. L. H. Dennis, Gas Analysis (1925) 115
Greiner and Friedrich stop cocks
The manifold which serves to connect the burette with the various pipettes is made of capillary glass tubing and the necessary glass stopcocks.

Absorption pipettes are of two common types, Francis auto-bubbler and Burrell contact. The former brings the gas into intimate contact with the solution in the form of fine bubbles. The foremost of the two chambers of the Burrell contact pipette is filled with glass tubes such that when the gas is forced into the pipette, the solution drops leaving the large surface of the tubes wet with the absorbing solution exposed to the gas. Various pipette arrangements are common, as one for each of the following: CO₂, H₂, and O₂, or else CO₂, O₂, and CO₂—according to the particular job for which the apparatus was designed.

The combustion pipette is made of a cylindrical Pyrex glass shell 1½ inches diameter and 5½ inches long with a capillary tube sealed longitudinally in the top and closed at the bottom with a number nine rubber stopper, thru which pass the glass-tube electrode-support posts and the leveling fluid entrance (connected by a rubber hose to the leveling bulb).

**Confining Liquids**

Certain authorities¹ say that for accuracy in measurement

¹ Burrell Manual For Gas Analysis, Burrell Tech Supp, Co.
of the gases, the confining fluid should be mercury, but that for ordinary work (including portable equipment) a 3% solution of sulphuric acid containing 20% sodium sulphate reduces the solvent power of water sufficiently to justify its use for CO₂ and the other gases present. The acidified sodium sulphate is then colored by an indicator, as phenolphthalein, or methyl orange, to make a more clearly defined level of the water in the burette against the graduations, and, further, the color will change to indicate the possibility of the liquid's having become alkaline and hence capable of absorbing CO₂, etc.

Hoffman¹ found that the saturating of the confining liquid with the gas was not satisfactory due to the changing composition during the analysis. He found that approximately 22% solution of sodium chloride was the best water solution and that it dissolved only about one-third as much as pure water. He states that acidified water is no better than pure water.

Dennis² says that on account of the solubility of gases in water and in the reagents, no great accuracy is attainable, even when the liquids are saturated with the gas mixture being analyzed, and that if very accurate results are desired, that the apparatus must unquestionably be filled with mercury.

¹. Feuerungstechnik (1926) 14, 98
². Dennis, Hempel's Gas Analysis (1912) 59
Order Of Analysis

The components of a gas mixture are usually removed in this order: CO₂, H₂O, CO, CH₄, and C₂H₆. However, some gas mixtures are adaptable to the scheme of analysis which determines CO₂, combustibles, and then O₂, in which event the O₂ in the original sample is accounted for as CO₂, H₂O, etc., in the combustible part before the absorption determines the residual O₂.

Where ethane and hydrogen are present, Burrell and Seibert¹ say that combustion by heated copper oxide in a U-tube is the approved method.

Methane and ethane are determined by combustion and measurement of the CO₂ formed. This procedure is necessary since these gases are not successfully removed by selective absorption as are most of the others.

The slow combustion of methane is by no means as simple as indicated by

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

Bone and Wheeler² in 1903 showed that the formation and decomposition of formaldehyde was one of the steps in the combustion of methane, and if sufficient oxygen is present, the oxidation proceeds on to CO₂ and H₂O. Armstrong³ suggested that methyl alcohol was the initial product, which rapidly decomposes to formaldehyde and steam. The mechanism

2. Trans. Chem. Soc. (1903) 83, 1074
3. Ibid., (1903) 83, 1088
of the reaction would be shown by:

$$\text{CH}_4 \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_2(\text{OH})_2 \rightarrow \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO}_2\text{CH} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

These products are methane, methyl alcohol, di-hydroxy methane, steam and formaldehyde, formic acid, carbonic acid, and finally carbon dioxide and water. H.D. Dakin (1912) gave a very similar theory differing in that formaldehyde decomposed into hydrogen and carbon monoxide, which on further oxidation gives water and carbon dioxide.

The various absorbing solutions and the methods of making them up and handling are given by Burrell and by Dennis.

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1. J.H. Friend (The Combustion of Combustion (1922)) says that the di-hydroxy methane is purely hypothetical, whereas the other products are evidenced experimentally.


