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GEOLOGICAL SURVEY OF PENNSYLVANIA.

J. P. LESLEY, STATE GEOLOGIST

*Compliments of
Francis C. Phillips*

THE COMPOSITION AND FUEL VALUE
OF
NATURAL GAS.

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Extract from Annual Report for 1886.

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The Chemical Composition of Natural Gas.

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Introduction.

Natural gas, as obtained from several of the most productive fields in Pennsylvania, according to the analytical data presented in this report, consists chiefly of the hydrocarbons of the paraffin series, together with nitrogen, a small proportion of carbon dioxide and traces of oxygen. Free hydrogen was found in minute quantity in Speechley gas. It is possible that by employing many thousand cubic feet of gas, traces of other constituents might be discovered. Inasmuch as the composition of natural gas possesses an interest for those who are not familiar with the strictly chemical aspect of the question, a few preliminary statements as to the more characteristic properties of its chief constituents will no doubt prove of value in this connection.

Hydrogen is obtained as a gas by the action of dilute sulphuric acid upon zinc. It is also produced during the putrefaction of vegetable matters buried under stagnant water. Its specific gravity is 0.069234 as compared with

NOTE.—Prof. Phillips has spent considerable time in the study and practical investigations of gaseous fuels, and at my request he was commissioned in the early part of the year to make analyses of the natural gas from eight of the most prominent pools in the State, and one analysis of the Fredonia gas in New York.

The first systematic investigation as to the composition of natural gas in the State, was made by the Geological Survey in 1875, the results of which were published in a Report on the Use of Natural Gas in Iron Manufacture, in 1876. Since 1883, when the use of natural gas for fuel became more general, numerous analyses of the different gases have been made by a number of chemists. The wide differences in the composition of the gases as shown by these analyses were so great that Prof. Phillips exercised more than special care in the collection of his samples and in the method of determining the individual constituents of the gases. All analyses were made in duplicate.

C. A. ASHBURNER,

Geologist in Charge.

air. One cubic meter weighs 0.089523 kilogram. One cubic foot weighs 39.12 grains. Hydrogen is odorless and tasteless. It takes fire at a bright red heat, and more readily than other constituents of fuel gases.

Hydrogen in burning generates 34180 heat units per unit weight burned. The product of its combustion is water.

In fuel gases hydrogen may occur in two very different forms.

In its *free* or *uncombined* state, it is often reported in the analyses of natural gas, and constitutes generally from 30 per cent. to 40 per cent. by volume of ordinary coal gas, being a product of the destructive distillation of coal at very high temperatures. The presence of a large proportion of *free* hydrogen in a gas fuel causes it to burn with a relatively small admixture of air, since one volume of hydrogen requires only one-half volume of oxygen, or two and one-half volumes of air for complete combustion. The hydrogen flame is non-luminous.

In *combination with carbon*, in the form of hydro-carbons, hydrogen constitutes about one-fourth by weight of the combustible portion of the natural gas now being used as fuel in Pennsylvania.

These hydro-carbons, which represent approximately nine-tenths by volume of natural gas, are divided into two classes: Paraffins and Olefines. Of the paraffins, the best known and most abundant is methane ($C'H_4$) consisting of 25.03 per cent. hydrogen, and 74.97 per cent. carbon by weight.

Methane is, like hydrogen, a product of the destructive distillation of coal, and consequently constitutes a large proportion of ordinary coal gas. It is also produced with hydrogen when plants decay at the bottom of rivers and swamps, and hence its older name of marsh gas. Methane, when pure is odorless, and not poisonous. Its specific gravity is 0.55297. One cubic meter weighs 0.7148 kilogram. One cubic foot weighs 312.36 grains. It is converted into a liquid under a pressure of about 2700 lbs. per square inch at $12^\circ F.$, or at 263° below zero $F.$, under atmospheric pressure. Methane requires twice its volume of oxygen or ten

volumes of air for its complete combustion, and the products are carbon dioxide and water vapor.

The Hukill well, Lyon's run, south of Murrysville, as already stated, yields this gas in a nearly pure condition. Methane contains *in one cubic foot, two cubic feet of hydrogen*, and hence in the union of the carbon and hydrogen, a considerable condensation occurs. Methane is the typical and best known member of a large group of hydro-carbons, which exhibit a remarkable resemblance in chemical relationships. The following list includes several of the most important :

Methane,	C ₁ H ₄
Ethane,	C ₂ H ₆
Propane,	C ₃ H ₈
Butane,	C ₄ H ₁₀
Pentane,	C ₅ H ₁₂
Hexane,	C ₆ H ₁₄
Heptane,	C ₇ H ₁₆
Octane,	C ₈ H ₁₈

	C _n H _{2n + 2}

The first four hydro-carbons are gases, but are more and more easily condensable to the liquid form in proportion as the amount of carbon is greater. The higher paraffins are solid. Common "paraffin wax" contains several of the highest members. While Methane (C₁ H₄) constitutes from 50 per cent. to 90 per cent. or more of Pennsylvania natural gas, Ethane, (C₂ H₆), the next member of the series occurs in smaller quantity. Concerning the higher members, Propane, (C₃ H₈), and Butane, (C₄ H₁₀), very little is as yet known, but there is reason to think that they are of common occurrence. Pentane, (C₅ H₁₂), is found in the lightest distillates from petroleum, and the higher members are found in abundance in crude oil. It may be said concerning the gaseous hydro-carbons of the series that they possess higher specific gravity, fuel value and illuminating power, and also stronger odor in proportion as the percentage weight of carbon is greater.

The illuminating power of pure methane, artificially prepared, has been determined as 5.15 to 5.20 standard candles

per 5 cubic feet burned per hour. (Wright, Chemical News, 1885, p. 102.)

The second class of hydro-carbons found in gas and petroleum includes the Olefines. Of these the typical member is Ethylene or Olefiant gas, ($C_2 H_4$). Ethylene is one of the products of the action of heat upon coal and various vegetable substances. It is a gas having a specific gravity of 0.96744. Condensable to a liquid at a temperature of 166° below zero F. According to Frankland its illuminating power is equal to 68 standard candles, and hence the name "illuminating hydro-carbons" often give to the group. One cubic foot in burning requires 3 cubic feet of oxygen, or 15 cubic feet of air. On account of their limited occurrence, olefines in many cases have no influence upon the fuel value of natural gas. They appear to be more abundant among the less volatile hydro-carbons of petroleum.

Whether hydrogen occurs in the *free state* in a gas fuel, or as a hydro-carbon, the product of combustion will invariably be water vapor, mixed in the latter case with carbon dioxide.

Carbon Dioxide, CO_2 . Well known as a universal product of decay, and as a gaseous furnace product, Carbon Dioxide, or Carbonic Acid is everywhere present, in the air, in water and in the soil and rocks.

A suffocating gas, having a specific gravity of 1.5241. 1 cubic meter weighs 1.9650 kilogram.

Condensable to a liquid under 780 lbs. pressure at 60° F.

Being incombustible its presence in gas (varying from a trace to 4 or 5 per cent.) tends to reduce to a corresponding degree the fuel value. Its presence may readily be shown by causing the gas to stream slowly through lime water, in which a milky deposit of carbonate of lime soon begins to form.

Nitrogen.—As a diluent of greater influence upon fuel value, we must regard nitrogen, on account of its occurrence in larger quantity. Constituting $\frac{1}{4}$ of atmospheric air, it is well known for its chemically indifferent character. In gas fuels it reduces the heating power in proportion to its quantity.

Gas from the Hukill well, Lyon's run, contained 2.02 per cent. while gas from Houston (near Canonsburg) contained 15.30 per cent. of nitrogen. Should the natural gas supply ever become seriously diminished, it is probable that a time will come when the actual calorific power will be an important factor in determining the market value. In that event the proportion of carbon dioxide and nitrogen, as well as the character of the hydro-carbons, will possess great interest for the gas companies and the consumers.

