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## United States Steel Corporation

METHODS FOR THE TECHNICAL SAMPLING AND ANALYSIS OF GASES

# THE METHODS 

OF THE

United States Steel Corporation

FOR THE

TECHNICAL SAMPLING AND ANALYSIS
OF GASES

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BY
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## PREFACE TO THE SECOND EDITION.

The interval since the publication of the first edition of this pamphlet has proved to be a period of notable industrial progress, and this statement is particularly applicable to the maufacture and use of by-product coke oven gas. This fact made the enlargement and revision of the pamphlet very desirable while the success and consequent exhaustion of che first edition made the preparation of a new edition necessary to meet the demands for copies of the book. Except for changes in the phraseology, the methods of the first edition for the analysis of the gases treated therein have been retained with but few changes of real importance. The use of a $10 \%$ sodium chloride solution for sampling is recommended, and the measuring burette has been graduated and marked to read from the top downward instead of from the bottom upwatd, but it is evident that these changes affect the methods but slightly. As to the additions to the text, the method for the analysis of by-product gas is made as nearly as possible like that for producer and blast furnace gases, but a method for the analysis of natural gas has been incorporated that differs slightly from that given for other fuel gases in that larger quantities for explosion are employed. This feature of the method is of decided advantage, because no error is introduced by the high percentage of resulting carbon dioxide.

The committee appointed for the preparation of this revised edition of the gas pamphlet was composed of the following gentlemen: Mr. W. D. Brown, Chemist of the Duquesne Works, Carnegie Steel Company; Dr. J. R. Harris, Chemist of the Tennessee Coal, Iron and Railroad Company; and Mr. J. V. Freeman, Chemist of the Central Laboratory, Joliet Works, Illinois Steel Company.

## PREFACE TO THE FIRST EDITION.

This pamphlet is descriptive of the methods selected by the chemists of the Corporation, acting through the Chemists' Committee, for the technical sampling and analysis of gases. With the increased significance attached to the economic control of those industrial processes involving the combustion of fuels and with the application of keen scientific research to the various problems involved, it becomes readily apparent that accurate knowledge of the composition of the gases encountered is a matter of prime importance. This fact is exemplified by the rapid increase in the use of internal combustion engines, using blast furnace or producer gas as a fuel, and by the increasing necessity for greater watchfulness upon the efficiency of boilers, stoves, and furnaces. The need is obvious, for use by the laboratories of the United States Steel Corporation, of a standard system of sampling and analysis of gases, in order that comparable results may be obtained with the maximum degree of accuracy, consistent with the minimum of time requisite for execution.

This description was consummated through a review of the practices, especially written for this purpose, of all the laboratories of the Corporation engaged in the sampling and analysis of gases. The apparatus shown for the analysis is to be considered only as a type of the permissible form. The essential points are the exclusive use of the capillary tubes, the permanency of connection of the auxiliary gases, compactness, and the applicability of the apparatus to the accompanying description. This form of apparatus and the methods as here described are to take precedence over all others employed for the analysis of gases throughout the laboratories of the Corporation.

It is the desire of the Chemists' Committee here to acknowledge their grateful appreciation of the services of Mr. D. A. Barkley and Mr. R. J. Wysor, assistants in the Duquesne Laboratory, in the preparation of this pamphlet.

The Chemists' Committee.

## INTRODUCTION.

In the preparation of the accompanying standard methods for the sampling and analysis of gases, there has been an unwavering purpose to eliminate, so far as possible, tedious analytical procedure and the use of cumbersome forms of apparatus. It has been desired to adopt methods, inherently correct in principle, which, in conjunction with simplified apparatus, will insure the requisite expediency, at times so necessary in commercial work, without an appreciable sacrifice in accuracy of results. While no notable originality is claimed in general for the subject matter of this pamphlet, it is believed that the application of well known methods, coupled with certain novel features in execution and in the forms of apparatus used, will be presented. No apology is offered for the unabridged nature of the descriptions and explanations appearing in this pamphlet. The delineation of the methods has been made in considerable detail so as to be clearly intelligible to amateurs as well as to those better versed in the subject.

## SAMPLING.

It is impossible within the compass of this pamphlet to give a detailed method, for sampling gases, that would be applicable to all the works of the Corporation and the various manufacturing operations therein. It is preferred to make this description general, leaving to each individual operator the solution of the details to meet his own particular conditions. In the sampling of gases two kinds of samples are recognized; namely-the accumulative and the control. The accumulative comprises all samples taken continuously during uninterrupted periods that may vary from one-half to twenty-four hours, and the results obtained from samples taken in this manner will constitute the official analysis, that is, they only will be considered in making comparisons with like results from other works. Under the head of the control samples are included all those samples taken for a shorter period of time than the minimum given above, and will represent momentary conditions of the particular operation in question, and are for the guidance of the works only. All a nalytical reports shall show the duration of the time of sampling in order that the status of the results may be known.


In sampling blast furnace or producer gases, which are considered homogeneous in the cross section of the main, the gas is withdrawn through a petcock on a pipe threaded into the shell of the main and extending in beyond the brickwork lining. In the absence of lining the gas may be withdrawn through a petcock on the shell, or when the main is inaccessible, on a pipe leading from the main, through which a continuous current of gas passes.

In sampling flue gas it is necessary that the gas be withdrawn through a perforated pipe, which enters with air-tight connection and extends entirely across the flue. The pipe is closed at the anterior end and provided at the outer end with an aspirating device, operated by air, water, or steam (see sketch). The perforations in this pipe should be equal distances apart, and, to obtain an equal flow through all openings, their combined area should be less than the cross sectional area of the pipe, three to four being considered a safe ratio. The sample is withdrawn from the sampling pipe through a petcock situated between the flue and the aspirating device. This pipe may also be used in sampling blast furnace or producer gas; but, instead of aspirating, the gas is allowed to escape under its own pressure.

An apparatus for collecting an accumulative sample is shown in the accompanying photograph. This appliance which is but one of many that may be used, has the advantage of simplicity of construction and operation. When a sample is collected, the petcock, permanently attached to the main, the flue or the intermediary pipe before mentioned, is connected by a rubber tube with one hole of the doubly perforated stopper in the two gallon aspirator bottle. This aspirator bottle contains a $10 \%$ solution of sodium chloride, which has been saturated with the gas to be sampled. The lower opening of this bottle is connected by a rubber tube with a similar opening in another bottle placed on a lower level, the rate of flow of water from the upper to the lower bottle being controlled by a screw compressor. The petcock being open, the compressor is released, and the gas rapidly displaces the water in the upper bottle. On closing the petcock, reversing the bottles and opening the pinchcock on the rubber tube leading from the second hole in the rubber stopper, the gas is rapidly expelled into the air until the rubber tube constituting the exit is full of water. The pinchcock is closed, the bottles reversed, and the upper one filled with gas, the rate of inflow of gas being so controlled by the compressor that the bottle is filled in the designated time, varying from one-half to twenty-four hours as previously stated.


Apparatus for the Sampling of Gases.

A portion for analysis is transferred from the bottle to the small sample tube (No. 2, Analytical Apparatus). This tube may be of glass or metal. It is approximately two inches in diameter and eight inches in length, with a capacity of about 300 c . c. Its ends are conically shaped and are terminated by petcocks. The sample tube, including the upper petcock, is filled with a $10 \%$ solution of sodium chloride, and is attached to the rubber tubing constituting the exit from the gas bottle, which is also full of the solution. The position of the aspirator bottles is reversed, thus placing the gas under pressure, the pinchcock is opened, the upper, then the lower cocks on the sample tube are opened, and the gas is allowed to displace the solution in the tube and flow through for a short time to saturate the moisture adhering to the sides. The lower, then the upper cock on the tube is closed, leaving the gas under slight pressure. The sodium chloride solution in the sample tube may be used repeatedly. The sample is delivered to the laboratory and analyzed as soon as possible. To prevent entrance of air, the ends of the tube may be dipped in molten paraffine.

When desired, a gasometer may be used for withdrawing a larger sample of such size that calormetric determinations may also be made. If uncleaned gas is to be sampled continuously, it is first passed through a suitable filter for removing the dust. The water in the gasometer is used continually and as long as practicable. A small sample for analysis is forced through a petcock on the holder and then through a rubber tubing connection into the sample tube in the manner previously described.

When it is desired to obtain a control sample, representing momentary conditions in the main, a sample tube filled with water or sodium chloride solution is connected by a rubber tube to the petcock on the main or intermediary pipe. If the gas be under pressure, the petcock, the upper, then the lower cock on the sample tube are opened, and the gas is allowed to displace the water and flush through. If the gas be under vacuum, an aspirator, for which another sample tube answers well, is connected with the lower end of the sample tube. With both vessels filled with water, the cocks are opened, and the gas is drawn into the sample tube.


Apparatus for the Analysis of Gases.

## ANALYSIS.

## THE APPARATUS.

The apparatus shown in the accompanying photograph has been designed with particular reference to its adaptation to the methods subsequently described. The distinguishing features in its design are the capillary tube of 1 mm . bore, the accessibility of the auxiliary gases, oxygen and hydrogen, and the central location of the burette in the apparatus, thus decreasing the error due to the capillary space. Drawings of this apparatus, which have been copyrighted, have been supplied to Messrs. Eimer and Amend of New York, the authorized makers, who are prepared to supply it in whole or in part.

The general disposition of the apparatus is obvious. On the extreme left end of the capillary is placed the rubber tubing connection leading to the Kipp apparatus (No. 9), while the connection to the oxygen supply (No. 7) is made on the end of the first stopcock. To the first capillary stem is attached the explosion pipette (No. 8); next in order is placed the pipette containing potassium hydroxide solution (No. 4), which is followed by the burette (No. 3). To the right of the burette are situated the pipettes containing stick phosphorus and fuming sulphuric acid (No. 6) and (No. 5), respectively.

The stem of each pipette is ground so as just to clear the corresponding stem of the capillary with which it is connected. The stem of the burette must not be altered, but is to be precisely adjusted to the stem of the capillary tube by regulating the height of the support at the bottom. The numerations are from the top downward, and since the majority of readings are made in the lower part of the burette, the first 20 cc . are graduated in fifths, but by interpolation, tenths may be read; the remaining 80 cc . are graduated in tenths, but may be read in twentieths. The burette is surrounded by a water jacket, thereby maintaining practically a constant internal temperature throughout the analysis, provided care is taken that the apparatus be not subject to great and sudden change of temperature.

The pipettes have two compartments, and to the open side a thin rubber bulb is attached. This protects the reagent from the atmosphere. The pipettes will conveniently hold 100 cc . of gas and 260 cc c. of the reagent, with the exception of the one for phosphorus. This pipette was designed for the use of stick phosphorus, and when loosely filled with this reagent, will hold 100 cc .
of gas and sufficient water to form a seal. Thus the gas is exposed to the maximum surface area of the phosphorus, facilitating the absorption of oxygen. In filling the pipette, the phosphorus is introduced through an opening at the lower end. The stem rises into the base of the pipette for a distance of about one-fourth inch, thus preventing the sticks from obstructing the orifice. The explosion pipette contains platinum terminals partly covered with glass to prevent the sparks from short circuiting. In case the terminals become coated, thus preventing the passage of the spark, they are cleaned by allowing the pipette to stand inverted in a mixture of concentrated sulphuric acid and chromic acid. In the same manner the burette should also be cleaned occasionally.