3. J.H. Dennis, Gas Analysis (1925)
PART II

HOT FILAMENT METHOD FOR SLOW COMBUSTION
Heating Elements

The resort to the combustion of methane and ethane in hopes of completeness, and the accurate measuring of the CO₂ formed, in the absence of satisfactory selective absorption methods, since methane is fairly inert chemically, the temperature of combustion is rather high, thus the source of ignition must be quite hot. The following table gives the most important electrically heated wire spiral heating elements experimented with.

<table>
<thead>
<tr>
<th>Wire metal</th>
<th>Wire size</th>
<th>Maximum current (amp.)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>28</td>
<td>5</td>
<td>barely red; too low temp.</td>
</tr>
<tr>
<td>Platinum</td>
<td>60</td>
<td>?</td>
<td>burned out too readily</td>
</tr>
<tr>
<td>Platinum</td>
<td>60</td>
<td>1.5</td>
<td>slightest extra heat from combustion burns it out.</td>
</tr>
<tr>
<td>Nichrome</td>
<td>26</td>
<td>6</td>
<td>good, but burns out in air or O₂ on about the second heating; embrittles easily.</td>
</tr>
</tbody>
</table>

In each of these experiments, the ends of the heating element wire were stuck into the mercury columns, which served as mechanical support and electrical contact, similar to the design shown by Fielder, Jones, and Holbrook. Smaller diameter spirals (1/8 to 1/4 inch diameter) serve much better than the larger ones. Due to the melting down of the spiral's core.

1. Platinum wire, twisted pair.
to help maintain its shape is desired. Thin Pyrex tube as a core melted and gave way; heavier Pyrex caused the element wire to sag too much. Porter and Ovitz used the spiral without a core, with the terminals of the spiral connected to heavy platinum wires, which scaled thru the glass electrode supports at the lower ends. These heavy platinum wires, which served as mechanical support and electrical contact for the heating element, were inside the now mercury filled glass electrode support tubes.

All heating element temperatures were such that the ends of the spiral boiled the mercury out from the mercury legs, since yellow to white heat of the platinum or nichrome is necessary for combustion. This lead to a resort to the porcelain core, platinum spiral (supplied by Burrell) about 1/8 inch diameter and 5/8 inch long consisting of five turns of about number 30 size wire. This element requires about 6 amperes to heat it sufficiently for the combustion of methane; this requires about 5 volts. This type element clips into a spring contact at its ends after the fashion of a cartridge to facilitate replacements. This brought up the problem of a suitable type of heating element support and suitable material for its construction.

Heating Element Support

A number of requirements are found necessary to be satisfied in order to produce a satisfactory support for such an element. The spring-clip metallic portion of the support must be of the order of \( \frac{3}{4} \) inch in length in order to minimize the gas space necessary above the leveling fluid and yet give sufficient spring action to serve as the clip as well. The support wires should not lose too much of their springiness nor rigidity on becoming red hot, must not oxidize enough to give too poor an electrical contact, nor expand enough to cause the glass sealed joint to crack or start a gas leak. The glass to metal joint must stand rather sudden changes of temperature.

Stiff copper wire sealed thru glass is wet by the glass according to Housekeeper, of the Western Electric Company\(^1\), but it is found to oxidize too easily when in use and give poor electrical contact to the heating element. He showed how flattening the copper wire in certain experiments gave relief to the mechanical stresses set up in the joint. Almost any sort of heat expansion difficulty can be overcome with the use of nickel-iron alloys which can even be made with a negative coefficient of heat expansion\(^2\), or the same as common glass, or the same as Pyrex glass etc., but the oxidation difficulty when in use has not yet been met.

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2. Guillaume produced these a number of years ago, among which is the well known Invar.
The British General Electric Company coated this with copper (20% of the wire) to form the 'dumet' wire, and Dundon\textsuperscript{1} prepared high temperature seals by bronzing the wire, but both these have yet the disadvantage of the oxidation difficulty when subject to the temperature of the operation of the heating element when in use. Kaye\textsuperscript{2} recommends stainless steel for equipment where oxidation causes some difficulty, but the coefficient of thermal expansion is too great for glass, or Pyrex which would stand the temperature changes. Tungsten is too brittle for the work and it also oxidizes rather easily. In general platinum seals thru ordinary glass quite well, and for special high temperature and high pressure work McKelvey and Taylor\textsuperscript{3} produced large platinum to glass joints which worked well.

Cemented joints of various commercial types were tried with but little success.