Oxygen being well known as the constituent of atmospheric air which is the active cause in all cases of combustion slow or rapid, its presence in natural gas would seem improbable. Contact of oxygen with the oxidizable elements of gas under high pressure would appear likely to cause its absorption and the formation of a corresponding amount of carbon dioxide or water. Nevertheless minute traces are constantly found and are indicated with great positiveness in gas as it flows directly from the wells and under high pressure. It has been experimentally shown that oxygen and nitrogen may be dissolved and held in mechanical solution by petroleum, and that oxygen is even more soluble in petroleum than in water. (St. Guiewosz, Reports of the Berlin Chemical Society, 1887, p. 188.)

For its liquifaction methane requires, as already stated, a pressure of at least 2,700 lbs. at common temperatures. Ethane is liquified under a pressure of 690 lbs. Carbon dioxide requires a pressure of 780 lbs.

Far greater pressures are needed for the liquifaction of oxygen, nitrogen and hydrogen.

It is a fact of much interest in this connection that in the case of methane, the principal constituent of natural gas, the pressure under which liquifaction takes place is about four times that found in the most productive gas wells.

If in the reservoir tapped by the well a pressure exists four times greater than that at the well mouth, it is probable that the expansion there resulting would cause a marked lowering of the temperature in the well.

It is commonly found however that the main leading from the well mouth does not possess a temperature much lower

than the air. From this it seems probable that methane cannot exist in a liquified state in the rocks.

The carbon dioxide and ethane, on the other hand, may occur constantly in liquid form in the rocks to which many of the wells penetrate.

Collection of Samples.

Glass vessels having a capacity of 250 to 400 cubic centimeters were carefully dried by a current of warm air, and in order to obtain the gas as nearly as possible free from moisture the following method was employed:

Glacial phosphoric acid, partially cooled from fusion, was drawn out into fine threads. A considerable number of such threads, in short pieces, could be pushed through the glass stopcocks, by which the vessels were closed, and left in the vessels which were then ready for the reception of gas samples. It is of importance to state that these vessels had been long in use for the same purpose and had been proved to be air-tight by thorough and repeated tests.

In collecting the samples several of these glass cylinders were connected in a series with the well or main by a short rubber hose, and gas allowed to flow for twenty minutes through them all.

The stopcocks were then closed in such a manner as to leave a slight excess of gas pressure in each vessel.

The stopcocks (which had previously been well greased with a mixture of tallow and wax) were then wound over and completely covered by fine cord, so that each resembled a ball of cord. The capillary ends of the cylinders were then closed by short pieces of thick rubber hose plugged with glass rods.

By this mode of wrapping all movement of the stopcocks during transportation on railroads is prevented.

The gas thus left in contact with the glacial phosphoric was gradually dried and ready for analysis on reaching the laboratory.

The common method of taking a gas sample in a glass cylinder having finely drawn out ends, which are to be sealed by a flame when the vessel is filled, is not applicable

in the case of natural gas. The constant escape of gas about a gas well renders the use of a flame absolutely impossible on account of the danger of accident. Vessels closed by glass stopcocks are now supplied by dealers capable of holding a gas sample for many weeks without risk of leaking.

Method of Analysis.

The determination of carbon and hydrogen existing in combustible form in the gas was conducted by combustion over oxide of copper in a porcelain tube, which was kept at a bright red heat, and the resulting carbon dioxide and water collected separately and weighed.

One of the glass cylinders, filled with gas at the well, was placed in a vertical position and the temperature observed at intervals.

When it was found that the temperature had remained constant for two hours, the lower stopcock was opened for a moment to allow the excess of gas to escape and secure equilibrium between the pressure of the gas inside and that of the atmosphere. At the same time the temperature and the height of the barometer were recorded. The glass cylinder was then connected with a porcelain tube containing oxide of copper, and already heated to intense redness in a furnace, and the gas forced out of the cylinder by dry mercury. As the gas escaped from the cylinder it was carried through the porcelain tube by a slow stream of nitrogen previously dried by suitable means.

The gas was thus burned completely to carbon dioxide and water which were collected and weighed by the usual methods, using a balance plainly sensitive to $\frac{1}{100000}$ gram.

After the combustion, the glass cylinder was accurately calibrated by means of mercury at a known temperature, and thus was determined the exact volume of gas which had been burned.

As it appeared possible under the conditions of the method that some nitrogen might undergo an oxidation, the water produced in the combustion of the gas was carefully tested, but in no case was the water found to have an acid reaction.

In the above described method are determined the weights of carbon and hydrogen per unit volume of gas. In conducting the combustion great care was taken to secure complete oxidation of the combustible constituents, and absorption of the products.

For the absorption of the water sulphuric acid of 1.71 Sp. Gr., followed by phosphoric anhydride, was used, and for the carbon dioxide a solution of caustic potash in glycerine.

For the determination of nitrogen the following method was employed: A porcelain combustion tube containing oxide of copper was brought to a yellow heat, and a stream of carbon dioxide conducted through the tube until the last traces of air were expelled.

The expulsion of the air was considered complete when it was found that the carbon dioxide escaping from the tube was wholly absorbed by a solution of caustic potash,—100 cubic centimeters of such gas not leaving a visible quantity unabsorbed by the alkaline solution. Then, after expulsion of the last traces of air, a quantity of natural gas (100 c. c. were generally employed), was allowed to flow slowly into the stream of carbon dioxide as it entered the combustion tube. In this manner the gas was burned and a mixture of nitrogen and carbon dioxide collected in a eudiometer over caustic potash solution. After the absorption of the carbon dioxide the volume of the residual nitrogen was measured. This nitrogen was carefully tested for carbon dioxide, oxygen and carbon monoxide, and was frequently repassed through the heated combustion tube a second time and again measured, in order to insure the complete combustion of all hydrocarbons. This repetition demonstrated in all but one or two instances that the nitrogen was pure. It was found that with a sufficiently slow stream of gas the oxidation by the oxide of copper is easily rendered complete, although the rate of flow must be regulated with great care.

By the common endiometric methods of analysis no determination is more difficult than that of nitrogen when occurring in small quantities in admixture with hydrocarbons of the paraffin series. In the method above described

large quantities of gas can be employed, and the results are accurate.

The determination of free oxygen in natural gas cannot well be made with the quantity of gas commonly at disposal. A test was made in every instance in about 100 cubic centimeters of gas, using an Elliott apparatus, and as an absorbent a solution of caustic soda and pyrogallic acid. In all cases the results were negative.

I have found it necessary to conduct the tests for oxygen at the wells, and this was done in the following manner:

A slow stream of gas was caused to flow (directly from the well or main) successively through solutions of caustic potash and pyrogallic acid, for 10 minutes, in order to expel dissolved air. Then by a simple contrivance the two fluids were mixed without interrupting the current of gas, which continued some time longer through the mixture. If the mixed fluids then exhibited a brown color, gradually increasing in depth, it was considered that the presence of oxygen was established.

The direct determination of free hydrogen has generally been considered a matter of such difficulty, that in many published analyses its quantity has been estimated by a calculation based upon the total carbon and hydrogen contained in the gas. For the present purpose a direct determination seemed very desirable and the process of Hempel has been used in the manner described below. 100 cubic centimeters of gas, after the removal of carbon dioxide, were washed with strong alcohol until the higher hydrocarbons, ethane, propane, &c. were removed. This was carried out in an Elliott apparatus, having a water jacket. Then the residual gas mixed with two or three times its volume of air was passed over asbestos coated with 30% of Palladium sponge at a temperature of 90°C.

By this treatment the hydrogen alone is burned, provided the higher paraffins, including ethane are previously removed by washing with alcohol. From the contraction in volume, after passing the palladium, the proportion of free hydrogen is easily determined.

The method is very accurate when methane is the only

hydro-carbon present. It is inaccurate in presence of ethane and the higher members of the series, and when these are present the washing with alcohol must be long continued. As it is a matter of great difficulty to retain hydrogen, even by the help of the most carefully ground stopcocks, the tests for this element were made in all cases at once after the arrival of the samples in the laboratory.

The olefines, as a group and carbon monoxide, are much more easily determined in natural gas than the paraffins and free hydrogen.

The olefines are quickly absorbed and removed by bromine water and carbon monoxide by a solution of cuprous chloride. These reagents are used in the order named. Unfortunately, however, these fluids are likewise solvents, in less degree, for the paraffins,—ethane, propane &c. Hence a gas perfectly free from olefines and carbon monoxide is liable, on being washed with the above named fluids, to undergo a reduction in volume, leading to a wrong conclusion.