The following auxiliary apparatus are used:-

1. A one-half pint Kipp apparatus for generating hydrogen from C. P. stick zinc and dilute hydrochloric acid.
2. An aspirator bottle containing oxygen and nitrogen in predetermined proportion.
3. An induction coil of sufficient size to give a one-eighth inch spark. The current required for this coil is deived either from dry cells, a storage battery, or from a direct current lighting circuit with a rheostat connection.

## SOLUTIONS.

1. Potassium Hydroxide. The pipette used for this reagent is filled with 260 c c. of a solution of approximately 1.27 specific gravity. The absorbing power is in excess of 40 cc . of carbon dioxide per c c . of solution. In place of potassium hydroxide, a solution of sodium hydroxide may be substituted.
2. Stick Phosphorus. This reagent is obtainable in sticks $3 / 6 \mathrm{in}$. in diameter. It may also be prepared from larger sticks by melting the phosphorus under water in a test tube immersed in a vessel of water at a temperature of about $50^{\circ} \mathrm{C}$. A glass tube of the proper internal diameter is inserted in the molten phosphorus, and a column of phosphorus is drawn into the tube by
means of suction to the desired height, when the tube is withdrawn and immediately dipped into a beaker of cold water. The solidified phosphorus is then pushed out with a glass rod into the reagent pipette, also filled with water. Extreme care must be taken to avoid spilling the phosphorus on the floor. When in use, the water in the pipette is renewed occasionally to remove the oxides of phosphorus in solution. The need for this removal is indicated when the fumes in the pipette are slowly or incompletely absorbed in one or two minutes. The chamber of the pipette containing the phosphorus is enclosed with a piece of black paper to protect it from the action of light.
3. Fuming Sulphuric Acid. Two hundred sixty cubic centimeters are required. The acid should contain at least $20 \%$ of the sulphur trioxide in excess. It will become discolored owing to its action upon the rubber tubing, but this does not appear to interfere with its efficiency. This action tends to harden the tubing, and then apparently ceases.
4. Dilute Hydrochloric Acid. A mixture of 100 cc c. hydrochloric acid and 400 c c. distilled water is poured into the Kipp apparatus, the middle chamber of which is well filled with C. P. stick zinc.
5. Saturated Water. This water is used to fill the burette, the explosion pipette and the leveling bottles. It is obtained by bubbling the gas through $20 \%$ solution of sodium sulphate slightly acidified with sulphuric acid. Care should be taken not to contaminate this water with any of the reagent solutions. The addition of methyl orange to this solution will indicate its becoming alkaline.

## AUXILIARY GASES.

1. Hydrogen. This gas is generated in the middle chamber of the Kipp apparatus by the action of dilute hydrochloric acid (1:4) upon C. P. stick zinc. The apparatus should be flushed several times with freshly generated hydrogen to remove all traces of air, and the rubber tubing connected to the left end of the main capillary tube.
2. Oxygen and Nitrogen Mixture. This mixture should contain from $35 \%$ to $45 \%$ oxygen and from $55 \%$ to $65 \%$ nitrogen. A mixture of one-fifth compressed or tank oxygen, containing between $95 \%$ and $100 \%$ oxygen, and four-fifths air will approximate $35 \%$ in oxygen content. Connections are
made between two aspirator bottles, one being filled with water, and the other containing enough water to form a seal, and the rubber tubing connecting the two bot tles is closed with a pinchcock. The volume of water in the former above the lower outlet is determined and a mark made at that point. Four-fifths of this amount is returned to the bottle, a mark being made on the side even with the water level, and the bottle is then filled with water. A connection is made with the oxygen supply, the pinchcock between the two bottles released, and the oxygen is allowed to pass slowly into the bottle until the water reaches the indicated mark, the overflow passing into the second aspirator bottle. At this point, the rubber tubing leading to the oxygen supply is disconnected, the second aspirator bottle is immediately lowered, and the air drawn into the upper bottle until the water level is even with the outlet. The end of the rubber tubing on the upper bottle is closed with a pinchcock, and the gases thoroughly mixed by agitation. The bottles are placed on their shelves, and the tubing connected to the stem of the three-way cock at the left of the gas apparatus. If the oxygen used contains carbon dioxide, it must be purified before use by passing through sodium hydroxide or soda lime.

## METHODS OF ANALYSIS.

## 1. PERCENTAGE OF OXYGEN IN OXYGEN AND NITROGEN MIXTURE.

In the application of the following methods, it has been found that a mixture of oxygen and nitrogen, in the proportion given before, is the most practical for use in the combustion of the component gases. but it is necessary to know the exact percentage of oxygen in this mixture in order that the amount of oxygen used for the explosions may be known. The object in introducing this mixture, instead of oxygen alone, is that a larger volume of the former can be added, and only a normal excess of oxygen will be present after the first explosion, thereby keeping the explosion ratio as high as practicable and reducing the flame temperature, thus minimizing ertors due to the oxidation of nitrogen. The explosion ratio is the proportion of the inert to the total gases entering into the combination. The oxidation of nitrogen cannot be entirely avoided, since oxides of nitrogen are formed in all explosions in amounts varying chiefly with the temperature attained. The design of explosion pipette, owing to its eudometric shape, is an aid in avoiding the combustion of nitrogen in that the flame movement is slower, and necessarily the pro-
duction of heat is lower than in the spherical form of pipette. Experiments have been made on the gases discussed in this pamphlet, and approximate quantitative determinations made of the oxides of nitrogen formed in the combustions. It has been found that with this mixture, and the explosive ratios as high as practicable, the errors due to oxides of nitrogen are negligible. The formation of oxides of nitrogen cannot be avoided by not adding nitrogen as this gas is contained to a greater or less extent in all gases herein analyized.

With the data of analysis at hand, the explosion ratio for the first explosion is found by dividing the gas residue after Contraction II by the sum of Contraction I and Contraction II, and the ratio for the second explosion by dividing the residue after Contraction III, by Contraction III. The most practical ratios of inert to the combining gases are those lying between 1.5 to 1 and 3 to 1 ; with producer gas and by-product gas the ratio obtained in the first explosion should approach as near as possible the latter ratio, since the amount of heat liberated in the combustion of methane is relatively great.

Before beginning the analysis, it is advisable each day to agitate the bottle containing the oxygen and the nitrogen mixture, and to flush out the connecting rubber tubing by lowering the leveling bottle ( L ) drawing in about $25 \mathrm{c} . \mathrm{c}$. each of hydrogen and oxygen and nitrogen mixture, and discarding through the three-way cock at the right. The solutions in the reagent pipettes are drawn even with the main capillary tube, care being exercised that there are no unfilled spaces in the capillaries of the pipettes. The left half of the capillary is filled with water drawn over from the explosion pipette, the leveling bottle is raised and any portion of the solutions that may have been drawn into the main capillary is expelled through the stem of the three-way cock at the right, to which is attached a piece of rubber tubing discharging into a waste receptacle. While the leveling bottle is still raised, the three-way cock is closed, and in this manner the capillary tube remains filled with water. The leveling bottle is placed at the base of the apparatus, and approximately 75 c c. of hydrogen are aspirated. The left side of the capillary is then filled with water from the explosion pipette and after the burette has drained for one minute, the water in the leveling bottle is brought level with that in the burette and a reading taken. Likewise 25 c c. of the oxygen and nitrogen are added and measured after the capillary has been filled and the burette has drained one minute. The leveling bottle is raised and the cock leading to the
explosion pipette (8) is opened, when the gas is passed over and back two or three times to insure a thorough mixture, as an imperfect mixture may prevent the desired explosion.

The electric circuit is then closed causing the explosion. The bottle (Y) which receives the overflow from the explosion pipette, and the location of which on the lower shelf is never changed, the gases thereby being kept under partial vacuum, is connected to the latter by a piece of strong rubber tubing about a foot long, partly constricted by a screw compressor near the bottles. The degree of the constriction is determined by increasing it until no bubbles apf ear in the pipette after an explosion. All the conditions of this arrangement tend to diminish the force of the resultant explosion.

After the explosion, the gas is immediately drawn back into the burette until the water from the pipette fills the left half of the capillary tube. The cock in the pipette is then closed and, after an interval of one minute to allow the gas to cool, a reading is made. This, less the previous reading, represents the contraction due to the formation and condensation of water and is known as Contraction I. The oxygen that enters into the explosion is equal to one-third of the contraction, since,

$$
\begin{aligned}
& 2 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O} . \quad 2 \text { volumes }+1 \text { volume }=\text { liquid (disappearing) } \\
& \text { Percentage of oxygen in the mixture }=
\end{aligned}
$$

$\frac{\text { Oxygen found }}{\text { Oxygen and Nitrogen Mixture added }} \times 100$

Example-Data

> Burette Readings
0.0


## Calculatıons.

$\frac{\text { Oxygen found }}{\text { Oxygen and Nitrogen Mixture added }} \times 100=36.5 \%$ Oxygen.

Explosion ratio, 2.6.

Two or more determinations are made which should agree within .1 or $.2 \%$. The percentage of oxygen in the mixture should be determined once each day while in use, as it is subject to change.

## 2. BLAST FURNACE GAS.

Before the analysis is started, the solutions in the pipettes are brought flush with the capillary tube, while the latter and burette are filled with water. During all analyses the capillary to the left of the burette is always filled with water before a reading is taken. The petcock on either end of the sample tube containing the gas sample (No. 2 Analytical Apparatus) is filled with water and attached to the rubber tubing leading from the shelf bottle (No. 1) which contains a $10 \%$ solution of sodium chloride. The other end of the sample tube is attached to the rubber tubing at the end of the main capillary, and the sample tube is placed in its rack on the side of the apparatus. The leveling bottle is then placed on top of the apparatus, the pinchcock on the water supply, the lower, then the upper cock on the sample tube, and the three-way cock on the capillary tube, are opened; the water from the shelf bottle forces the gas into the burette against its pressure from the leveling bottle, which is lowered it necessary, the gas being constantly under pressure.

About 25 c c. of gas are thus forced into the burette, and then expelled through the stem of the three-way cock, by turning it, all connections remaining as they are. This sample is rejected because it contains the air that was in the rubber connection between the capillary and sample tube. A second sample is forced in until it reaches the base of the burette, and one minute is allowed for the burette to drain and the temperatures to equalize; duing this period the sample tube may be disconnected from the apparatus. With the leveling bottle on top of the apparatus, the tube leading from it is pinched between the thumb and finger and the three-way cock opened, the pressure of the gas being thus released. The remaining portion is slowly forced out by
releasing the pressure on the tube until the meniscus just reaches the 100.0 cc . mark in the burette, then the three-way cock is closed. If the water in the leveling bottle is brought to the same level as that in the burette, the meniscus of the latter should be exactly at 100.0.