The final form of the heating element support was made from half inch diameter Pyrex tubing 1/16 inch thick walls, using number 18 nichrome wire as the support wires. The preparation of the final support does not require the services of an expert glass blower, yet certain technique is manifestly required. The Pyrex tubing is heated in an oxygen-methane flame and a one-half inch section of the end flattened by

\begin{itemize}
\item[1.] Jnl. Amer. Chem. Soc. (1923) 45, 716
\item[2.] Kaye, High Vacua (1927) 59
\item[3.] Jnl. Amer Chem. Soc. (1920) 42, 1364
\end{itemize}
Combustion Pipette For Hot Filament Ignition
means of one inch broad faced tongs to just admit the freshly polished and shaped nichrome wires. With the wires quickly inserted, the Pyrex is heated further by the one inch broad flame and the tongs used to shape the flattened glass compactly about the wire. Compressing the plastic mass about the wires is better than depending on wetting the wire by higher temperature glass, which would frequently cause the glass to crack on cooling. No great heat is applied in order to prevent gassing at the glass to metal joint and subsequent leaks. Housekeeper\(^1\) reports that if the metals to be used for sealing thru glass are kept at 800\(^\circ\) in a laboratory vacuum for ten to twenty minutes, the gassification during the scaling process is reduced to a low minimum and the metal may be used any time within the next ten days for the scaling work.

Flames of the necessary temperature to work Pyrex are hot enough to melt the nichrome quickly, which means that the wire must be kept out of the direct flame. With this the manipulation precautions may be summarized as follows:

1. Avoid heating the nichrome in air; its oxides do not stick to the glass well.
2. Avoid overheating the Pyrex; gas bubbles form leaky joints around the wires.

\(^1\)Jnl. Amer. Inst. Fleet. Engrs. (1923) 42, 877
3. Plastic Pyrex compressed about this sort of wire is better than trying to wet the wire with hotter glass.

4. Anneal the joint in a very smoky flame until a heavy coat of soot is accumulated, then set on a steam hot-plate for an hour or more.

When in use, this heating element support is quite durable and the leveling fluid can be brought up and over the metal to glass joint and very near the heating element even while the latter is quite hot. Discretion must be used as to how long the equipment has had time to heat before this drastic test of quality is applied.

Comparison Of Hot Filaments

One of the earlier analytical setups for slow combustion utilizing a hot filament was proposed by Coquillion\(^1\) in 1876 from the laboratory of M. Wurtz. It consisted of an electrically heated platinum spiral over which passed small amounts of mine air of low hydrocarbon content. Frequent explosions resulted, which seemed to be entirely avoided by the use of palladium spirals. The addition of a measured quantity of hydrogen\(^2\) apparently gave smoother combustion, but with most his experiments, he found deposits of free carbon\(^3\) when using this palladium heating element. The author of this present thesis found (as are also the commercial laboratories finding today) this type of deposit from the

1. Comptes rendus (1876) 83, 394
2. Ibid 84, 458
3. Ibid 84, 1503
use of platinum spirals as well, when analyzing large samples (30 cc) of nearly pure methane. Hempel placed a small platinum spiral inside a small quartz tube, while White put a small platinum heating element in a transparent quartz capillary 4 mm. internal diameter and 125 mm. long; each obtained nearly the same results. Drehschmidt used a platinum capillary tube 0.7 mm. internal diameter (3 mm. external diameter) externally heated by a flame with largely the same results. All these attempts at developing a method of gas combustion had to be confined to small quantities of gas of low combustible content.

**Analysis Method**

The following is the general method for the combustion of gas with the hot filament type of combustion equipment, commonly known as the Hempel method.

1. **Precautions:**
   - a. Do not get in a hurry for explosions result.
   - b. Be sure that you are right then go ahead.
   - c. Observe the following rules closely.

2. Put 70.0 cc. O₂ into the combustion pipette, this gas remaining at atmospheric pressure due to the level of its leveling bottle in the system; open the pinch-cock on this