For the determination of these substances the following process was used, based on the solubility of both in a cuprous chloride solution. At the gas well a stream of gas was caused to bubble for two hours or more through 100 cubic centimeters of a solution of cuprous chloride. The solution was preserved for examination in the laboratory.

A quart flask, provided with a gas delivery tube and a funnel tube reaching to the bottom, was filled with boiled water and then the cuprous chloride, prepared as above described, was poured into the flask through the funnel tube. The flask was then heated to the boiling point and the water caused to boil for three hours. A small quantity of gas was invariably collected from the cuprous chloride solution by this treatment.

The gas so collected was transferred to an Elliott apparatus and carefully tested for olefines and carbon monoxide by bromine water and cuprous chloride solution. In this way the quantities of these two constituents in a very large quantity of gas could be collected in concentrated form, convenient for a qualitative test.

Carbon dioxide was determined by means of moist potash in a eudiometer over mercury, and also in the Elliott apparatus over water, by caustic potash solution. The latter method yields very correct results.

In addition to the determinations carried out in the laboratory, the gas at the well was caused to pass in a slow stream through lime water. The stream of gas was made approximately the same by using the same delivery tube, depth of lime water and shape of containing vessel, and by counting the number of bubbles per minute, and then noting the rapidity with which the lime water became milky.

For the detection of ammonia the gas at the well was caused to bubble through 100 c. c. of water, which had been carefully purified by distilling with addition of sulphuric acid and permanganate of potash. This water was afterwards tested by Nessler's solution, after the common method in use in the examination of drinking water, for ammonia.

The presence of exceedingly minute traces of ammonia could thus be shown with great accuracy. As solid masses of ammonium carbonate are reported to have been thrown out from the pipes leading from gas wells in the Murrysville field this test seemed very important.

In the statement of the results of analyses all gas volumes are to be understood as "normal,"—that is the volumes observed under different conditions of temperature and pressure are all reduced to zero, Centigrade, and 760 millimeters mercury pressure; and, where measured in a moist condition, are calculated as dry.

The temperatures were all measured by one and the same thermometer, of which the error was known from a comparison with the Yale Observatory standard. This thermometer was made by Green in New York and is divided to $\frac{1}{10}$ degrees centigrade.

The barometer used was made by Hicks, and indicated by vernier, changes of $\frac{1}{1000}$ inch. The constant error of this barometer was ascertained by comparison with the standard barometer of the Signal Service department, in Washington.

In all cases of gas measurements in eudiometers, the observations were made by means of a Grunow cathetometer, having a millimeter scale and vernier and reading easily to $\frac{1}{20}$ millimeter.

The etched scales upon the eudiometer tubes, as commonly supplied, are often very incorrect, both as regards uniformity and total length of scale, and are unsuited for accurate measurements of pressures or volumes.

The glass cylinders containing the gas samples for combustion were calibrated at a temperature not differing by one degree Centigrade from the temperature at which the gas was measured for analysis. In this way the calculation of errors due to expansion and contraction of the glass vessels was rendered unnecessary. This necessitated repeated calibrations after nearly every combustion.

In the calculation of the results of analyses, the following plan was adopted :

The percentage of Carbon dioxide was determined volumetrically. Having failed to find Carbon monoxide and olefines in any of the samples, they are necessarily left out of account in the calculation. Having found free hydrogen in only one of the gas samples, and here in traces, (Speechley,) it is also to be ignored in the calculations.

The quantities of carbon dioxide and water produced in the combustion of a known volume of gas were weighed. From the weight of the water the proportion of hydrogen in a unit volume of gas could then be calculated. The percentage volume of carbon dioxide contained in the gas being known, its weight was deducted from the weight of the total quantity obtained in the combustion. The difference is the quantity corresponding to carbon in the form of hydrocarbons. The nitrogen having been determined in a separate portion of gas, and the free hydrogen being also known, the volume of the hydrocarbons will be expressed by the following equation

$$\text{C \& H in form of hydrocarbons, . . } \} = 100 - (\text{CO}_2 + \text{N} + \text{H} + \text{etc.})$$

That is to say the actual volume of hydro carbons will occupy the entire space in the gas not occupied by CO_2 , N, H, O, and other constituents of the gas.

No attempt has been made to determine the proportion of individual members of the paraffin series.—methane, ethane, propane &c, for the reason that no sufficiently accurate methods are known for the estimation of these bodies. No reagent can be named which will absorb and remove from a mixture any one of these paraffins exclusively, so as to allow of its correct determination by difference.

In such a mixture, moreover, no decided chemical change can be produced in any given paraffin without more or less altering the others. They are remarkable for the resemblance existing between them in chemical relationships, and also for the great resistance which they offer towards reagents of every description, excepting chlorine which attacks them all readily.

Moreover a calculation of the relative proportions of the gaseous hydro carbons of this class, based upon eudiometric data, is only possible where the number of such bodies is known to be limited to two,—a condition never to be assumed in a gas of unknown composition. In illustration of the fact just stated it may here be mentioned that a mixture of 1 volume each of methane, ethane and propane yields, on complete combustion, the same products and in the same proportions as three volumes of the intermediate hydrocarbon ethane. This can be shown by a very simple calculation.

Selection of Samples.

It was originally proposed to take samples from mains drawing gas from a group of wells and in this way obtain an average of the entire group. This was sometimes done as in the case of the Raccoon Creek and Speechley territories, where a large number of wells, all producing from one sand, are joined to one main. In other fields the wells are often drilled to different sands and produce gas from different horizons as in the case of the Kane wells. In many cases, among a large number of productive wells, all but two or three are shut in, and are thus held in reserve. In such instances a sample was taken at a single well, and directly from the main at the well.

Of the samples examined, No. 1 was taken at Fredonia, N. Y., by Mr. E. J. Crissey, Secretary of the Fredonia Natural Gas Light Co., from the mains of the company. All the other samples were collected by myself. In view of the great extent of the Pennsylvania gas territory, and the number of small areas of highly productive gas wells, the selection of samples with a view to an approximate average is a matter of no small difficulty. For the present purpose, and in the absence of any scientific criteria, reference has been had chiefly to the technical importance of certain regions, such as Murrysville and Speechley. Fredonia, N. Y., was chosen on account of the great depth (geologically) of the gas rock.

Wilcox gas is remarkable for the long maintained high pressure exhibited in certain wells.

Baden and Raccoon creek lie on the same anticlinal.

Houston (Canonsburg) gas comes from a region 200 miles distant from the far Northern Fredonia gas field. All the samples are from regions where natural gas is being largely utilized on account of its fuel value.

Description of Samples.

No. 1. Fredonia, N. Y. From mains of the Fredonia Natural Gas Light Co., May 12th, 1887.

Mr. E. J. Crissey, Secretary of this Company, furnishes the following information :

Gas is obtained at an average depth of 200 feet. The rock is black and gray shale, alternating, to the depth of about 1000 feet, where a limestone is found. No gas has been found below 250 feet until a depth of between 1700 and 1800 feet is reached, when gas and salt water are met. At 2250 feet gas is again found, which burns with a very white flame, whiter than that of the shallow gas. The sample examined comes from the depth of 200 feet.

Two determinations of nitrogen in this gas gave 9.58% and 9.50% respectively. Mean, 9.54%.

In two determinations of carbon dioxide there were found 0.38% and 0.44%. Mean, 0.41%.

Results of Analysis of Fredonia Gas.

Nitrogen,	9.54 per cent.
Carbon dioxide,	0.41
Olefines,	0
Carbon monoxide,	0
Free hydrogen,	0
Ammonia,	0
Hydrocarbons of the paraffin series,	90.05

 100.00

343.47 cubic centimeters of Fredonia gas yield on combustion, by the method already described :

H ₂ O.—0.6254 gm., corresponding to, H—0.06964 gm=21.83 per cent.
C O ₂ —0.9144 gm., “ “ “ C—0.24938 gm=78.17 per cent.

