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## REPORT ON THE CHEMICAL COMPOSITION OF NATURAL GAS.

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The following experiments were tried at the valve house of the Philadelphia Company, in the rear of the office building, on Penn Street, Pittsburgh, beginning on March 22, 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 Murrysfield field. The gas was passed very slowly, so that three 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  $\frac{1}{200,000,000}$  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     "
	<hr/>
	100.00     "

Hence this 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 2, 1887, from the high pressure main of the Bridgewater Natural Gas

Company, at Rochester, Pa. The pressure at the time was sixty-seven pounds.

The gas is produced wholly from one sand, which is about 1,200 feet below the surface, on Raccoon Creek, in Beaver County. The Bridgewater Company owns twenty-three wells, and supplies the towns of Beaver Falls, Rochester, New Brighton, Phillipsburg, Van Port, Bridgewater, New Sheffield and Shannopin.

The Youngstown Company owns twelve 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 twenty minutes the fluid remained perfectly clear. After forty 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 per cent.

#### RESULTS OF ANALYSIS OF RACCOON CREEK GAS.

Nitrogen, . . . . .	9'91
Hydrogen, . . . . .	0'
Carbon dioxide, . . . . .	trace.
Carbon monoxide, . . . . .	0'
Olefines, . . . . .	0'
Ammonia, . . . . .	0'
Oxygen, . . . . .	trace.
Sulphuretted hydrogen, . . . . .	trace.
Paraffins, . . . . .	90'09
	<hr/> 100'00

In a combustion of Raccoon Creek gas, 325'48 cubic centimetres yielded—

H <sup>2</sup> O — 0'5108 gm.,	corresponding to H, — 0'05688 gm. = 23'60 per cent.
CO <sup>2</sup> — 0'6755 gm.,	“ to C, — 0'18422 gm. = 76'40 “
	<hr/> 100'00 “

Hence the paraffins in this gas contain per litre—

0.62827 gm. carbon.  
0.19398 gm. hydrogen.

In a second combustion, 398.08 cubic centimetres gas yielded—

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

Hence the paraffins contain per litre—

0.63010 gm. carbon.  
0.19418 gm. hydrogen.

The means of these two results are per litre paraffins—

0.62918 gm. carbon, = 76.42 per cent.  
0.19408 gm. hydrogen, = 23.58 “  
100.00 “

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

No. 8, Baden. Six miles southeast from Rochester, on the Pittsburgh, Fort Wayne and Chicago Railroad, Beaver County. The samples were taken May 18, 1887, from the Bryan well No. 2, one of four wells belonging to the Baden Gas Company. This gas is produced wholly from one sand, which is 1,396 feet deep, or about 1,300 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	12.38	12.32 per cent.
Carbon dioxide, . .	0.41	0.41	0.41 “

#### RESULTS OF ANALYSIS OF BADEN GAS.

Nitrogen, . . . . .	12.32
Carbon dioxide, . . . . .	0.41
Oxygen, . . . . .	trace.
Hydrogen, . . . . .	0.
Carbon monoxide, . . . . .	0.
Olefines, . . . . .	0.
Ammonia, . . . . .	0.
Paraffins, . . . . .	87.27
	100.00

317.17 cubic centimetres of Baden gas yield on combustion—

H<sup>2</sup>O — 0.4892 gm., corresponding to H, — 0.05447 gm. = 23.48 per cent.  
CO<sup>2</sup> — 0.6510 gm.,                   "           to C, — 0.17754 gm. = 76.52 "  
100.00 "

Hence the paraffins of Baden gas contain per litre—

0.64142 gm. carbon.  
0.19681 gm. hydrogen.

In a second combustion, 332.70 cubic centimetres yield—

H<sup>2</sup>O — 0.5130 gm., corresponding to H, — 0.057127 gm. = 23.56 per cent.  
CO<sup>2</sup> — 0.6843 gm.,                   "           to C, — 0.18663 gm. = 76.44 "  
100.00 "

Hence the paraffins contain per litre—

0.64276 gm. carbon.  
0.19674 gm. hydrogen.

The means of these two results are per litre of paraffins—

0.64209 gm. carbon,   = 76.48 per cent.  
0.19677 gm. hydrogen. = 23.52 "  
100.00 "

No. 9, Houston well, Houston Station, two miles south of Canonsburg, on the Pittsburgh, Cincinnati and St. Louis Railroad, Washington County.

This well is situated one-third mile west of the Station, on Plum Run. It is drilled nearly through the Gantz sand, and is 1,794 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 superintendents 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 wells. The sample was collected on March 18, 1887.