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2. White, Gas Analysis (1913) 49
connecting hose to allow for later expansion of the gas.  
2. With 30.0 cc. of the gas to be analyzed in the measuring burette at atmospheric pressure, pinch its leveling bottle tube with a Mohr's pinch-cock and suspend the leveling bottle on the support some eight inches above the top of the burette, with the cock closed tightly; open stopcocks to connect the burette with the gas combustion pipette—this should not result in any gas flow since both were at atmospheric pressure.  
4. Heat the ignition element rather quickly to prevent unnecessary gas expansion. This temperature is bright yellow.  
5. Open the Mohr's pinch-cock very slightly so as to allow the combustible gas flow into the combustion zone at about one cc. per minute. Tiny audible and visible explosions take place as the gas enters; if this is not observed from the very start, then the sample must be discarded due to explosive mixtures being formed. The equipment is allowed to set for two or so minutes after all the gas has entered the combustion zone, or else the gas is run over the electrode several times to try to insure complete combustion.  
6. After these minutes of post combustion heating, or running over the hot element, the gas is slowly brought back into the measuring burette, allowing time for the element to cool a minute or so. The gas is cooled to constant volume.  
7. When this gas is in the CO₂ absorber pipette, a new sample of 40.0 cc. of O₂ is put in the combustion pipette to make ready for the second attempt at completeness of
combustion.

After complete absorption of the CO$_2$, the known volume of partly spent gas is passed into the combustion pipette as before, and the procedure is as before.

Combustion Rate And Completeness

Due to the size and convenience of the laboratory apparatus, 30.0 cc. CH$_4$ and 70.0 cc. O$_2$ (Commercial) were taken as standard volumes and the combusted products added to 40.0 cc. O$_2$ (after absorption of the CO$_2$ from the first combustion) during the second attempt of combustion. These proportions and this procedure gave superior results.

Obviously the rate of flow of CH$_4$ into the combustion zone during the first attempt is of great importance—this is more marked in the case of spark ignition as will be shown later. U.S. Bureau of Mines$^1$ recommends 10 cc. per minute while Ingelder$^2$ recommends 1 cc. per minute; the former gives CO which does not burn readily, while the latter gives free carbon which sticks on the sides of the pipette. This formation of carbon is augmented for longer times that the heating element remains hot during the first combustion, eventhough Ingelder recommends 10 minutes to allow for convection mixing and better combustion. Rhodes$^3$ failed to find compounds of nitrogen.

2. Ingelder, Gas Analysis (1931) 32
3. Dennis, Gas Analysis (1925) 153
from the air used for combustion, that were reported by White\(^1\) for long high temperature heating. Bunsen\(^2\), however, showed oxides of nitrogen from high temperature explosions, which showed up as though it was CO\(_2\) in the KCl solution.

In a study of the formation and the subsequent difficulty of CO, Schuften\(^3\) found CO to be active for combustion, or combine with H\(_2\) to form CH\(_4\) in a Ni-Al\(_2\)O\(_3\) catalyst only thru a certain critical temperature range (200\(^\circ\) to 300\(^\circ\)C) and concentration range. It is evident on inspection that carbon deposited on the walls of the combustion pipette will not combust, even though the simultaneously released H\(_2\) burns freely.

Taking precautions as to the duplication of conditions, and using mercury as the leveling fluid, the combustion of a gas may be checked to within a few tenths per cent error, run after run, even when the actual error may run as high as 2 to 5 per cent of the total gas present. Commercial laboratories employing this sort of equipment are demonstrating constant error by the deposits of free carbon in the top of the combustion pipette. This is sufficient to become quite visible on some four or five combustions using some 30 cc. or nearly pure CH\(_4\).

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2. Bunsen, Gasometrische Methoden (1877) 73
PART III

SPARK IGNITION METHOD FOR SLOW COMBUSTION
The method of explosion of relatively large quantities of combustible gas with commercial oxygen and utilizing an electric spark for ignition (proposed by Himan and endorsed by Gill and Hunt\(^1\)) involves much greater danger of blowing up the pipette than the other methods. In the use of air to supply the oxygen, the high temperature of explosion tends to form oxides of nitrogen and thus produce errors, and the other possibility of the incompleteness of combustion is just as with the hot filament ignition. White\(^2\) added pure H\(_2\) and reports to have had almost absolute assurance of complete combustion. He further prepared pure CH\(_4\) from which he reports an error of 1.6\% using 7 to 10 cc. samples of CH\(_4\).

Decomposition Of The Gas

In the use of commercial oxygen for slow combustion, the problem of nitrogen is avoided, but the other problems are yet to be solved. If the spark gap is too high up in the combustion pipette, the CH\(_4\) has too little time to mix with the essential oxygen, and is consequently broken up into free carbon and hydrogen while passing thru the spark (which was a continuous arc from a spark coil). The H\(_2\) burns freely while the carbon deposits out in the top of the pipette.