 100.00

Making allowance for the 9.95% of nitrogen and carbon dioxide contained in the gas, it is calculated that the 90.05% paraffins present contain

Per liter.—0.80627 gm carbon.
0.22515 gm hydrogen.

In a second combustion of Fredonia gas 326.17 cubic centimeters yielded.

H ₂ O—0.5927 gm, corresponding to H—0.0660= 21.89 per cent.
C O ₂ —0.8635 gm, “ “ “ C—0.2355= 78.11 per cent.

 100.00

As these quantities of carbon and hydrogen belong exclusively to the paraffins in the gas, it is calculated that the paraffins—amounting to 90.05% of the total gas—will contain

Per liter.—0.80185 gm carbon.
0.2247 gm hydrogen.

In these calculations, as in the following, an allowance is made in the determination of the carbon for the very small quantity of carbon dioxide which always occurs in the original gas.

The means of the two results above cited are per liter of paraffins,—

0.80406 gm Carbon = 78.14 per cent.
0.22492 “ Hydrogen= 21.86 per cent.

 100.00

In the case of the Fredonia gas no tests were made at the wells. An actual test made at one of the wells in August, 1884, showed traces of oxygen. In the limited quantity at disposal for the above analysis no positively certain indication for oxygen could be obtained.

No. 2. From valve house close to well No. 1, of the Sheffield Gas Co., $\frac{1}{2}$ mile from Sheffield. Warren Co., Pennsylvania. Wells No. 1, 2 and 3 were connected with the main at the time, so that the sample represents the average of the three wells.

Well No. 1 has been flowing since 1875; No. 2 was drilled two years later; No. 3. in 1885. The gas comes wholly from one and the same sand. The record of No. 1 is given on page 23 of Mr. Carll's Report on Warren Co. for 1883.

The sand from which these wells produce gas is about 1400 feet deep, and very nearly at ocean level.

The Sheffield Company own six wells. In the newer wells the pressure is even greater than in No. 1.

The pressure in No. 1 has remained constant since it was drilled, and amounts to 550lbs in 4 minutes when the gas is shut in.

In the Sheffield region there are about 64 square miles of gas-producing territory, and the gas pressure varies between 500 and 800lbs. per square inch.

The Sheffield gas wells supply Sheffield, Iona, Brookston, Clarendon, Warren, Corry, Erie and Jamestown, N. Y.

The wells in this region have been remarkably persistent.

Determinations of	(1)	(2)	Mean.
Nitrogen,	9.00	9.12	9.06 per cent.
Carbon dioxide,	0.33	0.27	0.30 per cent.

Results of Analysis of Sheffield Gas.

Nitrogen,	9.06
Carbon dioxide,	0.30
Oxygen,	Trace.
Hydrogen,	0
Olefines,	0
Carbon monoxide,	0
Ammonia,	0
Paraffins,	90.64
	100.00

305.27 cubic centimeters of Sheffield gas yield on combustion.

H₂ O.—0.4960, corresponding to H,—0.05523 gm= 23.36 per cent.
 C O₂ —0.6645, “ “ “ C,—0.18123 gm= 76.64 per cent.

100.00
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From these results it is calculated that the paraffins present in the Sheffield gas contain per liter :

0.65495 gm carbon.
 0.19960 gm hydrogen.

In a second combustion, 314.44 cubic centimeters of Sheffield gas yield :

H₂ O—0.5090 gm, corresponding to H,—0.05668 gm= 23.27 per cent.
 C O₂—0.6851 gm, “ “ “ C,—0.18684 gm= 76.73 per cent.

100.00
 =====

The paraffins will therefore contain per liter :

0.65557 gm carbon.
 0.19887 gm hydrogen.

The means of these two analysis are per liter of paraffins :

0.65526 gm carbon = 76.69 per cent.
 0.19923 gm hydrogen= 23.31 per cent.

100.00
 =====

No. 3.—Wilcox Gas Well, 3 miles from Wilcox, McKean Co. Sample collected Jan. 29, 1887. Originally known as “Wilcox well, No 1,” now called No. 7. Was drilled in 1878, and produces gas from the fourth sand exclusively.

This well was the first in this region, and has maintained a continuous pressure of 500 lbs. when shut in.

The United Natural Gas Co. own 24 wells in the Wilcox field, which occupies an area of about 2 miles square, No. 1 being in the southwest end. All are very productive, and some are remarkable for unusually high pressures, the gauge registering in one well 900 lbs. All exceed 500 lbs. Very little salt water is produced. The gas exhibits a decided oxygen reaction, turns lime water rapidly milky, and has a strong odor. Pipe lines carry the gas from these wells

to Bradford, Jamestown, N. Y.; Hornellsville, Salamanca, Buffalo, but the supply is largely in excess of the demand at present.

Determination of	(1.)	(2.)	Mean.
Nitrogen,	9.32	9.50	9.41 per cent.
Carbon dioxide,	0.21	0.20	0.21 per cent.

Results of Analysis of Wilcox Gas.

Nitrogen,	9.41 per cent.
Carbon dioxide,	0.21
Oxygen,	trace
Carbon monoxide,	0
Olefines,	0
Ammonia,	0
Hydrogen,	0
Paraffins,	90.38
	100.00
	100.00

374.2 cubic centimeters of Wilcox gas yield on combustion.

H₂ O.—0.6022 gm, corresponding to H,—0.06706 gm=23.48 per cent.

C O₂.—0.8014 gm, corresponding to C,—0.21856 gm=76.52 per cent.

100.00
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Hence 1 liter paraffins contains :

0.64622 gm carbon.

0.19828 gm hydrogen.

In the case of the Wilcox gas, an accident to some of the sample vessels prevented a second combustion, so that but a single result can be presented.

No. 4.—Kane well, No. 1, at Kane, McKean Co. Gas collected Jan. 30th, 1887.

The well was drilled in 1884. The pressure then was 550 lbs when shut in for 40 minutes. It was allowed to blow off for 8 months, and then shut in, when the pressure increased to 630 lbs. This gain in pressure has been permanent, up to October, 1886, when the last test was made. The Kane Natural Gas Co. own two other wells in addition to this. The gas exhibits decided oxygen and carbon dioxide reactions.

Determination of	(1.)	(2.)	Mean.
Nitrogen,	9.67	9.91	9.79
Carbon dioxide,	0.20	0.20	0.20

Results of Analysis of Kane Gas.

Nitrogen,	9.79 per cent.
Carbon dioxide,	0.20
Oxygen,	trace
Olefines,	0
Carbon monoxide,	0
Hydrogen,	0
Ammonia,	0
Paraffins,	90.01
	<u>100.00</u>

349.03 cubic centimeters of gas yield on combustion.

H ₂ O,—0.5600 gm, corresponding to H,—0.06236 gm=23.18 per cent.	
C O ₂ —0.7580 gm, “ “ C,—0.20672 gm=76.82 per cent.	
	<u>100.00</u>

Hence 1 liter of the paraffins contains :

0.65801 gm carbon.
0.19849 gm hydrogen.

248.1 cubic centimeters of the same gas yield on combustion.

H ₂ O,—0.3987 gm, corresponding to H,—0.04439 gm=23.28 per cent.	
C O ₂ ,—0.5366 gm, “ “ C,—0.14634 gm=76.82 per cent.	
	<u>100.00</u>

Hence the paraffins of Kane gas contain per liter :

0.19883 gm hydrogen.
0.65537 gm carbon.

The means of these two analysis are per liter of paraffins.

0.65669 gm carbon = 76.77 per cent.
0.19866 gm hydrogen=23.23 per cent.
<u>100.00</u>

No. 5. Speechley. This field has been a remarkably productive one, as regards quantity and pressure of gas and number of wells. These wells are situated on a N. E. & S. W. line about 6 miles S. E. from Oil City.

The sand rock from which the gas is obtained averages 1900 feet in depth, and is about 900 feet below the third oil sand of Venango county.

This latter sand also produces gas, but in much smaller quantity, and it is consequently cased off, so that the gas in this territory is wholly obtained from one and the same

sand rock. The Northwestern Gas Co. of Oil City have 60 wells, and a large number of wells are owned by other companies.

