There seems to be no doubt but that this substance is durene, notwithstanding the results of the analysis. In order to further identify it the dibromo and dinitro compounds were made and found to agree in every respect with the dibromo and dinitro compounds prepared by Anschütz.

That the above reaction with mesitylene is complex is evident from the formation of benzene, toluene, xylene and durene. This unusual reaction was observed by Anschütz,[1] who first showed that benzene homologs are formed from a single benzene derivative by the action of aluminium chloride. But as already stated, no anthracene derivatives had ever been prepared from mesitylene. There can be no doubt but the compound described above is an anthracene derivative. We have represented it as a tetramethyl compound, although analysis really agrees better for a hexamethyl derivative. We have so represented it because a hexa compound can only be formed from a isomer of mesitylene like pseudo-cumene or hemellithene. While we have not succeeded in identifying these latter compounds, both are within the range of possibility, and a hexamethyl derivative could therefore be formed. Experiments along this line are now under way.

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GAS ANALYSES BY FRACTIONAL DISTILLATION AT LOW TEMPERATURES.[2]

BY G. A. BURRELL AND F. M. SEIBERT.

Received April 30, 1914.

This paper describes experiments that resulted in the separation of a natural gas sample into the individual paraffin hydrocarbons present. This had not been accomplished hitherto.

Natural gases may contain only methane as the combustible constituent or may be mixtures that contain large quantities of the higher gaseous paraffins. In some samples the latter predominate. In addition, there may be vapors of the liquid paraffin hydrocarbons present, sometimes enough to warrant the installation of a plant for their extraction. The natural gas used in Pittsburgh is a complex mixture, and is typical of gas that is supplied to many cities to the extent of billions of cubic feet per year. The exact composition of this gas is of importance to the Bureau of Mines because it is used in testing explosives, safety lamps, electrical mining machinery, and other mining appliances. By the scheme shown herein, it is also possible to determine more closely the quantity of the vapors of the liquid paraffins in a natural gas mixture than has been possible heretofore.

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[1] *Ann.*, **235**, 178–190 (1886).

[2] Paper presented before the spring meeting of the American Chemical Society, April 7–10, 1914, by permission of the Director of the Bureau of Mines.

Gases that contain enough of these vapors are compressed and cooled at many plants and the condensate sold as gasoline.

It is generally known that ordinary combustion gas analyses give but little indication regarding the individual hydrocarbons present in a natural gas mixture. Only the two predominating paraffins are shown.

In the experiments reported herein, natural gas was first liquefied by means of liquid air and the different paraffin hydrocarbons separated by properly adjusting temperatures and removing the various fractions with a mercury pump. These fractions were analyzed by the ordinary slow combustion method. Advantage was taken of the work of P. Lebeau and A. Damiens,[1] who prepared various mixtures of the gaseous paraffins, liquefied them and partially separated them. This work is in advance over their work in that the separation was made into single constituents. The important part of this paper, however, is the application of the work to the determination of the constituents of natural gas. Such a separation is possible because, in the liquid condition, the boiling points of the gaseous paraffins are rather widely separated. These boiling points follow: Methane, —160°; ethane, —93°; propane, —45°; N butane, + 1°; and isobutane —10°. The two butanes were not separated. In order to finish the work with fractions large enough for accurate analyses, the experiment given herein was started with about $1^1/_2$ liters of gas (1531 cc.). Other experiments were performed with various natural gases in which smaller quantities were used. The sample, as analyzed by the ordinary slow combustion method, contained the following constituents:

Methane	79.2%
Ethane	19.6
Nitrogen	1.2
Total	100.0

There is also about 0.03 per cent. of carbon dioxide in the gas mixture. Carbon monoxide, hydrogen and olefine hydrocarbons are not present.

Experimental Procedure.—Fig. 1 shows the general arrangement of the apparatus. The Töpler pump is on the left of the photograph. (A) is a small glass vessel used for holding the liquefied gases. It could be enclosed in the Dewar flask (*B*). Surrounding this Dewar flask is shown another and larger one. This arrangement was adopted in order to provide better insulation than was afforded by only one flask, although the work can be conducted with only one Dewar flask. The gas sample, prior to liquefaction, was measured by weighing the water displaced from the glass vessel (*C*) then transferred to the gas buret (*D*) and from there passed into the liquefying bulb (*A*). At (*E*) is shown a mercury manometer for registering pressures in the pump. At the base of the

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[1] *Compt. rend.*, **156**, 325 (1913).