Too low a setting of the spark gap allows pockets of explosive

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1. Jnl. Amer. Chem. Soc. (1895) 17, 997
2. White, Gas Analysis (1913) 84
mixtures of the gas to form. The optimum value was found to be 1/2 to 5/8 inch below the gas inlet. This however, is not all the solution to the difficulties of decomposing the gas, since to quite a measurable degree it persists even at the best all round conditions with the spark method. The formation of CO during the first attempt at combustion, and the difficulty of burning further until the CO₂ is absorbed and the remaining mixture passed into the arc again in the O₂ atmosphere, is an outstanding difficulty. This is true even when the initial O₂ is quite well in excess of all the original CH₄.

The ensuing paragraph is to show the formation of CO during the first attempt at combustion. Even so, carbon deposits were in evidence in the top of the combustion pipette each time of experimentation. In each case the 30.0 cc. of CH₄ was run thru the arc, which was located as described in the 70.0 cc. O₂. After measuring and absorbing the CO₂, the mix was run thru the arc into 40.0 cc. of a new supply of O₂ now in the pipette; the gases were passed thru the arc on entering and leaving the pipette, thus they passed thru it eight times for each combustion attempt. Other experiments of letting the equipment set and depend on convection for stirring proved of little or no value.
Combustion Pipette For Spark Ignition
Table To Show CO Formation

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂ Found</th>
<th>CO₂ Found</th>
<th>Combustion based on vol. decrease</th>
<th>Ultimate Total comb. CO₂/CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>co.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>17.7</td>
<td>59.0</td>
<td>74.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.3</td>
<td>24.5</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.4</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>86.7</td>
<td>91.6</td>
<td>86.7%</td>
</tr>
<tr>
<td>2</td>
<td>16.9</td>
<td>56.3</td>
<td>79.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>5.4</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.6</td>
<td>22.2</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>3.7</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>93.1</td>
<td>97.6</td>
<td>88.1%</td>
</tr>
<tr>
<td>3</td>
<td>18.6</td>
<td>62.0</td>
<td>75.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.9</td>
<td>23.0</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>85.0</td>
<td>99.0</td>
<td>85.0%</td>
</tr>
</tbody>
</table>

Other factors causing ultimate low combustion were kept constant.

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1. Indicating possible CO, when getting more CO₂ than the theoretical O₂ consumed.
2. CH₄→ C + H₂ ; H₂ + ½O₂→ H₂O
3. Added the gas to the extra O₂ after the second combustion.
From sample number three of the preceding table comes the following mathematical analysis of the formation of CO.

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

The volume loss is two times CH\(_4\) burned, regardless of CO or CO\(_2\). 30.0 cc CH\(_4\) = 70.0 cc O\(_2\) gave 18.6 cc CO\(_2\) and 45.0 cc volume loss (corresponding to 23.5 cc CO\(_2\) if that fraction of CH\(_4\) had gone 100\% to give CO\(_2\) and H\(_2\)O).

The second combustion gave 6.9 cc CO\(_2\) and 8.4 cc volume loss, which was caused in part by the H\(_2\)O formed and the CO consuming O\(_2\) to give a volume of CO\(_2\) equal to the volume of CO burned to form it.

\[ (1) \text{CO}_2 \rightarrow \text{CO}_2 \quad (\text{1 volume}) \]
\[ (2) \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

Let \( x \) be the CO present from first combustion, and which did not combust during the second attempt.

\( y \) is the CH\(_4\) yet present after the first combustion which combusted during the second.

Gas volume balance:

\[ (3) x\text{CO} - y\text{CH}_4 = (\frac{x}{2} - 2y)\text{O}_2 - (x - y)\text{CO}_2 = 2y\text{H}_2\text{O} \]

Then from the second combustion and the CO\(_2\) from CH\(_4\), the CO\(_2\) balance:

\[ (4) x + y = 6.9 \text{ cc} \]

From the CO\(_2\) consumed by the CO, plus the H\(_2\)O from the CH\(_4\), the volume loss during the second combustion was:

\[ (5) \frac{x}{2} + 2y = 8.4 \text{ cc} \]

Simultaneous solution of (4) and (5) gives:

\( x = 3.60 \text{ cc CO present after first combustion} \)

\( y = 3.30 \text{ cc CH}_4 \) present after first combustion.
This is checked by equation (4) of $CO_2$ found from the theoretical equations of (1) and (2). Thus the value of

$$\frac{3.60}{30.0} = \text{initial CH}_4 \rightarrow CO \text{ at the first combustion.}$$