Determination of Carbon Dioxide. The leveling bottle is slowly raised after the cock in the first reagent pipette containing the solution of potassium hydroxide has been turned so that the gas will bubble through the solution. If the leveling bottle be not raised slowly, the bubbles which first appear may be lost by being carried into the other compartment of the pipette. When all but about 5 c c. of the gas has passed into the pipette, the cock is turned to a position for drawing the gas back into the burette, keeping the leveling bottle raised, and the instant the reagent has been expelled from the side capillary of the pipette by the remaining gas, the leveling bottle is lowered, and the gas is drawn back. Thus, the gas is forced in and drawn out of the pipette at least three times, the reagent finally being drawn to its initial point in the stem of the capillary. The capillary is filled with water from the explosion pipette, the burette is allowed to drain for one minute, and the reading taken. The difference between this and the initial reading represents the percentage of carbon dioxide in the gas. To make certain that all the carbon dioxide has been removed, the gas should again be passed through the solution of potassium hydroxide and a reading taken as before.

Determination of Oxygen. The passing of the residue from the absorption of carbon dioxide into the fuming sulphuric acid for the absorption of the illuminants or olefiant gases is usually omitted with blast furnace gas, as these are either entirely absent or present only in such small quantities that they can scarcely be detected in the usual way. Therefore, the residue is at once passed into the second pipette containing stick phosphorus and left there for one minute to remove the small amount, it any, of oxygen found in blast furnace gas. The difference between the burette reading obtained and that after the absorption of carbon dioxide, represents the percentage of oxygen present.

Determination of Carbon Monoxide, Hydrogen and Methane. One-half the above residue is used for the determination of these gases; if it is desired to duplicate the explosion, one-half of the residue is reserved in the phosphorus pipette. If not, the leveling bottle is placed on top of the apparatus, the
connecting rubber tubing pinched, and the residue to be rejected is slowly forced out through the stem of the three-way cock until the meniscus just reaches the calculated point. The three-way cock is closed and by the application of the leveling bottle the calculated reading should be obtained.

A volume of oxygen and nitrogen mixture containing about 16 c c. oxygen is now passed into the burette through the permanent rubber tubing connection, and, the capillary being filled with water, an exact reading is made. If the carbon dioxide, in the absence of oxygen, is low in the sample, it indicates a gas rich in combustibles, in which case a proportional increase is made irs the amount of the oxygen and nitrogen mixture added. The leveling bottle is raised, the cock leading to the explosion pipette opened, and the gases are passed over and back two or more times to insure a thorough mixture; the gases are then exploded, drawn back into the burette and, after one minute, Contraction I is noted.

The residual gas is passed through the potassium hydroxide pipette at least three times to remove all the carbon dioxide. After the burette has drained, a reading is made, which, less the preceding reading, gives Contraction II. The residual gas consists of nitrogen and oxygen, and, for the purpose of calculation, the oxygen must be known. About 25 c c. of hydrogen are added, an exact reading is taken, and the gases are passed back and forth into the explosion pipette until thoroughly mixed. The gases are exploded, drawn back into the burette, allowed to drain and cool, and a reading is noted. This reading, less the former, represents the contraction due to the combustion of hydrogen and oxygen. This result is known as Contraction III, and one-third of it represents the oxygen present prior to the last explosion.

In the analysis of all gases there should be an excess of hydrogen after Contraction III, hence two-thirds of Contraciion III should be less than the hydrogen added; if it is not less, oxygen still remains, which is removed by passing the residue into the phosphorus pipette. The contraction is noted, multiplied by three and added to Contraction III; one-third of this total is the oxygen present prior to the last explosion.

The remaining gas consists of nitrogen and hydrogen, which do not enter into the subsequent calculations, as all the necessary data have been obtained for calculating the amounts of carbon monoxide, hydrogen, methane and nitrogen that existed in the oiginal mixture. The reactions which take
place in the combustions are as follows: $2 \mathrm{CO}+\mathrm{O}_{2}=2 \mathrm{CO}_{2}$, or two volumes of carbon monoxide unite with one volume of oxygen forming two volumes of carbon dioxide, there being a contraction of one volume. Therefore, the contraction and the oxygen used are each one-half the carbon monoxide, and the carbon dioxide formed has the same volume as the monoxide. $2 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}$, or two volumes of hydrogen unite with one volume of oxygen forming water vapor which condenses, the contraction being three volumes. The contraction is then three-halves the hydrogen, and the oxygen consumed is one-half the hydrogen. $\mathrm{CH}_{4}+2 \mathrm{O}_{2}=\mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$, or one volume of methane unites with two volumes of oxygen forming one volume of carbon dioxide, the water condensing and the contraction being two volumes. The contraction and the oxygen used are each twice the methane and the carbon dioxide has the same volume as the methane.

From these facts the following equations are formed:
Contraction $I=1 / 2$ Carbon Monoxide $+3 / 2$ Hydrogen +2 Methane.
Contraction II = Carbon Monoxide + Methane.
Oxygen consumed $=1 / 2$ Carbon Monoxide $+1 / 2$ Hydrogen +2 Methane.
Also, Oxygen consumed $=$ Oxygen added- $1 / 3$ Contraction III.
From these equations, several formulae may be derived for calculating the components of the original mixture. The simplest are:

Hydrogen $=$ Contraction I $+1 / 3$ Contraction III - Oxygen added. Con. I $+(4 \times$ Con. II $)+$ Con. III.
Carbon Monoxide $=\frac{\text { Con. } 1+(4 \times \text { Oxygen added } . ~}{3}$ -
Methane $=$ Contraction II - Carbon Monoxide present.
As the analysis by explosion was performed on half portion, the results must be doubled for expression of percentage. Nitrogen is obtained by difference, $i$. e., it is equal to 100 minus the sum of the percentages of the other constituents of the gas.

Example-Data.
Burette Readings.
100.0

Potassium Hydroxide
13.0 Carbon Dioxide.
87.0

Stick Phosphorus
0.0 Oxygen.
87.0 Residue.


Occasionally it is found that the gas when mixed with hydrogen for the second explosion will not explode, due to the fact that, the gas sample being abnormally high in combustibles, an insufficient amount of oxygen remains after the first explosion. In such case the gas is drawn back into the burette and the oxygen and nitrogen mixture is added until the volume approaches 100 c c.; the gases are again mixed, exploded and the analysis completed as usual, the oxygen added being tound from the sum of the two additions. If, in the first explosion of any analysis, the explosion ratio of inert to combining gases is not sufficiently high, and doubt exists as to the formation of oxides of nitrogen, the explosion and resulting determinations may be duplicated, using a larger amount of oxygen and nitrogen mixture and the portion of the residue which has been reserved in the phosphorus pipette, or the residue from a new portion may be obtained in the following manner: One hundred cubic centimeters are taken from the original sample and the carbon dioxide, oxygen, and illuminants if present, are removed in the usual manner. The residue may not be the same as that obtained on the first sample on account of the reduction in volume of the carbon dioxide, due to its slight solubility in the solution in the sample tube, but a part of the residue is taken equal in volume to the gas used in the first explosion, and the analysis is continued as usual. When the apparatus is not in use, the leveling bottle is raised and the residue from the previous analysis is forced into each of the pipettes so as to clear the stop-cocks; this is done to prevent the stop-cocks from sticking.

## 3. PRODUCER GAS.

For the analysis of producer gas the method as described under Blast Furnace Gas is used with one or two modifications as subsequently described.

Determinations of Carbon Dioxide and Illuminants. A sample of exactly 100 c. c. is measured and the carbon dioxide removed. Next, the gas is bubbled twice through the fuming sulphuric acid pipette to absorb the unsaturated hydrocarbons, composed chiefly of ethylene and commonly called illuminants. Care must be exercised not to allow any water to enter the pipette. After the acid has been drawn to its initial point in the stem of the pipette, the gas is passed into the solution of potassium hydroxide two or three times to remove the white acid fumes, and a reading is taken. The decrease in volume indicates the percentage of illuminants present.

Determination of Oxygen. The gas is passed into the pipette containing stick phosphorus and left there while the oxygen and nitrogen mixture required for the combustion described below is introduced into the burette, measured, and transferred to the explosion pipette. The gas residue in the stick phosphorus pipette is then returned to the burette and measured; the diminution in volume is oxygen.

Determination of Carbon Monoxide, Hydrogen and Methane. The amount of oxygen, necessary for the combustion of the residue from producer gas is more than that for blast furnace gas, since the percentage of combustibles is greater. The oxygen used in the explosion with one-half the residue from 100 cc . of gas varies between 8 and 12 c c. and at least 8 or 12 cc c. should remain for the second explosion; therefore, $20 \mathrm{c} c$. oxygen (in the oxygen nitrogen mixture) are sufficient for both explosions. If this 20 cc . oxygen were added pure, the first explosion would be violent, endangering the pipette and causing the formation of oxide of nitrogen. If more oxygen were added, the addition of more hydrogen than described here would have to be made, and the resultant explosion would be violent.

A volume of the oxygen and nitrogen mixture containing about 20 cc . oxygen is drawn into the burette from the overhead bottle, while the gas residue is in the stick phosphorus pipette as described above. The capillary is filled with water from the explosion pipette, a reading is taken, and the gas is passed into the explosion pipette. The gas in the stick phosphorus pipette is transferred to the burette, and the oxygen determined; one-half is passed into the phosphorus pipette or discarded, and the other half is passed into the explosion pipette. The gases are mixed and then exploded; the gases are returned to the burette and allowed to cool, and a reading is taken. Contraction I is found by subtracting the gas volume remaining after the explosion from the sum of the residue taken for the explosion and the auxiliary gas added. Contraction II, the carbon dioxide formed during the explosion, is determined by the gases being passed through the potassium hydroxide solution. For the combustion of the remaining oxygen, hydrogen is added. Since 20 cc . oxygen were added, and at least 8 cc . were consumed in the explosion, the amount remaining is less than 12 cc ., and 25 cc . hydrogen are sufficient. The reading after Contraction II is generally less than 75 , and hydrogen is added to the capacity of the burette, when the gases are
passed into the explosion pipette. If the reading after Contraction II be more than 75 , the gas is passed into the potassium hydroxide pipette and $25-30$ c c. hydrogen drawn in and measured (the capillary, as always, being filled with water). The hydrogen is then passed into the explosion pipette, and the gas in the alkaline pipette drawn into the burette and forced into the explosion pipette. The gases are mixed, exploded, drawn back into the burette, allowed to cool, and a reading is taken. The reduction in volume is designated Contraction III.

Example-Data.

> Burette Readings.
100.0

Potassium Hydroxide......... 95.5
Fuming Sulphuric Acid....... 95.0

Stick Phosphorus
95.0
95.0 Residue.
$47.5 \quad 1 / 2$ Residue.
Oxygen and Nitrogen Mixture added while gas in Phosphorus Pipette.
55.0 Mixture added, $36.5 \%$ Oxygen. (20.1 Oxygen added.)
47.5
102.5 Volume

Explosion.
83.8
$83.8 \quad$ 18.7 Contraction I.
14.3. Contraction II.
69.5

Hydrogen added 95.8

Explosion

## Calculations:

18.7 Contraction I.
7.7 1/3 Contraction III.
26.4
20.1 Oxygen added.

Analysis.

| 6.3 | Hydrogen present. | Carbon Dioxide. | 4.5\% |
| :---: | :---: | :---: | :---: |
|  |  | Illuminants... | 0.5\% |
|  |  | Oxygen. | 0.0\% |
| 18.7 | Contraction I. | Carbon Monoxide | 25.8\% |
| 57.2 | $4 \times$ Contraction II. | Methane. | 2.8\% |
| 23.1 | Contraction III. | Hydrogen. | 12.6\% |
|  |  | Nitrogen. | 53.8\% |
| 99.0 Total. |  |  |  |
| 33.0 | $1 / 3$ Total. |  | 100.0\% |
| 20.1 | Oxygen added. |  |  |

12.9 Carbon monoxide present.
14.3 Contraction II.
1.4 Methane present.

Explosion Ratios:-I, 2.1; II, 3.1.