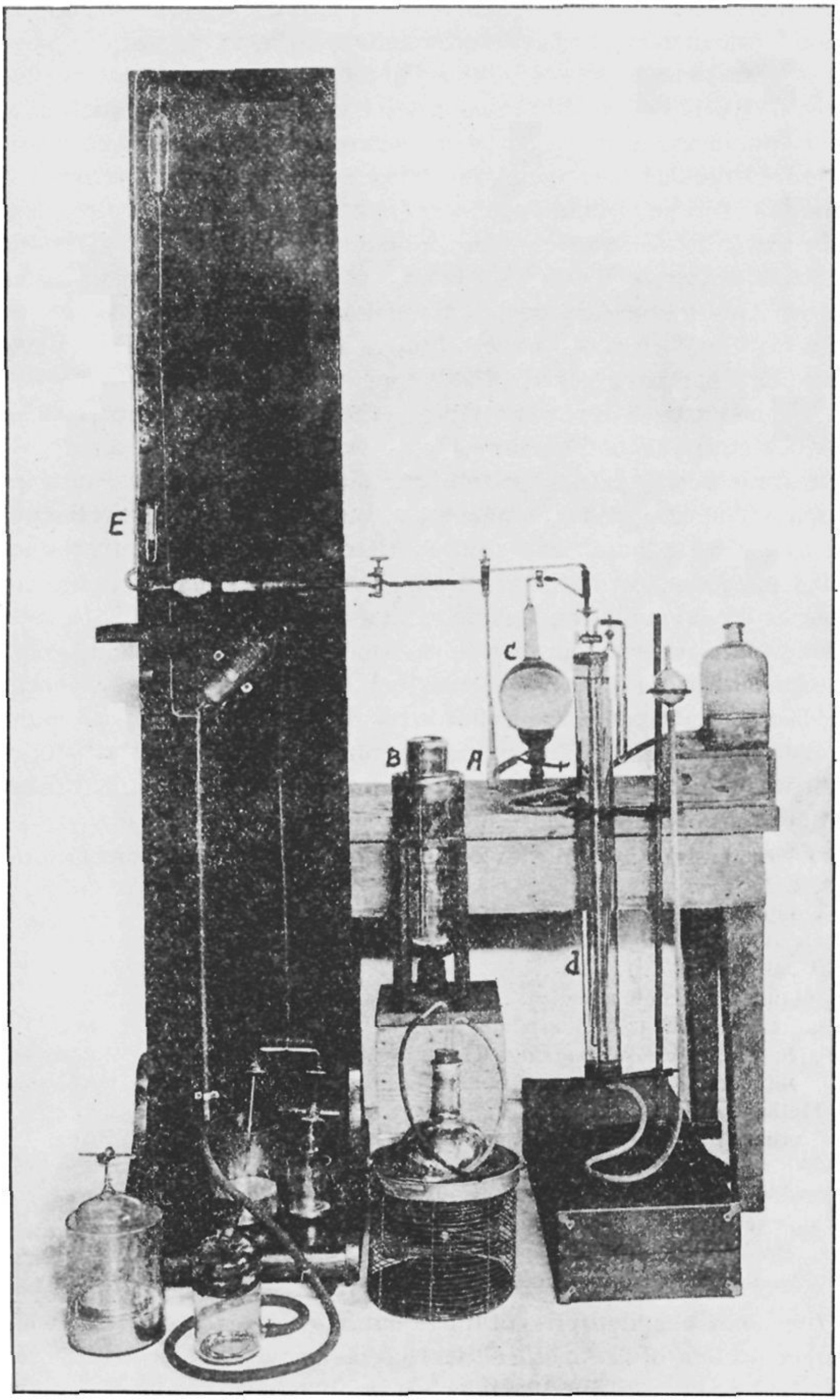

Fig. 1.—Apparatus for the liquefaction and fractionation of gas mixtures.

Topler pump are shown the glass vessels for trapping the different gas fractions over mercury as they were removed.