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

Determinations 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
Carbon dioxide . . . . .	0'44
Oxygen, . . . . .	trace.
Olefines, . . . . .	0'
Carbon monoxide, . . . . .	0'
Ammonia, . . . . .	trace.
Hydrogen, . . . . .	0'
Paraffins, . . . . .	84'26
	<hr/>
	100'00

310·20 cubic centimetres of Houston gas yielded on combustion—

H <sup>2</sup> O — 0'4601 gm.,	corresponding to H, — 0'05124 gm. = 23'20 per cent.
CO <sup>2</sup> — 0'6217 gm.,	“ to C, — 0'16955 gm. = 76'80 “
	<hr/>
	100'00 “

Hence the paraffins contain per litre—

0'64871 gm. carbon.  
0'19602 gm. hydrogen.

In a second combustion, 293·35 cubic centimetres yielded—

H <sup>2</sup> O — 0'4392 gm.,	corresponding to H, — 0'04891 gm. = 23'44 per cent.
CO <sup>2</sup> — 0'5855 gm.,	“ to C, — 0'15968 gm. = 76'56 “
	<hr/>
	100'00 “

Hence the paraffins contain per litre—

0'64604 gm. carbon.  
0'19786 gm. hydrogen.

The means of these two analyses are per litre of paraffins—

0'64737 gm. carbon,	= 76'68 per cent.
0'19694 gm. hydrogen,	= 23'32 “
	<hr/>
	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 group 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 simply of the hydrocarbons 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 hydrocarbons, it is evident that the higher paraffins are not present in notable quantity.

The method I have used in testing for the hydrocarbons 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 Murrys ville the least. Ammonia was found, in traces only, in Houston gas. Carbon monoxide 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 per cent. 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 Murrys ville, 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 composi-

tion 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.

TABLE I.

CONSTITUENTS.	Fredonia.	Sheffield.	Kane.	Wilcox.	Speechley.	Lyon's Run near Murrys ville.	Raccoon Creek.	Baden.	Houston.
Nitrogen, . . . . .	9.54	9.06	9.79	9.41	4.51	2.02	9.91	12.32	15.39
Carbon dioxide, . . . .	0.41	0.30	0.20	0.21	0.05	0.28	trace.	0.41	0.44
Hydrogen, . . . . .	0.	0.	0.	0.	0.02	0.	0.	0.	0.
Ammonia, . . . . .	—	0.	0.	0.	0.	0.	0.	0.	trace.
Oxygen, . . . . .	trace.	trace.	trace.	trace.	trace.	trace.	trace.	trace.	trace.
Sulphuretted hydrogen, .	—	0.	0.	0.	0.	0.	trace.	0.	0.
Paraffins, . . . . .	90.05	90.64	90.01	90.38	95.42	97.70	90.09	87.27	84.26
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
The paraffins contained in these gas samples have the following composition <i>by weight</i> :									
Carbon, . . . . .	78.14	76.69	76.77	76.52	77.11	74.96	76.42	76.48	76.68
Hydrogen, . . . . .	21.86	23.31	23.23	23.48	22.89	25.04	23.58	23.52	23.32
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

(3.) The carbon dioxide, which varies within very narrow limits. The only gas in which it disappears is that from Raccoon Creek, although Speechley gas contains barely more than at race.

At Oil City, a sand is found 582 feet below low water mark in the Allegheny River, which produces gas of low pressure, amounting, it is said, to twenty pounds when shut in for some time. This gas is used in the Oil Well Supply Company's works for heating purposes.

It bears the same relation to the Speechley gas-sand, 1,900 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.\*

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

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\* For the information of those who are not familiar with the chemistry of the subject, it may be of importance to call attention to the two very different modes of occurrence of hydrogen in fuel gases.

As *free* or *uncombined* hydrogen, it is often reported to occur in considerable quantity in natural gas, and constitutes often from thirty to forty per cent. of ordinary coal gas.

In this form of *free* hydrogen, it may be separated and removed more or less completely from the other gaseous constituents by exposure of the gas to a porous wall of plaster, through which the extremely light, *free* hydrogen more readily passes. In the above detailed analyses, *free* hydrogen was found in a single instance, and in traces only (Speechley gas).

In chemical union with carbon, hydrogen constitutes about one-fourth part by weight of all the natural gas now used as fuel in Pennsylvania. In this form of occurrence, as a hydrocarbon, hydrogen cannot be separated from the other constituents by mechanical means. The products of the combustion of all such gas will be the same in kind—carbon dioxide and water—whether the hydrogen be present wholly as a hydrocarbon, or partly as such and partly *free*.



## CALCULATION OF THE FUEL VALUE OF NATURAL GAS.

The calorific power of any combustible may be determined by measuring the number of kilogrammes of water heated from  $0^{\circ}$  to  $1^{\circ}$  by one kilogramme 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 and Silbermann (in 1849), 8,080 heat units, or one kilo. in burning will raise the temperature of 8,080 kilos. of water from  $0^{\circ}$  to  $1^{\circ}$  C.