## 4. BY-PRODUCT GAS.

Determination of Carbon Dioxide. One hundred cubic centimeters of the gas are measured, and the carbon dioxide is absorbed in the potassium hydroxide pipette.

Determination of Illuminants. The residue after carbon dioxide has been removed is passed through the fuming sulphuric acid pipette two or three times, care being taken to keep water out of the pipette. After the gas has been drawn to its initial point in the stem of the pipette, the fumes of sulphur trioxide are removed by being passed through the potassium hydroxide pipette. The contraction in volume is noted as illuminants and
consists of ethylene, $\mathrm{C}_{2} \mathrm{H}_{4}$, and its homologues and also benzene, $\mathrm{C}_{6} \mathrm{H}_{6}$. The latter may vary from $1 \%$ in the raw gas to $.2 \%$ in the debenzolized gas. It may be determined and deducted as described subsequently.

Determination of Oxygen. The gas, after the removal of illuminants. is passed into the phosphorus pipette for the absorption of oxygen. While here the oxygen and nitrogen mixture necessary for the combustion of the residue as subsequently described is drawn into the burette, measured, and passed into the explosion pipette. The gas in the phosphorus pipette is drawn backinto the burette and measured; the diminution in volume is oxygen.

Analysis of the Residue. The gas after the removal of the above absorbable constituents consists of carbon monoxide, hydrogen, and members of the paraffine group, $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{2 \mathrm{n}}+_{2}$, chiefly methane, $\mathrm{CH}_{4}$, but also some ethane, $\mathrm{C}_{2} \mathrm{H}_{6}$. The determinations of ethane would necessitate the removal of carbon monoxide and hydrogen before explosion as only two members of the paraffine group (hydrogen being considered the first member) can be determined by explosion. However, by the combustion of the residue of carbon monoxide, hydrogen, methane and ethane and calculation of the results, by the formulae given under blast furnace gas, to carbon monoxide, hydrogen and methane, no appreciable error is introduced. The carbon monoxide obtained is the same no matter what paraffines are present. Ethane is not determined separately, but is burned with the methane, so that the actual percentage of methane is increased and the actual percentage of hydrogen is decreased, that is, $\mathrm{H}_{2}+\mathrm{CH}_{4}$ (by analysis) $=\mathrm{H}_{2}+\mathrm{CH}_{4}+$ $\mathrm{C}_{2} \mathrm{H}_{6}$ (actual). Therefore, the sum of the combustibles and consequently the nitrogen remain true values.

## Example:

Gas Contains
$13.3 \%$
$31.0 \%$
$37.6 \%$
1.8\%
$4.7 \%$
$88.4 \%$

Analysis obtained by explosion.
$13.3 \%$
34.6\%
$35.8 \%$
$4.7 \%$
$88.4 \%$

The thermal values are nearly the same, being, for the iesidue exploded, 45b.8 B. t. u. Actual.
455.4 B. t. u. By Analysis.
1.4 B. t. u. Error of $.3 \%$ of the total heat value.

The amount of air necessary for combustion and the products of combustion as calculated from this analysis are correct, since the analysis is obtained by measurement of the oxygen used and the products of combustion formed.

The residue from absorption of by-product gas is very high in combustibles and consequently one-fourth is used for explosion. The oxygen required for the combustion of one-quarter of the residue from 100 c c. of gas is trom 20 to 25 c c. and there should be an excess of from 8 to 12 c c. to make proper explosion with the hydrogen subsequently added, a total of 33 с c. being required. That the proper explosion ratios be obtained, the oxygen is diluted with nitrogen as is done in the case of blast furnace and producer gas.

While the residue from 100 c c. of the gas is in the phosphorus pipette, as mentioned under determination of oxygen, a volume of oxygen and nitrogen mixture containing about 33 c c . oxygen is drawn into the burette, measured, the capillary being filled with water, and transferred to the explosion pipette. The gas in the phosphorus pipette is then brought back into the burette, measured, and all but exactly one-quarter discarded or forced into the phosphorus pipette.

If the entire quarter of the residue were passed into the explosion pipette, and the gases exploded after being mixed, the explosion ratio would be too low: 1.6 if $35 \%$ oxygen-nitrogen mixture were added and 1.0 if $45 \%$ mixture were used. To avoid this, 10 c c. of the gas are passed into the explosion pipette and exploded. The remaining gas is passed, the gases well mixed, and another explosion made. The ratio of the first explosion as calculated is very high, but it is probable that, the gases not being well mixed and the more combustible ones lying on the top, the actual ratio is lower. The second ratio is approximately 3 . The gas is passed into the burette and measured atter one minute for cooling and draining. Contraction I is calculated. The gas is then passed into the potassium hydroxide pipette for
the absorption of carbon dioxide; the diminution in volume is Contraction II. The residue is next passed into the potassium hydroxide pipette, and hydrogen sufficient to make a total volume of about 115 c c . is drawn into the burette and measured, the capillary being filled with water. The hydrogen is passed into the explosion pipette, and the gas in the potassium hydroxide pipette is drawn back into the burette and forced into the explosion pipette. The gases are mixed and exploded, then drawn back into the burette and measured. The difference in volume is designated Contraction III.

The volumes of oxygen and hydrogen given in the preceding paragraph will apply to all by-product gases generally analyzed. If gases rich in combustibles be encountered, the oxygen should be increased, likewise with a lean gas, the oxygen may be reduced.

Example-Data.


Calculations:

6.69 Methane.

## 5. FLUE GAS.

The repeated determination of large quantities of oxygen by stick phosphorus or pyrogallol solution introduces undesirable features with the use of either reagent. In the former case, unless care is exercised, the heat of reaction causes fusion with consequent disarrangment of the phosphorus sticks; with the use of the latter reagent there is a possibility of the incomplete absorption of all the oxygen. In such a case it would be absorbed in the cuprous chloride solution with the carbon monoxide, if this were used for the purpose, thus giving erroneous values to the carbon monoxide found. To overcome these difficulties the following method has been devised whereby the oxygen and carbon monoxide are determined by explosion; it has proven superior to the absorption method, which is usually followed in the analysis of flue gases.

Determination of Carbon Dioxide. This constituent is determined on exactly 100 c c. measured in the usual way, as described under Blast Furnace Gas.

Determination of Oxygen and Carbon Monoxide. One-half of the volume of the residual gases is rejected. To the remaining half, hydrogen is added to combine with the oxygen. More oxygen must be added to insure sufficient for the first and second explosions. A total of 18 c c. oxygen should be present. The oxygen in the residual gas varies inversely with the carbon dioxide and also according to the source from which the flue gas was derived. The following table shows approximately the amount of oxygen present in 50 c c. of gas and the amount to be added in the form of the oxygen and nitrogen mixture. (" $\mathrm{CO}_{2}$ " is per cent. found.)

| Source of Flue Gas | $\mathrm{O}_{2}$ present in $50 \mathrm{c} . \mathrm{c}$. | $\mathrm{O}_{2}$ to be added |
| :--- | :---: | :---: |
| Coal and Producer Gas | $10 \mathrm{c} c .-.5 \mathrm{CO}_{2}$ | $8 \mathrm{cc} .+.5 \mathrm{CO}_{2}$ |
| Blast Furnace Gas | $10 \mathrm{cc}-.4 \mathrm{CO}_{2}$ | $8 \mathrm{cc} .+.4 \mathrm{CO}_{2}$ |
| By-Product Gas | $10 \mathrm{c} .-\mathrm{CO}_{2}$ | $8 \mathrm{cc} .+\mathrm{CO}_{2}$ |
| Natural Gas | $10 \mathrm{cc}-.8 \mathrm{CO}_{2}$ | $8 \mathrm{cc} .+.8 \mathrm{CO}_{2}$ |

The method of procedure is as follows: To one-half the residue, 16 c c . of hydrogen are added, the capillary is filled with water, and a reading is taken. The oxygen and nitrogen mixture containing the calculated amount of oxygen is then added, and a reading is taken. The gases are passed into the explosion pipette, well mixed and exploded. The residue is drawn into the burette and measured, the decrease in volume is Contraction I. Contraction II is found by passing the gas through the potassium hydroxide pipette. Hydrogen is added to the capacity of the burette (at least 26 c c. must be added). A reading is taken, and the gases are transferred to the explosion pipette, mixed and exploded. The residue is returned to the burette and measured; Contraction III is thus obtained.

The data necessary for the calculation of the percentage of oxygen and carbon monoxide in the sample have thus been obtained. From the reactions given under the determination of carbon monoxide, hydrogen and methane in blast furnace gas, it is seen that when one volume of oxygen unites with two volumes of carbon monoxide, there is a contraction of one volume and the formation of two volumes of carbon dioxide, which on absorption causes a
further contraction of two volumes; the total contraction is, therefore, three volumes for one volume oxygen, or the oxygen is one-third the total contraction. The carbon monoxide was also shown to have the same volume as the dioxide formed. In the combustion of hydrogen and oxygen, it was shown that the oxygen is one-third the contraction. Then the oxygen entering the two explosions, or the total oxygen, is one-third the sum of the three contractions, and the oxygen in the sample is found by subtracting the oxygen added from this total oxygen. These facts are expressed in the following equations:

Carbon Monoxide $=$ Contraction II.
Oxygen in sample $=\frac{\text { Con. I + Con. II + Con. III }}{3}$-Oxygen added.
The absence of methane and hydrogen in a flue gas may be proven by the application of this formula:

$$
\mathrm{H}_{2}+\mathrm{CH}_{4}=\frac{2(\text { Con. I) }- \text { Con. II }}{3}-\mathrm{H}_{2} \text { added for the first explosion. }
$$

Example-Data.

> Burette Readings.

$$
100.0
$$

Potassium Hydroxide. ..... . $10.0 \%$ Carbon Dioxide.

|  | 90.0 |  |
| :---: | :---: | :---: |
|  | 45.0 | 1/2 Residue. |
| Hydrogen added......... . . . |  | 16.2 c c. Hydrogen. |
|  | 61.2 |  |
| Oxygen and Nitrogen Mixture |  | 35.8 - 13.07 c c. Oxygen added |

24.7 Contraction I.
72.3

Potassium Hydroxide
. 8 Contraction II.
71.5

Hydrogen added.
99.5

Explosion
2ri. 0 Contraction III.