The samples of gas for examination were taken April 13th, 1887, from the high pressure main at South Oil City, belonging to the Northwestern Natural Gas Co. At this time the pressure in the main was 100 lbs.

This sample may be considered to represent approximately the average of the gas from a large number of wells.

The tests at the main indicated the presence of oxygen, but less of carbon dioxide than found in the Warren and McKean county gas.

Determination of.	(1)	(2)	Mean.
Nitrogen,	4.61	4.41	4.51 per cent.
Carbon dioxide,	0.05	0.05	0.05
Hydrogen,	0.02	0.02	0.02

Results of Analysis of Speechley Gas.

Nitrogen,	4.51 per cent.
Carbon dioxide,	0.05
Hydrogen,	0.02
Carbon Monoxide,	0
Olefins,	0
Oxygen,	trace.
Ammonia,	0
Paraffins,	95.42
	100.00
	100.00

304.24 cubic centimeters Speechley gas yield on combustion.

H ₂ O,—0.5423 gm, corresponding to H,—0.06039 gm=22.93 per cent.	
CO ₂ ,—0.7441 gm, “ “ C,—0.20293 gm=77.07 per cent.	
	100.00
	100.00

Hence the paraffins of this gas contain per liter

0,69900 gm Carbon
0,20801 gm Hydrogen

In a second combustion of the same gas, 310.52 cubic centimeters yield

H ₂ O,—0.5500 gm, corresponding to H,—0.06125 gm=22.85 per cent.	
CO ₂ ,—0.7585 gm “ “ C,—0.20686 gm=77.15 per cent.	
	100.00
	100.00

Hence the paraffins contain per liter :

0.20671 gm Hydrogen.
0.69815 gm Carbon.

In a second combustion, 306.28 cubic centimeters of gas yield

H₂O,—0.4818 gm, corresponding to H,—0.05365 gm=25.02 per cent.
CO₂,—0.5895 gm “ “ C,—0.16074 gm=74.98 per cent.
100.00
=====

The means of these two results are per liter of paraffins :

0.69857 gm carbon = 77.11 per cent.
0.20736 gm hydrogen = 22.89 per cent.
100.00
=====

No. 6. Hukill well, on the Dick Farm, Lyons Run District, southern end of Murrysville field, and one of 60 wells belonging to the Philadelphia Company.

This well was drilled in 1883 and was allowed to blow off for a long time. The well is very productive and has a pressure as it flows through the main of 285 lbs.

The well has extra heavy casing and there is good reason to suppose that the gas comes exclusively from the Murrysville sand. The sample was taken April, 8, 1887.

The gas produces a decided carbon dioxide reaction but exhibits a very slight reaction for oxygen.

This gas has a very faint odor, free from the pungent character noticed among some of the gas samples. The well yields no oil, but a very little salt water.

Determinations of,	(1)	(2)	Mean.
Nitrogen,	2.13	1.91	2.02
Carbon dioxide,	0.26	0.30	0.28

Results of Analysis of Murrysville Gas.

Nitrogen,	2.02 per cent.
Carbon dioxide,	0.28
Oxygen,	trace
Carbon monoxide,	0
Olefines,	0
Ammonia,	0
Hydrogen,	0
Paraffins,	97.70
	<u>100.00</u>
	<u>=====</u>

346,94 cubic centimeters of Murraysville gas yielded on combustion.

H ₂ O,—0.5473 gm,	corresponding to H,—0.06095 gm=	25.06 per cent.
CO ₂ ,—0.6682 gm,	“ “ C,—0.18224 gm=	74.94 per cent.
		100.00
		====

Hence the paraffins in Murraysville gas contain per liter :

0,53763 gm Carbon.
0.17981 gm Hydrogen.

In a second combustion 306.28 cubic centimeters of gas yield

H ₂ O,—0.4818 gm,	corresponding to H,—0.05363 gm=	25.02 per cent.
CO ₂ —0.5895 gm,	“ “ C,—0.16074 gm=	74.98 per cent.
		100.00
		====

Hence the paraffins contain per liter :

0.53718 gm Carbon.
0.17922 gm Hydrogen.

The means of the above analyses are per liter of paraffins :

0.53741 gm Carbon	=	74.96 per cent.
0.17950 gm Hydrogen	=	25.04 per cent.

100.00

====

The following experiments were tried at the valve house of the Philadelphia Company, in the rear of the office building on Penn street, Pittsburg, beginning on March 22d, 1887. A Woulfe's bottle containing 200 c. c. purified water, and a second bottle containing cuprous chloride were connected with a gas meter, and gas allowed to stream slowly through them until 190 cubic feet had passed. The gas thus used comes directly from the Murraysville field. The gas was passed very slowly, so that 3 days were occupied in the transmission of the volume above named. The water was then tested for ammonia by Nessler's reagent. No trace could be detected, although as is well known this reagent is capable of detecting $\frac{1}{200000}$ part of ammonia in water, with great certainty.

The cuprous chloride was tested for both olefines and

carbon monoxide by the method I have detailed, but no trace could be detected of either.

The composition of methane gas by weight is

Carbon,	74.97 per cent.
Hydrogen,	25.03 per cent.
	100.00

Hence this Hukill well produces gas approximating in composition to pure methane, and in this respect differs from all those from which samples have been taken. It may be here stated that at the time the sample was collected there was every reason to believe that the gas came exclusively from this one well.

No. 7. Raccoon Creek District.

The sample was taken May 2d, 1887, from the high-pressure main of the Bridgewater Natural Gas Co. at Rochester, Pa. The pressure at the time was 67 lbs.

The gas is produced wholly from one sand, which is about 1200 feet below the surface on Raccoon Creek, in Beaver county. The Bridgewater Company owns 23 wells and supplies the towns of Beaver Falls, Rochester, New Brighton, Phillipsburg, Vanport, Bridgewater, New Sheffield, Shannopin.

The Youngstown Company own 12 wells in the same region. The gas is almost odorless, and the wells produce little or no salt water, and no oil.

On causing the gas to bubble through lime water, for 20 minutes the fluid remained perfectly clear. After 40 minutes a rapid stream of gas caused the lime water to become faintly milky, as seen in a bright light. The proportion of carbon dioxide was far too small to allow of an accurate eudiometric determination. The oxygen reaction was faint but decided.

This gas on being passed for one hour into a nitrate of silver solution produced a faint but decided reaction, indicating a trace of sulphuretted hydrogen.

In the statement below, the result of the carbon dioxide test at the main is given.

Determination of	(1)	(2)	Mean.
Nitrogen,	10.00	9.82	9.91

Results of Analysis of Raccoon Creek Gas.

Nitrogen,	9.91 per cent.
Hydrogen,	0
Carbon dioxide,	trace.
Carbon monoxide	0
Olefines,	0
Oxygen,	trace
Ammonia,	0
Sulphuretted hydrogen,	trace
Paraffins,	90.09
	<hr/>
	100.00
	<hr/> <hr/>

In a combustion of Raccoon creek gas 325.48 cubic centimeters yielded :

H ₂ O,—0.5108 gm, corresponding to H,—0.05688 gm=	23.60 per cent.
C O ₂ ,—0.6755 gm, “ “ C,—0.18422 gm=	76.40 per cent.
	<hr/>
	100.00
	<hr/> <hr/>

Hence the paraffins in this gas contain per liter: .

0.62827 gm carbon.
0.19398 gm hydrogen.

In a second combustion 398.08 cubic centimeters gas yielded

H ₂ O,—0.6254 gm, corresponding to H,—0.06964 gm=	23.56 per cent.
C O ₂ ,—0.8286 gm, corresponding to C,—0.22598 gm=	76.44 per cent.
	<hr/>
	100.00
	<hr/> <hr/>

Hence the paraffins contain per liter:

0.63010 gm carbon.
0.19418 gm hydrogen.

The means of these two results are per liter paraffins:

0.62918 gm carbon =	76.42 per cent.
0.19408 gm hydrogen=	23.58 per cent.
	<hr/>
	100.00
	<hr/> <hr/>

This is the only gas which contains traces of sulphuretted hydrogen among those I have examined.