By the same authors it was found that one kilo. of hydrogen in burning, generates a quantity of heat sufficient to warm 34,462 kilos. of water from  $0^{\circ}$  to  $1^{\circ}$  C.; that is, 34,462 heat units. Later determinations have been made by various authors, the most important being by Thomsen, who found 34,180 (*Berichte der deutschen chemischen Gesellschaft*, 1873, p. 1883), and by Berthelot, who obtained the number 34,600 (*Comptes Rendus*, 1880, p. 1240). The value assigned by Thomsen, viz., 34,180, is probably the more correct.

If it were possible that a fuel should contain pure hydrogen and charcoal, 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 13,270.5 heat units, but if the same quantities of carbon (as charcoal) and hydrogen were burned separately in a calorimeter, 14,613 heat units would result (assuming that the carbon produces 8,080 and the hydrogen 34,180 heat units per kilo. burned).

This difference between the calculated amount of heat, and the actually available heat,  $14,613 - 13,270 = 1,343$  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 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.	Available Heat as determined by Calorimetric Measurement.	Percentage of Available on Theoretical Maximum of Heat Units.
		Per Kilo. of Paraffin.	Per Kilo. of Paraffin.	
Methane, . . . . .	CH <sup>4</sup>	14,613	13,270	90.81
Ethane, . . . . .	C <sup>2</sup> H <sup>6</sup>	13,310	12,373	92.95
Propane, . . . . .	C <sup>3</sup> H <sup>8</sup>	12,835	12,052	93.89

It has been shown by Thomsen that isomeric hydrocarbons, or those which differ in properties, though having identical composition, may produce different quantities of heat when burned. Thus—

	Symbol.	Heat Units.
Propylene, . . . . .	C <sup>3</sup> H <sup>6</sup>	11,757
Trimethylene, . . . . .	C <sup>3</sup> H <sup>8</sup>	10,917
Difference, . . . . .		840

The chemical formulæ 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 hydrocarbons 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 (C H<sup>4</sup>).

Berthelot has stated that a second hydrocarbon isomeric with ethane (C<sup>2</sup>H<sup>6</sup>) exists, which produces on burning 12,776 heat units, instead of 12,373, 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 effect the calculated results.

The calorific power of methane was determined by Andrews in 1848, as 13,108 heat units (*Philosophical Magazine*, 1848, p. 321), and by Favre and Silbermann in 1853 as 13,063 heat units.

In 1880, Thomsen assigned it the value 13,345.6, and this number agrees closely with that obtained by Berthelot in the same year, viz., 13,343.8. More recently Thomsen has corrected his former result, and now gives 13,270.5 as the most probable number (Berthelot, *Comptes Rendus*, 1880, p. 1240). Thomsen (*Berichte der deutschen chemischen Gesellschaft*, 1880, p. 959 and 1321, ref., and 1887, p. 77, ref.).

The elaborate researches of Julius Thomsen in thermo-chemistry (*Thermo-chemische 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 condensable vapor of higher paraffins occur in the gas

in some places, as is evident by the condensation of benzine in pipes. The 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 <sup>4</sup>	74.97	25.03
Ethane, . . . . .	C <sup>2</sup> H <sup>6</sup>	79.96	20.04
Propane, . . . . .	C <sup>3</sup> H <sup>8</sup>	81.78	18.22
Butane, . . . . .	C <sup>4</sup> H <sup>10</sup>	82.72	17.28
Pentane, . . . . .	C <sup>5</sup> H <sup>12</sup>	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 of Murrys ville gas contain—

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

and in case of Fredonia gas—

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

From the tabular statement of the composition of the lower paraffins, it appears that Murrys ville 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, . . . . .	21.70    "    "
	<hr/> 100.00    "    "

By this I do not imply that it actually contains these two paraffins in the proportions named, for it is possible that the gas in question contains more of methane and a very small quantity of some 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 theoretical heat of combustion is greater in the case of methane 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 remained constantly the same.

This error would be small in most instances, but in the extreme case of the two gases, consisting of methane and ethane, respectively, the error from this source would exceed one per centum. I have attempted to correct this error, as will be shown below.

The curious and intimate relationship of the paraffins is well illustrated by the fact that a mixture of one cubic metre 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  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as three cubic metres of the intermediate hydrocarbon ethane.

1 cubic metre of methane weighs 0.7148 kilos., and generates	
heat units, . . . . .	9,485
1 cubic metre of ethane weighs 1.34016 kilos., and generates	
heat units, . . . . .	16,582
1 cubic metre of propane weighs 1.9656 kilos., and generates	
heat units, . . . . .	23,688
Total, . . . . .	49,755
3 cubic metres of ethane generate on burning heat units, .	49,746
Difference, . . . . .	9

The numbers expressing the heat produced are obtained by

multiplying the weight of the cubic metre by 13,270, 12,373 and 12,052, respectively, as given in Table II.