## Calculations:



## r. NATURAL GAS.

The analysis of natural gas by the methods given for the other fuel gases described herein is not very satisfactory. If but little, say 10 c c., of the methane and ethane are exploded with oxygen, any error in reading is multiplied many times. Again on combustion of a large quantity with oxygen, the resultant gas is nearly pure carbon dioxide and, its solubility in water varying with its percentage, consequently a relatively large quantity is dissolved. The second contraction, i. e., on absorption of carbon dioxide, being low, the result is that the sum of the methane and ethane obtained by calculation is over 100, and the nitrogen a minus quantity. To overcome these defects, use is made of the following method in which the contraction on explosion and on absorption of the carbon dioxide is treated as one known factor and the oxygen entering into combination the other factor.

Percentage of Oxygen in Commercial Oxygen. Commercially pure oxygen is used instead of the oxygen and nitrogen mixture of previous methods. This practice is necessary on account of the great amount of oxygen required for combustion. The determination of the percentage of oxygen is made by exploding a large quantity of it with hydrogen and noting the resultant contraction, of which one-third equals the oxygen. The determination is best accomplished in the following manner: about 100 c c. of pure hydrogen are forced into the burette, the capillary is filled with water from the explosion pipette, a reading is taken, and the gas is forced into the explosion pipette until the water level is at zero; about 100 c c. more hydrogen are introduced, and a reading is taken, the gas is then forced into the explosion pipette
until the water level is again at zero. About $60-65 \mathrm{c}$ c. oxygen are then added, a reading is taken, and 15 c c. portions are successively introduced into the explosion pipette and exploded, the gases being well mixed before the last explosion. After the final explosion, the residue is drawn over, the capillary being filled with water, and a reading is taken. One-third of the contraction is oxygen, from which the percentage can be calculated.

Determination of Carbon Dioxide. Exactly 100 c c. are forced into the burette from the sampling tube, as described previously. A reading is taken, and the gas is passed through the potassium hydroxide pipette for the absorption of carbon dioxide, then returned to the burette, and the capillary filled with water from the explosion pipette. A reading is taken; the contraction in volume is the percentage of carbon dioxide.

Determination of Illuminants. The use of fuming sulphuric acid is not advisable here as it absorbs the higher members of the paraffine group. In its place is substituted a pipette containing a $1 \%$ solution of palladium chloride. The gas is passed three times through this solution and returned to the burette, the contraction being illuminants, ethylene and its homologues. The contraction in volume would also include hydrogen and carbon monoxide, if present; however, the rate of absorption of these gases is comparatively slow. They are generally absent, and their absence is proved by the method described later. One passage of natural gas through fuming sulphuric acid gives about the same contraction as the method described herein, but repeated passages take out more and more of the paraffines. No definite result is obtained.

Determination of Oxygen. After absorption of illuminants, the gas is passed into the phosphorus pipette for the absorption of oxygen, and while it is there, the requisite amount of oxygen is measured in the burette and transferred to the explosion pipette. The gas in the phosphorus pipette is then returned to the burette, and the contraction due to absorption of oxygen is noted.

Determination of Methane and Ethane. The gas residue consists, besides the small quantity of nitrogen, of methane, ethane and perhaps other higher homologues. It is impossible by any method to determine more than two gases of the paraffine group by combustion, and the gases are assumed to consist of methane and ethane. No error is introduced by this assumption, as proven later.

While the gas is in the phosphorus pipette as described above, oxygen is drawn into the burette to its capacity, the capillary is filled with water, and a reading is taken. The gas is then forced into the explosion pipette until the water is at the zero mark, the capillary containing gas. The ight hand capillary tube is flushed with water, and 50 c c. of air are drawn into the burette and measured; about 15 c c. oxygen (sufficient to make the total 122 c c.) are then added, and the gas is forced into the explosion pipette. The right hand capillary is flushed out, and the gas in the phosphorus pipette is drawn into the burette and measured, as described under Determination of Oxygen. One-half the residue is discarded or reserved in the phosphorus pipette. About 10 cc . of the half reserved for analysis are forced into the explosion pipette and exploded. This operation is repeated with successive portions of the gas until the last is added, when the gases are thoroughly mixed before explosion. The resultant gas is very rich in carbon dioxide, which, if the gas were passed into the burette, might be absorbed by the water. Later on this dissolved carbon dioxide may be given off by the water. Therefore, a compressor is placed on the rubber tubing from the burette to the bottle, and the gas in the explosion pipette is forced to bubble through the potassium hydroxide pipette by raising the bottle connected to the explosion pipette. After the gas has been passed several times it is transferred to the burette, and a reading is taken. The sum of the diluted oxygen added and the gas residue taken for explosion, minus the volume remaining after the absorption of carbon dioxide, is Contraction "A." Hydrogen is then added to the capacity of the burette, a reading is taken, and the gases are passed into the explosion pipette, well mixed and exploded. The residue is passed into the burette and measured, the decrease in volume is Contraction "C."

From the above contractions ("A" and " C ") and from a knowledge of the amount of oxygen in the commercial oxygen, the methane and ethane may be calculated. The reactions of burning methane and ethane are as follows:

$$
\begin{aligned}
& \mathrm{CH}_{4}+2 \mathrm{O}_{2}=\mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \\
& 2 \mathrm{C}_{2} \mathrm{H}_{6}+7 \mathrm{O}_{2}=4 \mathrm{CO}_{2}+6 \mathrm{H}_{2} \mathrm{O}
\end{aligned}
$$

From these reactions it is seen that the total contraction on combustion and absorption of methane and ethane are 3 and $9 / 2$ times the volume of the
respective gases; or that " A " $=3 \mathrm{CH}_{4}+9 / 2 \mathrm{C}_{2} \mathrm{H}_{6}$. Likewise the oxygen
 $\mathrm{Oc}=2 \mathrm{CH}_{4}+7 / 2 \mathrm{C}_{2} \mathrm{H}_{6}$. Also it is evident that the oxygen consumed
 which is $1 / 3 \mathrm{C}$. or $\mathrm{Oc}=\mathrm{Oa}-1 / 3 \mathrm{C}$.

From these equations the following formulae are derived:

$$
\begin{gathered}
\mathrm{CH}_{4}=7 / 3 \mathrm{~A}+\mathrm{C}-3 \mathrm{Oa} . \\
\mathrm{C}_{2} \mathrm{H}_{8}=(\mathrm{A}+1 / 3 \mathrm{C}-\mathrm{Oa})-\mathrm{CH}_{4} .
\end{gathered}
$$

Example-Data.
Burette Readings.
Puity of Oxygen.
0.0

Commercial Oxygen added.... 61.8 Commercial Oxygen added.
$61.8 \quad 257.6$ Total volume.
Explosion
77.0 Residue.
$77.0 \quad 180.6 \quad$ Contraction.
60.2 1/3 Contraction or Oxygen.
$60.2 \div 61.8=97.4 \%$ Oxygen in Commercial Oxygen. Gas Analysis.
100.0

Potassium Hydroxide......... . $2 \%$ Carbon Dioxide.
99.8

Palladium Chloride........... $.4 \%$ Illuminants.
99.4

Stick Phosphorus. . . . . . . . . . . $0 \%$ Oxygen.
99.4
49.7 1/2 Residue.


Determination of Hydrogen and Carbon Monoxide. These gases are generally absent. If present, they reduce palladium chloride somewhat slowly, water and carbon dioxide being formed. If the diminution in volume caused by the passage of the gas through palladium chloride is considerable, the presence of hydrogen or carbon monoxide would be indicated, in which case their determination is advisable. For this purpose, the apparatus for supplying hydrogen is disconnected, and a palladium tube is connected to the end of the gas apparatus,-the other end of the palladium tube is connected to an absorption pipette containing water. The palladium tube is immersed in a beaker of water at $90-100$ degrees C ., and oxygen is passed through the tube to oxidize any hydrogen present. The water is drawn to a specified point in the stem of the absorption pipette, and the capillary tube of the apparatus is filled with water from the explosion pipette. Fifty c c. of natural gas are then introduced into the burette and measured, the carbon dioxide is removed, and the gas is passed through fuming sulphuric acid. About 10 cc . of oxygen are added, and a reading is taken. The gases are then passed back and forth through the palladium tube, whichis immersed in hot water at first and then in cold water to cool the gas. The gas is finally brought back into the burette, the water in the pipette being at the previous level, and a reading is taken. The decrease in volume is noted as Contraction "a." The gases are then passed into potassium hydroxide, drawn back and measured; the diminution in volume is Contraction "b." From a study of the contractions formed in the combustion of carbon monoxide and hydrogen, it is seen that

$$
\begin{gathered}
\mathrm{CO}=\mathrm{b} \\
\mathrm{H}_{2}=\frac{2 \mathrm{a}-\mathrm{b}}{3}
\end{gathered}
$$

Error in Assuming the Gas to be Methane and Ethane. The basis of the determination is in reality the volume of combustible gas (equal to A Oxygen consumed) and the oxygen necessary for combustion (Oxygen consumed $=$ Oxygen added $-1 / 3 \mathrm{C}$ ). Both are accurately determined, consequently the combustibles present and the amount of air necessary for their combustion as calculated from the analysis is correct. The carbon dioxide formed on combuscion has not been determined but can be calculated for any and all paraffines which have the general formula $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{2 n}+{ }_{2}$. If n represents the number of carbon atoms in the molecule, and $p$ the total
volume of paraffines, then, by reasoning analogous to that given when the formulae were derived, $n p$ equals (Oxygen consumed - $1 / 3 \mathrm{~A}$ ). But np equals the carbon dioxide and is independent of any particular paraffines that may be assumed to be present, therefore, the carbon dioxide formed on the combustion of the gas, as calculated from the analysis, is correct. As regards the heat value calculated from the analysis, Thomsen has shown that the heat value of a paraffine is equal to $\mathrm{K}+\mathrm{nD}$ where K and D are constant factors. The heating value of the unabsorbed portions of natural gas then is $(K+n D) p$ or $K p+D n p$. It has been shown that $p$ and $n p$ are correct, depending upon the factors $\mathrm{A}, \mathrm{C}$ and Oa . Therefore, the heating value of natural gas as calculated from the analysis is correct.

## BENZOL IN BY-PRODUCT GAS.

Unwashed by-product gas contains about $.8 \%$ to $1.0 \%$ benzol, and the washed gas contains about $.2 \%$. It is determined by passing the gas through paraffine oil in a series of bottles and distilling the absorbed benzol as described on Page 80 of the "Coal, Coke and By-Product" pamphlet. The result so obtained is converted into pounds and divided by the number of cubic feet of gas at standard temperature and pressure. This result, when divided by the weight of a cubic foot of benzol (gas) at 62 degrees and 30 inches (Table "A") and multiplied by 100, gives the percentage. This percentage is subtracted from the illuminants as obtained by volumetric analysis, the difference being ethylene and possibly its homologues.