Optimum Oxygen For Second Combustion

The optimum amount of oxygen for the second combustion was found as indicated by the second table; in each case 30.0 cc. $CH_4$ was added to 70.0 cc. $O_2$ during the first combustion, and after absorbing the $CO_2$, the mix was attempted to be combusted a second time as indicated by passing it into the pipette, thru the spark in the recorded volume of new $O_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$O_2$ in pipette just before 2nd, cc.</th>
<th>$CO_2$ Found, cc.</th>
<th>$CO_2$ Found, %</th>
<th>$CO_2$ Theoret. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1.6</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>3.0</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>3.7</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>6.4</td>
<td>21.4</td>
<td></td>
</tr>
</tbody>
</table>

Other factors that might cause variation as $CH_4$ rate of flow into pipette, changing position of spark gap, time of exposure to spark, etc., were kept constant throughout. These are but averages of many runs, and are for second combustions only.

Rate Of $CH_4$ Flow Into Spark

Concurrent with the study of the formation of $CO$ and free carbon, was the observations of the effect of the rate
of flow of \( \text{CH}_4 \) into the combustion zone during the first combustion. These data are for the first combustion only.

<table>
<thead>
<tr>
<th>( \text{CH}_4 ) rate into arc in cc/sec</th>
<th>( \text{CO}_2 ) found cc</th>
<th>( \text{CO}_2 ) found %</th>
<th>( \text{CO}_2 ) theor. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>18.1</td>
<td>60.5</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>21.6</td>
<td>70.0</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>21.7</td>
<td>72.3</td>
<td></td>
</tr>
</tbody>
</table>

Faster flow rate of \( \text{CH}_4 \) into the \( \text{O}_2 \) in the combustion zone, than one cc. per second is so fast that the explosions are violent and explosive mixtures of dangerous size accumulate in the pipette. The mixture was run thru the arc several times each attempt at combustion. The optimum \( \text{CH}_4 \) rate for this size of equipment is about one cc. per second, at which velocity, tiny flames about one inch long are visible and audible. Even with this, the depositing of carbon was shown as in the case of hot filament ignition. Thus, this method, similar to the hot filament method, is not satisfactory for large quantities of gas of high combustible content. The formation of \( \text{CO} \) is of little significance, for in time and in the presence of sufficient \( \text{O}_2 \) it will burn, unless perchance this is the reason for the formation of the deposited free carbon.
PART IV

COPTHR OXIDE METHOD FOR SLOW COMBUSTION
Campbell first utilized the principle of fractional combustion in gas analysis by contact with hot copper oxide, even though the combustion of many kinds of compounds had been accomplished in regular analysis by organic chemists for a long time. He determined accurately the minimum combustion temperature for various gases both with copper oxide alone and with palladinized copper oxide. His values are as follows:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Initial combustion point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pure CuO</td>
</tr>
<tr>
<td>H₂</td>
<td>175-180</td>
</tr>
<tr>
<td>C₆</td>
<td>100-105</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>315-325</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>270-280</td>
</tr>
<tr>
<td>C₄H₈(Iso)</td>
<td>320-330</td>
</tr>
<tr>
<td>CH₄</td>
<td>No combustion @ 455°C.</td>
</tr>
</tbody>
</table>

Jaeger first proposed a convenient scheme for utilizing this principle in ordinary analysis of gas and the method usually bears his name. He takes advantage of the wide difference of minimum combustion temperatures of CO and H₂ as compared with CH₄ to separate the gases by fractional combustion. He used hard Jena glass (recommended transparent quartz) for the combustion chamber with an

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1. Amer. Chem. Jnl. (1895) 17, 628
2. White, Gas Analysis (1913) 84, cites Jour. Gasbeleucht (1898) 41, 764
internal diameter of about 10 mm and a length of 200 mm. It is filled thru its middle section with granulated copper oxide kept in place with wads of asbestos fiber. With the CO₂, CH₄, and O₂ previously removed, the whole volume of gas was flushed thru the CuO into a phosphorus pipette which had been previously filled also with air and now contained nitrogen. For computation he quotes these equations:

\[
\begin{align*}
H₂ + CuO & \rightarrow H₂O + Cu \\
CO + CuO & \rightarrow CO₂ + Cu
\end{align*}
\]

Thus it is evident that after the gas has been heated to 250°C, the contraction in volume is equal to the H₂, since the CO₂ volume is equal to the CO, and the CuO is practically equal to the Cu. Since CH₄ burns slowly, Jaeger passed it back and forth several times to insure combustion:

\[
CH₄ + 4CuO \rightarrow 4Cu + CO₂ + 2H₂O.
\]

Jaeger initially proposed 250°C for the combustion of H₂ alone. Even with Uhlig praising Jaeger's work very highly and recommending it, the author of this present thesis found it unnecessary to pass the gas more than once with the equipment shown in the following pages. Engelder greatly endorses the practice of preferential combustion, for more than two gases, over hot copper oxide.