No. 8. Baden, six miles S. E. from Rochester on the Pittsburgh, Fort Wayne and Chicago R. R., Beaver county. The samples were taken May 18th, 1887, from the Bryan well, No. 2, one of the four wells belonging to the Baden Gas Co. The gas is produced wholly from one sand which is 1396 feet deep, or about 1300 feet below the Ohio river. This well was drilled in May, 1886.

The Baden wells are on the same anticlinal axis as the Raccoon creek wells. This same axis continues northward a few miles east of the Speechley wells near Oil City.

The gas exhibits a decided carbon dioxide and also an oxygen reaction.

Determinations of	(1.)	(2.)	Mean.
Nitrogen,	12.26	22.38	12.32 per cent.
Carbon dioxide,	0.41	0.41	0.41

Results of Analysis of Baden Gas.

Nitrogen,	12.32 per cent.
Carbon dioxide,	0.41
Oxygen,	trace
Hydrogen,	0
Carbon monoxide,	0
Olefines,	0
Ammonia,	0
Paraffins,	87.27
	<hr/>
	100.00
	<hr/> <hr/>

317.17 cubic centimeters of Baden gas yield on combustion :

H₂O,—0.4892 gm, corresponding to H,—0.05447 gm= 23.48 per cent.
C O₂,—0.6510 gm, corresponding to C,—0.17754 gm= 76.52 per cent.

100.00

Hence the paraffins of Baden gas contain per liter :

0.64142 gm carbon.
0.19681 gm hydrogen.

In a second combustion 332.70 cubic centimeters yield :

H₂O,—0.5130 gm, corresponding to H,—0.05712 gm= 23.56 per cent.
CO₂,—0.6843 gm, corresponding to C,—0.18663 gm= 76.44 per cent.

100.00

Hence the paraffins contain per liter :

0.64276 gm carbon.
0.19674 gm hydrogen.

The means of these two results are per liter paraffins :

0.64209 gm carbon = 76.48 per cent.
0.19677 gm hydrogen= 23.52 per cent.

100.00

No. 9. Houston well, Houston station, 2 miles south of

Cannonsburg, on the Pittsburgh, Cincinnati and St. Louis. R. R., Washington county.

This well is situated $\frac{1}{3}$ mile west of the station on Plum run.

It is drilled nearly through the Gantz sand and is 1794 feet deep. An upper, gas producing, sand is found at 850 feet, but this is cased off so that the well may be considered to yield gas from the Gantz sand exclusively.

The gas from the upper sand is said by well superintendants to burn with a whiter but more sooty flame than that from the greater depth.

According to the statements generally heard at the wells, the occurrence of an upper, less productive gas sand, yielding gas of greater illuminating power, is a very common feature in many gas fields. The sample was collected on March 18, 1887.

The gas exhibits an oxygen reaction and causes a rapid precipitation in lime water.

Determination of	(1.)	(2.)	Mean.
Nitrogen,	15.23	15.37	15.30 per cent.
Carbon dioxide,	0.42	0.46	0.44

Results of Analysis of Houston Gas.

Nitrogen,	15.30 per cent.
Carbon, dioxide	0.44
Oxygen,	trace
Olefines,	0
Carbon monoxide,	0
Ammonia,	trace
Hydrogen,	0
Paraffins,	84.26
	<hr/>
	100.00
	<hr/> <hr/>

310.20 cubic centimeters of Houston gas yielded on combustion.

H₂ O,—0.4601 gm, corresponding to H,—0.05124 gm,= 23.20 per cent.
C O₂—0.6217 gm, “ “ “ C,—0.16955 gm,= 76.80 per cent.

100.00

Hence the paraffins contain per liter :

0.64871 gm carbon.
0.19602 gm hydrogen.

In a second combustion 293.35 cubic centimeters yielded :

H₂ O,—0.4392 gm, corresponding to H,—0.04891 gm= 23.44 per cent.
 C O₂ —0.5855 gm, “ “ “ C,—0.15968 gm= 76.56 per cent.

100.00
 =====

Hence the paraffins contain per liter :

0.64604 gm carbon.
 0.19786 gm hydrogen.

The means of these two analyses are per liter of paraffins :

0.64737 gm carbon = 76.68 per cent.
 0.19694 gm hydrogen = 23.32 per cent.

100.00
 =====

The analyses above detailed were carried out with great care, and every known precaution observed in order to secure accuracy.

The results represent the character of the gas from particular wells or groups of wells, scattered over a large region, and as it flowed from the wells on a single day.

It is questionable whether they can be considered to represent the average composition of natural gas, for the reason that the gas territory is so vast in extent.

According to the above results natural gas is not so complex a substance as has been heretofore supposed.

The samples examined may be said to consist mainly of the hydro-carbons of the paraffin series, among which methane predominates.

It is to these bodies that the fuel value of the gas is due.

Inasmuch as most of the gas conveyed through pipe lines, deposits little or no liquid hydro-carbons, it is evident that the higher paraffins are not present in notable quantity.

The method I have used in testing for the hydro-carbons of the olefine series enables me to state with much confidence that these bodies,—ethylene, propylene, butylene, etc., are absent. Hydrogen I have found in Speechley gas alone, although the utmost care has been taken in the examination.

Perhaps still smaller quantities may have escaped detection in other gas samples.

Sulphuretted hydrogen was found only in Raccoon creek gas, but in faint traces.

Oxygen is present in all, but in such small quantities that I have never succeeded in accurately determining its real percentage.

As nearly as I can estimate, the Wilcox contains more oxygen than any other, and Murrysville the least.

Ammonia was found, in traces only, in Houston gas. Carbonic oxide was not found in any of the samples.

A comparison of the results in the accompanying table shows that the different gas samples differ mainly in the following particulars.

1.—The proportion of carbon to hydrogen in the contained paraffins—that is to say the ratio of the lower to the higher paraffins. Fredonia is seen to be the richest gas in carbon.

2.—The proportion of nitrogen, which varies between 2.02% and 15.30%. The three gas fields, Speechley, Baden and Raccoon Creek approximately on the same anticlinal (according to Mr. I. C. White) produce gas having very different quantities of nitrogen.

The resemblance between the Fredonia, Sheffield, Kane, Wilcox, and Raccoon Creek gas as regards the proportion of nitrogen is a matter of interest, although not explainable.

In the case of Murrysville, Speechley and Fredonia gas the density, richness in carbon, and calorific power of the contained paraffins are inversely as the proportion of nitrogen. It is a curious fact that there is a certain continuity as regards composition in the case of the Fredonia, Kane, Sheffield and Wilcox gases, which disappears on reaching the Speechley field, in proceeding southward. South of Speechley much greater differences occur.

3.—The carbon dioxide, which varies within very narrow limits. The only gas in which it almost disappears is that from Raccoon creek although Speechley gas contains barely more than a trace.

At Oil City a sand is found 582 feet below low-water mark in the Allegheny river, which produces gas of lower pressure, amounting, it is said, to 20 lbs. when shut in for some time. This gas is used in the Oil Well Supply Co's works for heating purposes. It bears the same relation to the Speechley gas sand—1900 feet deep—as the shallow gas sands usually to the deeper, and more productive sand rocks.

A determination of the nitrogen in the gas from this upper rock gave 5.62 per cent. Speechley gas contains 4.51 per cent. The sample was collected on April 13th, the day on which the Speechley samples were taken.

The Speechley gas wells are six miles distant from this well. Tests for hydrogen, olefines, carbon monoxide and dioxide and ammonia in this gas all led to negative results.

Calculation of the Fuel Value of Natural Gas.

The calorific power of any combustible may be determined by measuring the number of kilograms of water heated from 0° to 1° C. by 1 kilo of the fuel in burning, or by a calculation. The difficulties and inconveniences encountered in the first method necessitate commonly a resort to the second.

Pure charcoal in burning produces, according to the researches of Favre & Silbermann (in 1849), 8080 heat units, or 1 kilo in burning will raise the temperature of 8080 kilos of water from 0° to 1° C.