## Example:

Gas metered (reduced to Standard conditions) . . $=75.4$ Cubic Feet.
Benzol obtained...................................... . . . $=.152$ Pounds.
Benzol per Cubic Foot. . . . . . . . . . . . . . . . . . . . . . . $=.002016$ Pounds.
Per cent. of benzol $(.002016 \div .21152 \times 100) \ldots=.95 \%$

## TOTAL SULPHUR IN BY-PRODUCT GAS.

The sulphur occurring as hydrogen sulphide is removed and determined by absorption in an acetic acid solution of lead acetate; the sulphur otherwise combined and known as organic sulphur is burnt with the gas in a Referees apparatus and determined as barium sulphate. The train consists of a gas meter, three gas washing bottles, containing each 100 c . c. of a solution of
lead acetate, and a Referees apparatus. The chimney and condenser of the Referees apparatus are rinsed with water and as much ammonium carbonate as will find place around the pillar of the burner is added. The meter reading, temperature, barometer and manometer readings, and time are taken. The burner is lighted, and as soon as the flame is adjusted, the trumpet tube is connected to the condenser. The gas is burned at the rate of about half a cubic foot per hour for a period of from two to four hours. The condensate from the chimney, condenser and trumpet is rinsed into the collecting breaker and filtered. Sulphur is determined by acidification of the solution with hydrochloric acid and precipitation as barium sulphate with barium chloride. The precipitate is removed by filtration, ignited and weighed; $13.73 \%$ of its weight is sulphur.

The wash bottles contain a precipitate of lead sulphide, which is collected on a filter, washed with hot water, and dissolved in nitric acid into a volumetric flask. The solution is diluted to a definite volume, then an aliquot part is withdrawn, heated to boiling and 10 c c . of dilute sulphuric acid ( $1: 1$ ) are added. Boiling is continued for about 30 minutes and the precipitate of lead sulphate is allowed to cool, when it is removed by filtration, washed, dried, and weighed; $10.57 \%$ of this weight is sulphur, and $11.24 \%$ of it is the equivalent in hydrogen sulphide. The lead acetate solution is made by dissolving 100 grams lead acetate in a liter of water containing 30 cc . of glacial acetic acid.

Hydrogen Sulphide in By-Product Gas. When hydrogen sulphide alone is to be determined, use is made of the following method: The gas is aspirated through two wash bottles of 300 c c. capacity, each containing 100 c c. of a $5 \%$ solution of sodium hydroxide, into a gasometer of about 15 liters capacity. A large aspirator bottle, graduated to 200 c c. may be conveniently employed as a gasometer. The top opening of the aspirator bottle is closed with a large three-holed rubber stopper for a gas inlet, manometer and thermometer. Through a one-hole rubber stopper, fitted into the bottom outlet of the gasometer, is placed one end of a one-fourth inch glass tube bent sharply at right angles and provided on the other end with a short rubber tube, on which is a pinchcock to regulate the flow of water from the gasometer into the receiver below.

About ten liters of gas are passed, the temperature and the pressure being recorded. The sodium hydroxide solutions are rinsed into a liter flask, made up to a definite volume, and an aliquot part taken for titration. Ten cubic
centimeters of starch solution and 10 c c. of a $.2 \%$ solution of potassium iodide are added, followed by dilute hydrochloric acid. The liberated hydrogen sulphide is titrated with standard iodine or iodate solution to the first permanent blue. The iodide is added to prevent the necessity, otherwise, of determining and deducting a blank. The starch solution is made as follows: Five grams starch (preferably soluble starch) are stirred into 25 c c. of water, and, while stirring is continued, 5 c c. of a solution containing 2.5 grams sodium hydroxide are added; the gelatinous mass, after having stood one hour, is poured into water and diluted to one liter. Starch may also be made by boiling, as described in the Corporation pamphlet on analysis of steel.

The standard iodine solution may be a deci-normal one or the same solution as is used in the titration of sulphur in steel. The latter solution is made by dissolving 4 grams iodine and 10 grams potassium iodine in 25 c c. cold water; the deci-normal solution is made by dissolving 12.7 grams iodine and 30 grams potassium iodide in 75 c c. water. When solution is complete, water is added to a volume of one liter. A solution of potassium iodate may be used instead of the iodine. It is made by dissolving 1.112 grams iodate and 6 grams potassium iodide in one liter of water. This solution and the iodine solution, containing 4 grams per liter, is such that 1 c c. equals .0005 gram sulphur and .0005314 gram or .00820 grain hydrogen sulphide. One cubic centimeter of deci-normal solution equals .0017038 gram or .0263 grain hydrogen sulphide.

The volume of gas measured is corrected for temperature and pressure as subsequently described, and the resultant number of cubic feet of gas at standard temperature and pressure is divided into the grains of hydrogen sulphide found by titration; the result should also be stated in percentage. One cubic foot of hydrogen sulphide gas weighs 636 grains, therefore, the grains of hydrogen sulphide found per 100 cubic feet, divided by 636 , gives the percentage.

## Example:

Gas corrected to standard conditions................ . . 382 Cubic Foot.
Iodate used in titrating an aliquot of $1 / 5 \ldots . . . . . .22 .4$ c c.
Iodate equivalent to total sulphide................... . . 112.0 c c.
Hydrogen sulphide present (. $00820 \times 112$.$) ........ . 9184$ Grain.
Hydrogen sulphide per 100 cubic feet
$\quad(.9184 \div .382 \times 100) \ldots \ldots \ldots \ldots \ldots \ldots .240 . \quad$ Grains
Hydrogen sulphide by volume $(240 . \div 636) \ldots \ldots . \quad .38 \%$

An alternative method consists in titrating the gas direct with a standard solution of iodine. One hundred c c. of gas are drawn into a suitable pipette containing starch solution, and iodine is added until a permanent blue is obtained. The iodine solution is made by dissolving 1.7076 grams of iodine and 20 grams potassium iodide in 25 cc c. water and diluting to one liter; 1 c c. of this solution used in titrating 100 c c. of gas is equivalent to 100 grains of hydrogen sulphide per 100 cubic feet of gas.

## CYANOGEN IN BY-PRODUCT GAS.

In this determination the cyanogen is converted into potassium ferrocyanide by being passed through a potassium hydroxide solution containing freshly precipitated ferrous hydroxide in suspension. After filtration, the potassium ferro-cyanide is determined in the clear solution by acidification and titration with a standard solution of ferric chloride.

Into each of three wash bottles are placed 60 c c. of a $10 \%$ potassium hydroxide solution and 30 cc c. of a ferrous sulphate solution ( $10 \%$ of the crystals). Gas is passed at the rate of two to three cubic feet per hour for about four hours. The precipitate and solution are transferred from the wash bottles to a 600 c c. beaker, and boiled. The solution is filtered while hot into a volumetric flask, and the precipitate washed, the washing going also into the flask. An aliquot part of the filtrate is transferred to a beaker and one drop of ferric chloride solution is added, followed by the careful addition of dilute sulphuric acid until the resultant precipitate just dissolves. The solution is now titrated with standard ferric chloride solution. The end point of the titration is indicated by the spot test; a few drops from the beaker containing the liquid under titration are placed on a white filter paper; a spot will be formed with the blue already precipitated surrounded by a circle of the clear solution. When neither ferric chloride solution nor potassium ferro-cyanide solution cause a blue color upon being placed on the clear circle, the end point is reached.

The ferric chloride solution is made by dissolving 25 grams of the salt in water, acidified slightly with hydrochloric acid, and diluting to 1 liter. It is standardized by titrating with a standard solution of potassium ferro-
cyanide made by dissolving 4.22 grams of $\mathrm{K}_{4} \mathrm{Fe}(\mathrm{CN})_{6}+3 \mathrm{H}_{2} \mathrm{O}$ in 1 liter of water. One hundred c c. of this solution are withdrawn with a pipette, transferred to a beaker, and titrated as described above; this aliquot part is equal to 0.156 grams of cyanogen. The cubic feet of gas as metered is corrected for pressure, temperature and moisture as hereafter described.

## REDUCTION OF VOLUME TO STANDARD TEMPERATURE AND PRESSURE.

In the determination of benzol, cyanogen or calorific value of a gas, a wet meter or tank is used for measuring the gas, and the temperature and pressure at the meter or tank are taken, so that the volume metered may be reduced to standard conditions of temperature and pressure. However, the gas is saturated with moisture which has a definite partial pressure.

To reduce the gas volume to dry gas under standard conditions, the procedure is the same as if dry gas were metered, except that the pressure of the dry gas is found by subtracting the vapor pressure from the total pressure of the mixture of gas and vapor.

Let $\mathrm{V}_{\mathrm{S}}=$ Volume of dry gas at $62^{\circ} \mathrm{F}$. and $30^{\prime \prime}$ mercury.
$\mathrm{V}=$ Volume as metered.
$b=$ barometer in inches of mercury.
$\mathrm{p}=$ pressure of meter in inches of mercury.
$\mathrm{e}=$ vapor pressure in inches of mercury at temperature of meter, as given in Table (B).
$\mathrm{t}=$ temperature in Fahrenheit of the meter.
( $0^{\circ} \mathrm{F}$. is considered $459^{\circ}$ Absolute.)
The pressure of the mixture of water vapor and dry gas in the meter is ( $b+p$ ), and since the pressure of water vapor is (e), the pressure due to dry gas is $(b+p-e)$.

Therefore, $\mathrm{V}_{\mathrm{s}}=\mathrm{V} \times \frac{521}{459+\mathrm{t}} \times \frac{\mathrm{b}+\mathrm{p}-\mathrm{e}}{30}$
The calculation may be simplified by applying a factor equal to $\frac{521}{459+\mathrm{t}} \times \frac{\mathrm{b}+\mathrm{p}-\mathrm{e}}{30}$ as found in Table C. This table gives the factor for reducing a given volume of gas to $62^{\circ} \mathrm{F}$. and $30^{\prime \prime}$ Mercury.

## Example:


$3.5 \times .0738=.26^{\prime \prime}$ Mercury, pressure of meter.
Pressure of dry gas is $29.40^{\prime \prime}+.26^{\prime \prime}-.73^{\prime \prime}=28.93^{\prime \prime}$ and the volume of dry gas at standard temperature and pressure equivalent to the wet gas metered is, therefore,

$$
2.813 \times \frac{521}{529} \times \frac{28.93}{30}=2.672
$$

Using Table "C," the factor for $70^{\circ}$ and $28.93^{\prime \prime}$ is found to be .9498 .
$2.813 \times .9498=2.672$ cubic feet of dry gas.

## THERMAL VALUES:

The thermal values may be determined by calorimeter or by calculation from the gas analysis. Considerable variations exist among the values commonly given as heats of combustion for the different gases; but it is believed that the following figures, calculated from Thomsen, will give results which are sufficiently reliable for all technical purposes. In Column III of Table "A," showing the British thermal units developed in the combustion of one cubic foot of the different gases, measured at $62^{\circ} \mathrm{F}$. and $30^{\prime \prime}$ Mercury, two values are given-the gross and the net-the difference between them being the latent heat of the water formed, which is not included in the latter. The temperature of the products of combustion in both cases are assumed to be $62^{\circ} \mathrm{F}$. For the purpose of comparison, all Corporation results should be expressed in terms of Net B. t. u. Where the illuminants contain gases having a higher heat value than ethylene, a higher value should be used, this being determined from the gas by analysis. The percentage of each combustible present is multiplied by its value in the table, and the sum of the products will represent the British thermal units evolved in the combustion of one cubic foot of the gas.