The difference is so slight, amounting to only nine heat units, that it is evident that it would have been sufficiently accurate to assume this mixture of three hydrocarbons 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 the natural gas (containing no hydrocarbon 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 per cent. of paraffins, together with 9.54 per cent. of nitrogen and 0.41 per cent. carbon dioxide. The paraffins in this gas consist of 0.80406 kilo. carbon and 0.22494 kilo. hydrogen per cubic metre.

The theoretical maximum of heat units for these paraffins is calculated as follows :

$$\begin{array}{r} 0.80406 \times 8,080 = 6,497 \\ 0.22494 \times 34,180 = 7,288 \\ \hline 13,785 \end{array}$$

When  $\text{CH}_4$  burns, only 90.81 per cent. of the theoretical heat is available. When  $\text{C}_2\text{H}_6$  burns, 92.95 per cent. can be utilized.

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

The available heat of combustion can be determined by multiplying the theoretical maximum by a factor which is intermediate between .9081 and .9295, 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.* equals the percentage of available on theoretical maximum heat for ethane, and

*Mt.* equals 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 13,785 heat units.

Then,  $13,785 \times 0.9224 = 12,715$  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  $12,715 \times 0.9005 = 11,450$ , the available heat produced by one cubic metre 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 four volumes of methane and one 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

$$\frac{2 \text{ Mt.} + \text{Et.}}{3 \times 100} = 0.9152.$$

This factor has accordingly been used in the case of the above-named gases. Speechley gas may be considered to contain five volumes of methane and two 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 .9081.

It is not implied in the above consideration that the actual proportions of what may be regarded as the most commonly occurring paraffins— $\text{CH}_4$ ,  $\text{C}^2\text{H}_6$ ,  $\text{C}^3\text{H}_8$ , 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 approximately correct values for the factors to be used in the calculation of the calorific power of gas.

The following table, IV, contains the results of the calculation carried out as explained. Column No. 2 in this table expresses the quantities of carbon and hydrogen contained in one cubic metre of each gas. In Column No. 3 are given the factors, the derivation and use of which has already been pointed out.

TABLE IV.  
FUEL VALUE OF NATURAL GAS.

GAS FIELDS.	2		3	4	5	6	7
	Weight in Kilos. of Carbon per Cubic Metre of Paraffins.	Weight in Kilos. of Hydrogen per Cubic Metre of Paraffins.	Factor.	Available Heat Units per Cubic Metre of Gas.	Available Heat Units per 100 feet of Gas.	Pounds of Water at Boiling Point, evaporated by 100 feet of Gas.	Pounds of Pure Charcoal, equal in Heating Effect to 100 feet of Gas.
Fredonia, . . . . .	0.80406	0.22492	0.9224	11,449	32,421	133.30	8.845
Sheffield, . . . . .	0.65526	0.19924	0.9152	10,040	28,430	116.89	7.756
Kane, . . . . .	0.65669	0.19866	0.9152	10,354	29,319	120.54	7.999
Wilcox, . . . . .	0.64622	0.19828	0.9152	9,925	28,102	115.54	7.667
Speechley, . . . . .	0.69857	0.20738	0.9173	11,144	31,554	129.73	8.609
Lyon's Run, near Murrys ville, . . . . .	0.53741	0.17950	0.9081	9,206	26,321	108.22	7.181
Raccoon Creek, . . . . .	0.62918	0.19408	0.9132	9,661	27,355	112.47	7.463
Baden, . . . . .	0.64209	0.19677	0.9152	9,515	26,941	110.77	7.350
Houston, . . . . .	0.64737	0.19694	0.9152	9,224	26,119	107.38	7.126

1 cubic metre = 35.3166 cubic feet.

1 kilogramme = 2.20462 pounds avoirdupois.

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, the number being ascertained 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 metre. 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 No. 3.

The numbers in Column No. 5 indicate kilogrammes of water which can be warmed from 0° to 1° C. when 100 cubic feet of the



respective gas, measured at  $0^{\circ}$  C., and under a barometric pressure of seventy-six centimetres, are burned at an initial temperature of  $18^{\circ}$  C., or  $64^{\circ}.4$  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 No. 6 are stated the numbers of pounds avoirdupois of water which, theoretically, should be boiled away at  $100^{\circ}$  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, *Comptes Rendus*, 1877, p. 646).

In the 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.

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 view of these reported changes, it is to be regretted that more abundant data are not at hand upon which to base a conclusion as to the real nature of the fluctuations in composition. If such changes occur, are they progressive or irregular? Are they of such a character as to cast any light upon the question of origin, which every one asks but no one can answer? Are they to be regarded as a factor in determining the durability of a gas well?