By the same authors it was found that 1 kilo of hydrogen in burning generates a quantity of heat sufficient to warm 34462 kilos of water from 0° to 1°C—that is 34462 heat units. Later determinations have been made by various authors, the most important being by Thomsen, who found 34180 (*Berichte der Deutschen chemischen Gesellschaft*, 1873, p 1533), and by Berthelot who obtained the number 34600, (*Comptes Rendus*, 1880 p 1240). The value assigned by Thomsen, viz: 34180, is probably the more correct.

If it were possible that a fuel should contain pure hydrogen and charcoal, *uncombined*, a calculation of its heating

power would lead to very correct results. It is found, however, that when a *compound* of carbon and hydrogen is burned, the number of heat units produced will not equal the number obtained when the same quantities of carbon and hydrogen are burned separately.

Thus a kilo of methane produces 13270.5 heat units, but if the same quantities of carbon (as charcoal) and hydrogen were burned *separately* in a calorimeter, 14613 heat units result (assuming that the carbon produces 8080, and the hydrogen 34180 heat units per kilo burned).

The difference between the calculated amount of heat, and the actually available heat— $14613 - 13270 = 1343$ heat units is 9.19 per cent. of the theoretical yield. For practical applications this is a loss of heat, which must be considered to represent the quantity of energy required to overcome the mutual affinity of the carbon and hydrogen, which are to be first separated, before they are burned to carbon dioxide and water.

With more complex compounds the available heat of combustion does not fall so far short of the theoretical maximum, and it may be stated in a general way that the greater the number of carbon atoms in the compound, the more closely will the available and actual number of heat units coincide. This statement is especially true of certain series of hydrocarbons. The following table (II) will serve to illustrate this in the case of the first three members of the paraffin series. For the higher paraffins no determinations have yet been made.

TABLE II.—Showing Ratio of Available to Calculated Heat of Combustion in the case of certain Hydrocarbons.

NAME.	SYMBOL.	Calculated heat units, assuming that the carbon and hydrogen produce the maximum of heat, and are burned separately. Per kilo of paraffin.	Available heat as determined by calorimetric measurement. Per kilo of paraffin.	Percentage of available on theoretical maximum of heat units.
Methane,	CH_4	14613	13270	90.81
Ethane,	C_2H_6	13310	12373	92.95
Propane,	C_3H_8	12835	12052	93.89

It has been shown by Thomsen that isomeric hydro carbons, or those which differ in properties, although having identical composition, may produce different quantities of heat when burned, thus :

	Symbol.	Heat Units.
Propylene,	$C_3 H_6$	11757
Trimethylene,	$C_3 H_6$	10917

Difference = 840

The chemical formulas given show them to have the same composition, and yet these hydrocarbons would be represented by different values if used as fuels.

The presence of isomers among the hydro carbons of natural gas would tend to interfere with the correctness of a calculation of its fuel value.

No isomers are known in the case of methane (CH_4).

Berthelot has stated that a second hydro carbon isomeric with ethane (C_2H_6) exists, which produces on burning 12776 heat units, instead of 12373, the number as determined by Thomsen.

Thomsen's researches have disproved this assertion, however, and have shown conclusively that ethane produced in a variety of ways invariably possesses the same calorific power. (Berichte der Deutschen chemischen Gesellschaft 1881, p 500). Isomers of the higher paraffins no doubt occur in gas, as well as in petroleum, but when it is considered that in gas the higher paraffins occur only in small quantity, and moreover that the calculated and the available calorific power differ much less in these higher members than in methane and ethane, the danger of error from the presence of such isomers cannot be considered likely to affect the calculated results.

The calorific power of methane was determined by Andrews in 1848 as 13108 heat units (Philosophical Magazine 1848 p 321), and by Favre and Silbermann in 1853 as 13063. heat units.

In 1880 Thomsen assigned it the value 13345.6, and this number agrees closely with that obtained by Berthelot in the same year, viz: 13343.8. More recently Thomsen has corrected his former result, and now gives 13270.5 as the

most probable number. (Berthelot, Comptes Rendus, 1880 p 1240. Thomsen, Berichte der Deutschen Chemischen Gesellschaft 1880, p 959 and 1321 Ref, and 1886 p 77, Ref.).

The elaborate researches of Julius Thomsen in thermochemistry, (Thermochemische Untersuchungen, Leipzig) have reached the fourth of a series of large volumes, and although designed primarily as a contribution to theoretical chemistry, they supply data likely to prove of great value in the study of fuels for metallurgical and other technical purposes.

The actual calorific power of a gas fuel may now, by the use of such data, be more satisfactorily determined by calculation, provided its composition is known, than by the use of a calorimeter. In this respect there is an important difference between gas fuels and the various kinds of coal. Coal being a compound of carbon, hydrogen and oxygen, of a highly complex character, or possibly a mixture of such compounds, no such plainly definable relationship exists between the theoretical maximum and the available heat quantity per unit weight burnt.

The percentage composition by weight of the paraffins likely to occur in natural gas is expressed in the following table. Small quantities of condensible vapors of the higher paraffins occur in the gas in some places as is evidenced by the condensation of benzene in pipes. These heavier vapors occur usually in very minute quantity, if at all:

TABLE III.—Showing the Composition by weight of some of the Lower Paraffins.

NAME.	Symbol.	Per cent. carbon.	Per cent. hydrogen.
Methane,	CH ₄	74.97	25.03
Ethane,	C ₂ H ₆	79.96	20.04
Propane,	C ₃ H ₈	81.78	18.22
Butane,	C ₄ H ₁₀	82.72	17.28
Pentane,	C ₅ H ₁₂	83.29	16.71

The analyses of natural gas above detailed show a variation in the proportion of carbon and hydrogen in the case of the two extremes of 3.18 per cent., thus :

The paraffins in Murrysville gas contain—

Carbon,	74.96 per cent. by weight.
Hydrogen,	25.04 “ “ “
	<hr/>
	100.00
	<hr/> <hr/>

And in the case of Fredonia gas—

Carbon,	78.14 per cent. by weight.
Hydrogen,	21.86 “ “ “
	<hr/>
	100.00
	<hr/> <hr/>

From the tabular statement of the composition of the lower paraffins, it appears that Murrysville gas, as obtained at the Hukill well, has nearly the composition of methane, while disregarding again the nitrogen and carbon dioxide present, the Fredonia gas, the richest in carbon, approximates in composition to a mixture of equal volumes of methane and ethane, of which the actual composition would be, by weight :

Carbon,	78.22 per cent.
Hydrogen,	21.78 per cent.
	<hr/>
	100.00
	<hr/> <hr/>

By this I do not imply that it actually contains these two paraffins in the proportion named, for it is possible that the gas in question contains more of methane and a very small quantity of some one of the higher paraffins, propane, or quartane, etc.

As I have stated in regard to the analyses, the exact determination of the percentage of individual paraffins is a matter of such extreme difficulty, that it may be considered practically impossible.

If we assume that Fredonia gas really contains equal volumes of methane and ethane, and calculate its calorific power accordingly, the following error may be committed. The gas may contain a larger amount of methane than was assumed, and consequently a very small quantity of quartane or pentane, *for although the percentage of carbon and hydrogen is definitely fixed by the analysis, it is still a question as to the arrangement of the carbon and hydrogen in the form of higher or lower paraffins.*

As the difference between the available and the theoretical heat of combustion is greater in the case of methane and less and less in the higher paraffins, an under estimate of the quantity of methane would lead to too high a value for the available heat of combustion. On the other hand, an under estimate of the proportion of the higher paraffins, would cause the available heat, as expressed in heat units, to be rated too low, supposing that in both cases the absolute quantities of carbon and hydrogen remain constantly the same.

This error would be small in most instances, but in the extreme case of 2 gases consisting of methane and ethane respectively, the error from this source would exceed 1%. I have attempted to correct this error, as will be shown below. The curious and intimate relationships of the paraffins are well illustrated by the fact that a mixture of 1 cubic meter each of methane, ethane and propane will contain the same proportions of carbon and hydrogen, and will consequently yield the same quantities on burning of $C O_2$ and $H_2 O$ as three cubic meters of the intermediate hydro-carbon, ethane,—

1 cubic meter of methane weighs 0.7148 kilo, and generates heat units,	9485
1 cubic meter of ethane weighs 1.34016 kilo, and generates heat units,	16582
1 cubic meter propane weighs 1.9656 kilos, and generates heat units,	23688
	<hr/>
	49755
3 cubic meters of ethane generate on burning heat units, .	49746
	<hr/>
	9
	<hr/> <hr/>

The numbers expressing the heat produced are obtained by multiplying the weight of the cubic meter by 13270, 12373 and 12052, respectively, as given in table II.