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2. Ibid. (1910) 29, 196
3. Engelder, Gas Analysis (1931) 35
Electric Furnace For Copper Oxide Combustion
With a porcelain combustion tube 1½ inches diameter about 20 inches long containing 300 grams of wire copper oxide (approximately number 30 B&W) and plugged at the ends with ignited long fiber asbestos, the following data were taken with 1 cc. per second as the CH₄ rate of flow into the combustion zone:

<table>
<thead>
<tr>
<th>Gas used cc.</th>
<th>Air to flush cc.</th>
<th>Temp. CuO °C</th>
<th>CO₂ found in grams</th>
<th>CO₂ found % CO₂ Theor.</th>
</tr>
</thead>
<tbody>
<tr>
<td>200.0</td>
<td>200</td>
<td>350</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200.0</td>
<td>400</td>
<td>460</td>
<td>.043</td>
<td>12</td>
</tr>
<tr>
<td>200.0</td>
<td>500</td>
<td>460</td>
<td>.029</td>
<td>3</td>
</tr>
<tr>
<td>200.0</td>
<td>600</td>
<td>570</td>
<td>.126</td>
<td>37</td>
</tr>
<tr>
<td>200.0</td>
<td>600</td>
<td>570</td>
<td>.127</td>
<td>40</td>
</tr>
<tr>
<td>200.0</td>
<td>600</td>
<td>700</td>
<td>.343</td>
<td>100.2</td>
</tr>
<tr>
<td>200.0</td>
<td>600</td>
<td>700</td>
<td>.343</td>
<td>100.5</td>
</tr>
</tbody>
</table>

The CO₂ was absorbed with Ascarite, a commercial CO₂ absorber. Using water as the leveling fluid in the burette, it saturates the gas and the air, which means that it is necessary to employ the vapor correction and then correct to normal temperature and pressure:

Room temperature was 30°C and water vapor pressure at this temperature is ≈ 31.5 mm mercury. Atmospheric pressure was 760.2 mm, so the 200.0 cc. corrected is found to be
\[ \frac{200.0 \times (760.0-31.8)}{760.0} \times \frac{273}{303} = 173 \text{ cc at NTP} \]

\[ \frac{173}{22.4} \times 16 = 0.1236 \text{ grams CH}_4 \text{ if pure} \]

\[ \frac{\text{CC}_{2}\text{H}_6}{\text{CH}_4} \times 44.00 \times 0.1236 = 0.3400 \text{ grams CO}_2 \text{ for 100\%} \]

from 200.0 cc CH\(_4\) at room conditions saturated with H\(_2\)O vapor.

Then to compute the C\(_2\)H\(_6\) from the apparent 100.5\% CH\(_4\) in the original gas sample:

Let \( x \) equal CH\(_4\) actual cc., then \( x \) equals the CO\(_2\)

\[ (100.0-x) \] is \( \text{C}_2\text{H}_6 \)

or, \( 2(100.0-x) \) cc is the \( \text{CO}_2 \) from the C\(_2\)H\(_6\)

CO\(_2\) balance:

\[ x + 2(100.0-x) \] equals 100.5

\[ x \] equals 99.5 cc or \% CH\(_4\)

and, 0.5 cc or \% C\(_2\)H\(_6\)

This gas analyzed by different means showed 0.1\% H\(_2\)S,

which, when burned to SO\(_2\), shows up as CO\(_2\) in the CO\(_2\) absorber.
COPPER OXIDE COMBUSTION OF METHANE

Temperature -vs- Per Cent Combustion
From the foregoing, it is evident that the copper oxide combustion method is to be favored over the numerous disadvantages of the other methods. Preferential combustion and the high order of accuracy are two of the most important features. Calculations, however, are complicated, but never the less are accurate. The difficulty of weighing the 100 gram absorber in order to measure accurately 0.1 milligram is merely a problem of laboratory technique.