## Example:

Gas Analysis. Thermal Value.
Carbon Dioxide. ..................... . . . 4.5
Illuminants.......................... . . . $5 \%$ of $1495=7.48$ B. t. u.
Oxygen......... . . . . . . . . . . . . . . . . . . 0.0
Carbon Monoxide..................... $25.8 \%$ of $322=83.08$ B.t. u.
Methane,............................ . $2.8 \%$ of $909=25.45$ B. t. u.
Hydrogen... . . . . . . . . . . . . . . . . . . . $12.6 \%$ of $274=34.52$ B. t. u.
Nitrogen
53.8\%
150.5
B. t. u.

## WEIGHT OF A CUBIC FOOT OF GAS.

Column II of Table " C " shows the weight in pounds of a cubic foot of the constituent gases at a temperature of $62^{\circ} \mathrm{F}$. and a pressure of $30^{\prime \prime}$ mercury. The weight of a cubic foot of gas is the sum of the values, found by multiplying the weight per cubic foot of each of the constituent gases by its percentage of volume. The weight of a cubic foot of moist gas is found by adding the weight of the cubic foot of dry gas at its temperature and partial pressure to the weight of a cubic foot of water vapor at its partial pressure.

## Example:

Gas has been washed at $70^{\circ}$ and $29.66^{\prime \prime}$ and was, therefore, saturated. Pressure of moisture is $.73^{\prime \prime}$, pressure of dry gas is $29.66-.73=28.93^{\prime \prime}$.

Gas Analysis.
Carbon Dioxide............. $13.0 \%$ of $.11671=.015172$
Carbon Monoxide. .......... . $25.8 \%$ of $.07365=.019002$
Hydrogen. . . . . . . . . . . . . . . $5.8 \%$ of $.00531=.000202$
Nitrogen. . . . . . . . . . . . $.07368=.042292$

Weight of 1 cubic foot dry gas at $62^{\circ}$ and $30^{\prime \prime}=.07667$ Pound.
$\times .9498$ (See Table "C")
Weight of 1 cubic foot dry gas at $70^{\circ}$ and $28.93^{\prime \prime}=.07282$ Pound.
Weight of 1 cubic foot moisture at $70^{\circ}$ and $.73^{\prime \prime}=$
(Table B) is 7.98 Grains or . 00114 Pound.
Weight of 1 cubic foot wet gas at $70^{\circ}$ and $29.66^{\prime \prime}=.07396$ Pound.

By another method the weight of a cubic foot of wet gas is found by adding the weight of a cubic foot of dry gas to the weight of moisture accompanying it and dividing the sum by one, plus the volume of moisture accompanying one cubic foot dry gas; this latter volume is found by multiplying the grains of moisture by .00301 , the volume occupied by one grain of moisture at $62^{\circ}$ and $30^{\prime \prime}$.

## Example:

The gas contains 6 grains of moisture per cubic foot at $62^{\circ}$ and $30^{\prime \prime}$.
Conditions in the main were $70^{\circ}$ and $29.66^{\prime \prime}$.
Weight of 1 cubic foot of dry gas at $62^{\circ}$ and $30^{\prime \prime} \ldots=$.
At $62^{\circ}$ and $30^{\prime \prime}, 1$ cubic foot of water vapor theoretically weighs .04749 pound from which one grain would occupy .00301 cubic foot.
Volume of moisture $=6 \times .00301=.01806$ cubic foot.
Weight of .01806 cubic foot Moisture (. $01806 \times .04749$ or $6 \div 7000$ ) . . . . . . . . . . . . . . . . . $=.00086$ Pound.

Weight of 1.01806 cubic feet moist gas. . . . . . . . . . . . . $=.07753$ Pound.
Weight of 1 cubic foot of moist gas at $62^{\circ}$ and $30^{\prime \prime} \ldots . .=.07615$ Pound.
Weight of 1 cubic foot of moist gas at $70^{\circ}$ and $29.66^{\prime \prime}$.-
(. $07615 \times .9737$ ) (See Table C) . . . . . . . . . . . . . . . $=.07415$ Pound.

Specific Gravity and Percentage by Weight. When suitable apparatus is not available for determining the specific gravity of gas, it may be calculated from the volumetric analysis by means of Column I of Table "A," showing the specific gravity of various gases compared with air. The calculated specific gravity of a gas is found by adding the products obtained by multiplying the percentage by volume of each constituent gas by its specific gravity. The respective products thus obtained, divided by the specific gravity of the gas, yield the percentage by weight of the constituent gases.

The specific gravity of moist gas is found by adding the product of .6221 and the percentage of water vapor accompanying dry gas to the specific gravity of the dry gas, and dividing the sum by one, plus the percentage of water vapor. This latter value is found by multiplying the grains per cubic foot dry gas by .00301 , the volume occupied by 1 grain water vapor.

Example:
Gas Analysis.

| Carbon Dioxide | 13.0\% of | . $5288=$ | . 19874 |
| :---: | :---: | :---: | :---: |
| Oxygen. | . $0 \%$ |  |  |
| Carbon Monoxide. | 25.8\% of | $.9648=$ | . 24892 |
| Methane. | .0\% |  |  |
| Hydrogen.. | 3.8\% of | $.0695=$ | . 00264 |
| Nitrogen. | . $57.4 \%$ of | $.9651=$ | . 55397 |
| Specific gravity |  |  | . 0043 |

Moisture on this gas was found to be 6 grains per cubic foot dry gas at $62^{\circ}$ and $30^{\prime \prime}$. Volume of moisture was, therefore, $6 \times .00301$ or .01806 cubic foot.

Therefore, specific gravity of dry gas

$$
=1.0043
$$

.01806 cubic foot moisture at .6221 specific gravity.... $=\frac{.0112}{1.0155}$
Specific gravity of moist gas is $1.0155 \div 1.01806 \ldots \ldots=.9975$
The specific gravity of gas over water varies with the temperature since the amount of water taken up varies.

## APPENDIX.

The Air Necessary for Combustion. Column IV of Table "A" gives the amount of oxygen necessary for combustion of the various gases. It may be repeated here and stated as an equation, thus:

Oxygen Necessary, $(\mathrm{On})=3 \mathrm{C}_{2} \mathrm{H}_{4}+.5 \mathrm{CO}+2 \mathrm{CH}_{4}+.5 \mathrm{H}_{2}+3.5$ $\mathrm{C}_{2} \mathrm{H}_{6}+7.5 \mathrm{C}_{6} \mathrm{H}_{6}-\mathrm{O}_{2}$.

Air is composed of $20.9 \%$ oxygen, the remaining $79.1 \%$ being considered nitrogen. The nitrogen is then 3.78 times the oxygen, and the air necessary for combustion is 4.78 times the oxygen. The above is in terms of cubic feet of dry air per cubic foot of dry gas at the same temperature and pressure.

The Products of Combustion. The products are given in Table "A", Column V. Placed as equations, they are:

$$
\begin{aligned}
& \mathrm{CO}_{2} \text { produced }=\mathrm{CO}_{2}+\mathrm{CO}+\mathrm{CH}_{4}+2 \mathrm{C}_{2} \mathrm{H}_{4}+2 \mathrm{C}_{2} \mathrm{H}_{6}+6 \mathrm{C}_{6} \mathrm{H}_{6} \\
& \mathrm{H}_{2} \mathrm{O} \text { produced }=\mathrm{H}_{2}+2 \mathrm{CH}_{4}+2 \mathrm{C}_{2} \mathrm{H}_{4}+3 \mathrm{C}_{2} \mathrm{H}_{6}+3 \mathrm{C}_{6} \mathrm{H}_{6} .
\end{aligned}
$$

$\mathrm{N}_{2}$ produced $=\mathrm{N}_{2}+3.78\left(3 \mathrm{C}_{2} \mathrm{H}_{4}+.5 \mathrm{CO}+2 \mathrm{CH}_{4}+.5 \mathrm{H}_{2}+\right.$ $3.5 \mathrm{C}_{2} \mathrm{H}_{6}+7.5 \mathrm{C}_{6} \mathrm{H}_{6}-\mathrm{O}_{2}$ ). The volumes above refer to volumes per dry volume of fuel gas, and the moisture in the fuel gas and in the air must be added.

## Example:

| Gas Analysis | Percentage | Oxygen <br> Necessary | Products of Combustion. |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\mathrm{CO}_{2}$ | $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{N}_{2}$ |
| Carbon Dioxide. | 1.8\% | 0.0 | 1.8 |  |  |
| Ethylene. | 2.2\% | 6.6 | 4.4 | 4.4 |  |
| Benzine. | . $2 \%$ | 1.5 | 1.2 | . 6 |  |
| Carbon Monoxide. | 4.8\% | 2.4 | 4.8 |  |  |
| Methane. | 26.8\% | 53.6 | 26.8 | 53.6 |  |
| Hydrogen.. | 53.1\% | 26.55 |  | 53.1 |  |
| Nitrogen. ...... | 10.9\% |  |  |  |  |
|  |  | 90.65 |  |  |  |
| Oxygen.... | . $2 \%$ | . 2 |  |  |  |
|  |  | $90.45 \%$ | $39.0 \%$ | 111.7\% |  |

$\mathrm{N}_{2}$ produced is $10.9+3.78 \times 90.45$. 352.80

Air necessary $=4.78 \times 90.45=432.35 \%$ or 4.3235 cubic feet per cubic foot of dry fuel gas at same temperature and pressure.

The moisture in fuel gas was found to be 6 grains per cubic foot at $62^{\circ}$ and $30^{\prime \prime}$, therefore, its volume is $6 \times .3=1.8 \%$ of the dry fuel gas. The air contains 4 grains per cubic foot; from Table " B " it is found that 4 grains compare with $.35^{\prime \prime}$ pressure, therefore, the pressure of air is the barometric pressure ( $29.40^{\prime \prime}$ ) minus $.35^{\prime \prime}$ or 29.05 . $^{\prime \prime}$ The volume of moisture is .35 $\div 29.05 \times 100=1.2 \%$ of the dry air. The total moisture is then $111.7+$ $1.8+(1.2 \%$ of 432.35$)=118.7 \%$ of the fuel gas or 1.187 cubic feet per cubic foot of dry fuel gas, measured at the same temperature and pressure.

The products are summarized as follows:

| $\mathrm{CO}_{2}$. | $39.0 \%$ of fuel gas. |
| :---: | :---: |
| $\mathrm{N}_{2}$ | $352.8 \%$ of fuel gas. |
| $\mathrm{H}_{2} \mathrm{O}$. | 118.7 \% of fuel gas. |

Composition of Perfect Flue Gas. The above figures show the products of perfect combustion of a volume of fuel gas. Their percentages of the flue gas are easily calculated by dividing each by the sum.

| Flue Gas | Dry | Moist |
| :---: | :--- | ---: |
| $\mathrm{CO}_{2}$ | $10.0 \%$ | $7.6 \%$ |
| $\mathrm{~N}_{2}$ | $90.0 \%$ | $69.1 \%$ |
| $\mathrm{H}_{2} \mathrm{O}$ |  | $23.3 \%$ |
|  | - | - |
|  | $100.0 \%$ | $100.0 \%$ |

For the purposes of comparison, data are given for the other fuel gases.

|  | Blast Furnace Gas | Natural Gas |
| :--- | :---: | ---: |
| $\mathrm{CO}_{\mathbf{2}}$ | $25.6 \%$ | $12.1 \%$ |
| $\mathrm{~N}_{\mathbf{2}}$ | $74.4 \%$ | $87.9 \%$ |
|  | - | - |
|  | $100.0 \%$ | $100.0 \%$ |

The products of combustion from burning pure carbon would contain $20.9 \%$ carbon dioxide, since it has the same volume as the oxygen used. The dry products of combustion of coals contain less $\mathrm{CO}_{2}$ than 20.9 due to the fact that the hydrogen of the coals requires oxygen from the air, resulting in more nitrogen than if pure carbon were burnt. The percentages of carbon dioxide in the products of combustion resulting from perfect combustion of various coals have been calculated and are given here for comparison.

| Anth | \% $\mathrm{CO}_{2}$ |
| :---: | :---: |
| Semi-Anthracite, Coalhill, Ark. | 19.0\% |
| Semi-Bituminous, Mora, W. Va. | 18.8\% |
| Bituminous Coking, Connellsville, Pa. | 18.8\% |
| Bituminous Non-Coking, Hocking Valley, Ohio | 18.7\% |
| Sub-Bituminous, Unita Co., Wyo | 18.9\% |
| Lignite, Milan Co., Texas... | 19.2\% |

Producer gas being derived from coal by partial combustion, the ultimate products of combustion (dry) are the same as if coal were used for fuel.