The difference is so slight—amounting to only 9 heat units, that it is evident that it would have been sufficiently accurate to assume this mixture of three hydro-carbons to consist of the intermediate member Ethane in so far as the calculation of the fuel value is concerned.

Or it may be more broadly stated that, with a view to

the calculation of the calorific power of natural gas, it is sufficiently accurate to assume that a natural gas, (containing no hydro-carbons of the olefine series) has the simplest constitution consistent with its percentage by weight of carbon and hydrogen, and then to determine its fuel value accordingly.

Fredonia gas, as shown in the table of analyses, consists of 90.05% of paraffins, together with 9.54% nitrogen and 0.41% carbon dioxide. The paraffins consist of 0.80423 kilo carbon and 0.22494 kilo hydrogen per cubic meter.

The theoretical maximum of heat units for these paraffins is calculated as follows, per cubic meter:

0.80406 × 8080,	6497
0.22494 × 34180,	7288
	13785
	13785

When $C H_4$ burns, only 90.81% of the theoretical heat is available. When $C_2 H_6$ burns 92.95% can be utilized.

Hence if Fredonia gas is to be looked upon as a mixture of equal volumes of the two hydro-carbons methane and ethane, it will contain about 1 and 1.87 parts by weight respectively, (or approximately two parts by weight) of methane and ethane.

The available heat of combustion can be determined by multiplying the theoretical maximum by a factor which is intermediate between $\frac{90.81}{100}$ and $\frac{92.95}{100}$, and as a very close approximation the fraction

$$\frac{2 \text{ Et} + \text{Mt}}{3 \times 100}$$

will, I think, be sufficiently accurate. In this Et = the percentage of available on theoretical maximum heat, for ethane and Mt = the same ratio for Methane.

Substituting in this fraction

$$\frac{2 \times 0.9295 + 0.9081}{3} = .9224$$

The theoretical maximum heat of combustion of the Fredonia gas, as calculated above, is 13785 heat units per cubic meter of contained paraffins.

Then $13785 \times 0.9224 = 12715$ as the available heat units due to the paraffins in the gas. As there are 90.05% of paraffins,

the remainder, consisting of nitrogen and carbon dioxide, the above number will be still further reduced, and $12715 \times 0.9005 = 11450$.— the available heat produced by 1 cubic meter of Fredonia gas.

In the case of the gas from Sheffield, Kane, Wilcox, Raccoon Creek, Baden and Houston, there is a general similarity as regards the percentage of carbon and hydrogen. Wilcox gas may be regarded as representing approximately the average, and as a calculation shows that a mixture of 4 volumes methane and 1 volume ethane contains carbon 76.54 and hydrogen 23.46, we may, for the purpose of the present calculation, assume that the above mentioned six gases contain approximately these proportions of the two named paraffins. For such a mixture the factor by which to obtain the available calorific value will be

$$\frac{2 \text{ Mt} + \text{Et}}{3 \times 100} = 0.9153.$$

This factor has accordingly been used in the case of the above named gases. Speechley gas may be considered to contain 5 volumes of Methane and 2 volumes of Ethane for the purpose of the present calculation, and the factor will be

$$\frac{3 \text{ Et} + 4 \text{ Mt}}{7 \times 100} = 0.9173.$$

Murrysville gas contains nearly pure methane, and consequently the factor will be 90.81.

It is not implied in the above considerations that the actual proportions of what may be regarded as the most commonly occurring paraffins,— CH_4 , C_2H_6 , C_3H_8 , etc., can be accurately stated, for this I believe to be impossible. These proportions have been assumed as not inconsistent with the analytical data, merely for the purpose of obtaining an approximately correct value for the factor to be used in the calculation of the calorific power of the gas. The following table (IV) contains the results of the calculations carried out as explained. Column No. 2 in this table expresses the quantities of carbon and hydrogen contained in 1 cubic meter of the paraffins in each gas. In column No. 3 are given the factors, the derivation and use of which have already been pointed out :

TABLE IV.—Fuel Values of Natural Gas.

GAS FIELD.	WEIGHT IN KILO-GRAMS PER CUBIC METER OF PARAFFINS.		Factor.	Available heat units per cubic meter of gas.	Available heat units per 100 cubic feet of gas.	Pounds of water at boiling point evaporated by 100 cubic feet of gas.	Pounds of pure charcoal equal in heating effect to 100 cubic feet of gas.
	Carbon.	Hydrogen.					
Fredonia,	0.80406	0.22492	0.9224	11449	32421	133.30	8.845
Sheffield,	0.65526	0.19924	0.9152	10040	28430	116.89	7.756
Kane,	0.65069	0.19806	0.9152	10354	29319	120.54	7.999
Wilcox,	0.64622	0.19828	0.9152	9925	28102	115.54	7.667
Speechley,	0.69857	0.20736	0.9173	11144	31554	129.73	8.609
Lyon's Run, near Murrysville,	0.53741	0.17950	0.9081	9296	26321	108.22	7.181
Raccoon Creek,	0.62918	0.19408	0.9152	9661	27355	112.47	7.463
Baden,	0.64209	0.19677	0.9152	9515	26941	110.77	7.350
Houston,	0.64737	0.19694	0.9152	9224	26119	107.38	7.126

This factor is a fraction. Its numerator represents the actual number of heat units produced in the burning of the unit weight of the total paraffins, from a consideration of the percentage of carbon and hydrogen in the gas. The denominator represents the number of heat units obtained when the quantities of contained carbon and hydrogen are multiplied by the numbers 8,080 and 34,180 respectively, and the products added.

Column No. 4 gives the actual fuel value of each gas expressed in heat units per cubic meter. These numbers represent the heat of combustion calculated for the carbon and hydrogen separately, these two added together, and their sum multiplied by the corresponding factor in column No. 3.

The numbers in column No. 5, indicate kilograms of water which can be warmed from 0° to 1° C, when 100 cubic feet of the respective gas, measured at 0° C and under a barometric pressure of 76 centimeters, is burned at an initial temperature of 18° C, or 64.4° F; (this last is the temperature assumed by Thomsen in his determinations,) and assuming that the products of combustion are liquid water and gaseous carbon dioxide.

In column 6 are stated the number of pounds avoirdupois of water which, theoretically, should be boiled away at 100° C. into steam at the same temperature, and under atmospheric pressure, when 100 cubic feet of gas are burned. The latent heat of evaporation of water in this calculation has been assumed as 536.2 heat units. (Berthelot, Compts Rendus, 1877, p. 646.)

In a seventh column a comparison is given between gas and pure charcoal, assumed free from ash.*

Charcoal has been chosen rather than coke or coal, for the reason that exact calorimetric data as to the latter fuels are as yet difficult to obtain, and calculated values are uncertain.

*As already stated the heat unit employed in the above calculations is the quantity of heat required to warm 1 kilogram of water from 0° to 1° C.

The plan of statement of results I have adopted will render it an easy matter, however, to substitute any other units or calorimetric values.

An impression prevails, based partly upon analytical data, and partly upon a supposed variation in the steam-producing power, that natural gas is subject to constant fluctuations in composition. To what extent such fluctuations are liable to affect the value of the results of the above calculations, I am wholly unable to state.

In conclusion I have to express my indebtedness for information and for facilities in conducting tests and examinations at wells to the following gentlemen: Mr. K. Chickering, of the Oil Well Supply Co., Oil City; Mr. W. C. Henry, of the United Natural Gas Co., Wilcox; Mr. Walter Horton and Mr. John McNair, of Sheffield; Mr. J. D. Bruder, of Kane; Mr. E. J. Crissey, of Fredonia; Mr. T. F. Gayley, of Rochester, and to the officers of the Philadelphia Gas Co., the Baden Gas Co. and the Pennsylvania Gas Co. of Pittsburgh, and to many others.

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