Excess Air. The complete combustion of a fuel with the proper amount of air is rarely obtained. In practice there is generally an excess of air and also incomplete combustion, some carbon monoxide being found in the flue gas. This carbon monoxide should have combined with oxygen present
forming carbon dioxide, according to the equation: $2 \mathrm{CO}+\mathrm{O}_{2}=2 \mathrm{CO}_{2}$. The oxygen which should have combined is one-half the volume of the carbon monoxide, the excess oxygen is then $\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}$ (to prevent confusion, prime ['] is placed over the formulae of the various flue gases). The excess air is $\frac{\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}}{.209}$ stated as percentage of the flue gas. The excess air, however, is usually stated as percentage of the air required or necessary. This is calculated from the nitrogen as follows: The excess nitrogen or Nx is 3.78 times the excess oxygen Ox or
(1) $\mathrm{Nx}=3.78\left(\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}\right)$

A flue gas is composed of two parts, the excess air and the perfect flue gas, consequently, the nitrogen of perfect flue gas ( Nt ), plus the nitrogen of excess air ( Nx ) equals the nitrogen of the flue gas $\left(\mathrm{N}_{2}{ }^{\prime}\right)$ from which $\mathrm{Nt}=\mathrm{N}_{\mathbf{2}}{ }^{\prime}$ - Nx. By substitution for Nx , its value shown in equation (1), the following is obtained:
(2) $\mathrm{Nt}=\mathrm{N}_{2}{ }^{\prime}-3.78\left(\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}\right)$

By dividing equation (1) by (2), a proportion is obtained,
(3) $\frac{\mathrm{Nx}}{\mathrm{Nt}}=\frac{3.78\left(\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}\right)}{\mathrm{N}_{2}{ }^{\prime}-3.78\left(\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}\right)}$

In burning a fuel containing no nitrogen, the nitrogen of perfect flue gas (Nt), coming only from air, is the nitrogen of air necessary for complete combustion (Nn). Therefore, substituting for Nt in equation (3) its equal Nn , the equation is derived:-
(4) $\frac{\mathrm{Nx}}{\mathrm{Nn}}=\frac{3.78\left(\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}\right)}{\mathrm{N}_{2}{ }^{\prime}-3.78\left(\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}\right)}$

This is the ratio of excess nitrogen to necessary nitrogen, and is the same as the ratio of excess air to necessary air. Coal contains a small amount of nitrogen, but the error introduced is negligible, and the foregoing formula multiplied by 100 shows the percentage of excess air, using coal as a fuel.

However in burning a gaseous fuel containing nitrogen, another factor is introduced, and the formula is more complicated. For a fuel gas the nitrogen from air necessary for combustion is 3.78 times the oxygen (On), which value was given under "Air Necessary for Combustion."
(5) $\mathrm{Nn}=3.78$ times On. The nitrogen of perfect flue gas ( Nt ) equals the sum of the nitrogen of the original gas $\left(\mathrm{N}_{2}\right)$ and the nitrogen of air necessary
for complete combustion (Nn) or $\mathrm{Nt}=\mathrm{N}_{2}+\mathrm{Nn}$, from which,
(6) $\mathrm{Nt}=\mathrm{N}_{2}+3.78$ times On. Now, if equation (3) be multiplied by the quotient of (6), divided by (5), a proportion referring to excess nitrogen results:
(7) $\frac{\mathrm{Nx}}{\mathrm{Nn}}=\frac{3.78\left(\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}\right)}{\mathrm{N}_{2}{ }^{\prime}-3.78\left(\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}\right)} \times \frac{\mathrm{N}_{2}+3.78 \mathrm{On}}{3.78 \mathrm{On}}$

Nx to Nn is the ratio of excess nitrogen to necessary nitrogen and is the same as the ratio of excess air to necessary air. It is noted that the first fraction refers to the flue gas alone, and the second fraction to the fuel gas and is fairly constant for any given fuel.

## Example:

| Flue Gas Analysis. |  |
| :---: | :---: |
| Carbon Dioxide. | 5.2\% |
| Oxygen. | 8.7\% |
| Carbon Monoxide. | . $8 \%$ |
| Nitrogen. | 85.3\% |
|  | 100.0\% |

This flue gas was derived from combustion of the by-product gas given in example under "The Products of Combustion."
Excess Oxygen $=8.7-.4=8.3 \%$ of flue gas.
Oxygen necessary for combustion $=90.45 \%$ of fuel gas previously given.
Ratio of excess air to necessary air $=$
$\frac{3.78 \times 8.3}{85.3-3.78 \times 8.3} \times \frac{10.9+3.78 \times 90.45}{3.78 \times 90.45}=58.2 \% \times 1.032=60.1 \%$
Correctness of Sampling and Analysis. As stated before, the flue gas may be considered as composed of excess air and of perfect flue gas; the sum of the two should equal $100 \%$ less the diminution in volume caused by contraction in volume if the CO were completely burnt; or, if $\left(\mathrm{CO}_{2} \mathrm{t}\right)$ represents the carbon dioxide of perfect flue gas, then.

$$
\frac{\mathrm{CO}_{2}{ }^{\prime}+\mathrm{CO}^{\prime}}{\mathrm{CO}_{2} \mathrm{t}}+\frac{\mathrm{O}_{2}{ }^{\prime}-1 / 2 \mathrm{CO}^{\prime}}{.209}+1 / 2 \mathrm{CO}^{\prime}=100 \%
$$

Example: Flue gas cited under "Excess Air" and by-product gas under "Products of Combustion."

$$
\frac{5.2+.8}{.10}+\frac{8.7-.4}{.209}+.4=100.1 \%
$$

TABLE "A"
Based on Standard Conditions of $62^{\circ} \mathrm{F}$ and $30^{\prime \prime}$ Mercury

| Column | Symbol | I.Specific <br> Gravity | $\begin{aligned} & \text { II. } \\ & \text { Wt. of } 1 \\ & \text { Cu. Ft. } \\ & \text { Lbs. } \end{aligned}$ | III. <br> Heat of Comb. B. t. u. per Cu. Ft. |  | IV. <br> Volume <br> of $\mathrm{O}_{2}$ <br> Necessary <br> for Comb. | v. <br> Products of Combustion |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | Gross | Net |  | $\mathrm{CO}_{2}$ | $\mathrm{H}_{2} \mathrm{O}$ |
| Air |  | 1.0000 | . 07634 | .... | .... | $\ldots$ | $\ldots$ | $\ldots$ |
| Carbon Dioxide. | $\mathrm{CO}_{2}$ | 1.5288 | . 11671 | .... | .... | .... | 1.0 | $\ldots$ |
| Ethylene | $\mathrm{C}_{2} \mathrm{H}_{4}$ | . 9752 | . 07445 | 1595 | 1495 | 3.0 | 2.0 | 2.0 |
| Oxygen. | $\mathrm{O}_{2}$ | 1.1052 | . 08437 | .... | .... | .... | .... | .... |
| Carbon Monoxide | CO | . 9648 | . 07365 | 322 | 322 | . 5 | 1.0 | $\ldots$ |
| Methane | $\mathrm{CH}_{4}$ | . 5544 | . 04232 | 1009 | 909 | 2.0 | 1.0 | 2.0 |
| Hydrogen. | $\mathrm{H}_{2}$ | . 0695 | . 005306 | 324 | 274 | . 5 | .... | 1.0 |
| Nitrogen | $\mathrm{N}_{2}$ | . 9651 | . 07368 | .... | .... | .... | .... | .... |
| Ethane | $\mathrm{C}_{2} \mathrm{H}_{6}$ | 1.0449 | . 07977 | 1773 | 1623 | 3.5 | 2.0 | 3.0 |
| Benzene. | $\mathrm{C}_{6} \mathrm{H}_{6}$ | 2.7708 | . 21152 | 3902 | 3752 | 7.5 | 6.0 | 3.0 |
|  |  |  |  |  |  |  | $\mathrm{SO}_{2}$ |  |
| Hydrogen Sulphide | $\mathrm{H}_{2} \mathrm{~S}$ | 1.1906 | . 09089 | 656 | 606 | 1.5 | 1.0 | 1.0 |
| Water Vapor... | $\mathrm{H}_{2} \mathrm{O}$ | . 6221 | . 04749 | .... | .... | .... | .... | 1.0 |
| Cyanogen | $\mathrm{C}_{2} \mathrm{~N}_{2}$ | 1.806 | . 1379 |  |  | $\ldots$ | . . . |  |

TABLE "B" AQUEOUS VAPOR
Pressure in inches of mercury at ( t ) degrees Fahrenheit.
Weight in grains per cubic foot at (t) degrees and (e) pressure.

Factors for Reduction of the Volumes of Gas to Standard Conditions of $62^{\circ} \mathrm{F}$. and $30^{\prime \prime}$ Mercury

TABLE "C"-Continued
Factors for Reduction of the Volumes of Gas to Standard Conditions of $62^{\circ} \mathrm{F}$. and $30^{\prime \prime}$ Mercury

Factors for Reduction of the Volumes of Gas to Standard Conditions of $62^{\circ} \mathrm{F}$. and $30^{\prime \prime}$ Mercury

TABLE "C"-Continued
Factors for Reduction of the Volumes of Gas to Standard Conditions of $62^{\circ} \mathrm{F}$. and $30^{\prime \prime}$ Mercury

Factors for Reduction of the Volumes of Gas to Standard Conditions of $62^{\circ} \mathrm{F}$. and $\mathbf{3 0 ^ { \prime \prime }}$ Mercury

TABLE "C"-Continued
Factors for Reduction of the Volumes of Gas to Standard Conditions of $62^{\circ} \mathrm{F}$. and $30^{\prime \prime}$ Mercury

Factors for Reduction of the Volumes of Gas to Standard Conditions of $62^{\circ} \mathrm{F}$. and $30^{\prime \prime}$ Mercury

TABLE "C"-Continued
Factors for Reduction of the Volumes of Gas to Standard Conditions of $62^{\circ} \mathrm{F}$. and $30^{\prime \prime}$ Mercury


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