The entire sample was first liquefied by means of liquid air. With the gas in the liquid condition, connection was made between it and the mercury pump and as much of the gas removed with the pump as possible. This process divided the original quantity into two portions; first, a gaseous portion, and second, a liquid residue.

In other words, the vapor pressure of liquid ethane (b.p.—93°) is so small at the temperature of liquid air that none could be detected in the distillate within the experimental error of making the analysis. It was found that, when liquid air was used which had stood for some time, so that its boiling point had risen near to the boiling point of oxygen (—183°), the methane and nitrogen were removed from the original mixture more quickly than when newly made liquid air was used. This is to be expected. The residue from this first fractionation was allowed to volatilize, measured and again liquefied at the temperature of liquid air. Connection was again made to the pump and more methane removed. In other words, although the residue from the first fraction was treated in exactly the same manner as the original sample more methane was obtained.

Upon volatilizing the entire residue, however, and again liquefying, a rearrangement of the solution occurred and chance for faster evaporation of this last methane portion was afforded. In no case could the last minute traces be obtained, so the attempts at complete recovery were stopped when it was found that only such a small proportion was being left behind as did not sensibly affect the results.

TABLE I.—ANALYSIS OF A PORTION OF THE TOTAL METHANE AND NITROGEN FRACTION.

	Cc.	Cc.
Sample taken	30.10	30.20
O_2 added	95.20	99.30
Total volume	125.30	129.50
Volume after combustion	66.30	70.10
Contraction due to combustion	59.00	59.40
Volume after CO_2 absorption	36.80	40.50
CO_2 produced by combustion	29.50	29.60
Methane from contraction[1]	29.44	29.64
Methane from CO_2[1]	29.59	29.67
	%.	%.
Methane from contraction	97.8	98.2
Methane from CO_2	98.3	98.2
Average per cent. methane	98.1	98.2

To this point, the first series of fractionations had reached a stage where the larger portion of the methane had been removed and where the first residue had been volatilized, reliquefied and pumped to obtain another

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[1] Corrected for molecular volume of carbon dioxide.

small portion of methane. The residue from the second liquefaction was treated again in the same identical manner and more methane obtained. A further identical treatment resulted in no additional recovery of methane. No indication of methane was found in the ethane portion, within the error of making the analysis.

The distillate obtained by the above scheme undoubtedly contained a trace of ethane, but it was so small that it could not be detected by analysis. The analysis of a portion of the total methane and nitrogen fraction is given in Table I, above.

Second Series of Fractionations.

The next step in the process involved the separation of the ethane from the methane-free residue. This necessitated the employment of a temperature such that practically all of the ethane could be separated from the still higher paraffins, propane, the butanes, etc. The temperature used could not be too low, else the ethane itself could not be separated, nor so high as to also remove all the propane. A natural gas condensate, obtained from a natural gas gasoline plant by subjecting natural gas (casing head gas) from an oil well to a pressure of 250 lbs. per square inch and then cooling it to ordinary temperature, proved excellent, when cooled by liquid air, for obtaining low temperatures higher than the temperature of liquid air. This condensate is known in the natural gas gasoline trade as "wild" gasoline. It contains large quantities of liquid propane and the butanes (especially the latter) as well as some of the ordinary gasoline constituents, the pentanes, hexanes, etc. Other substances tried for obtaining low temperatures, such as alcohol, ether, methyl, and ethyl chloride, etc., jellied so much at low temperatures that they could not be used satisfactorily. The mass did not remain of uniform temperature from top to bottom.

In order to obtain a temperature of —145°, for instance, the condensate was placed in a Dewar flask and stirred with a test tube into which liquid air was run until —145° was reached. Upon removal of the liquid air the condensate warmed up very slowly, about 5° to 10° per hour, thereby affording sufficient time for the withdrawal of vapors from the liquefaction bulb. In separating ethane from the methane-free residue, the latter was first cooled to a temperature of —145° and pumping was started and continued until the temperature had risen to —125°. By this process, there was obtained a distillate consisting of ethane and propane. In other words, some propane (b. p. —45°) is removed at —125° as well as the ethane (b. p. —93°). The residue was then treated twice in the same manner, the final separation of the ethane being made at a temperature of —155° to —140°. The temperature was purposely lowered to —125° the first time to obtain practically all of the ethane as well as some propane, because it was found quicker to separate the ethane from that part of the propane that came over than to attempt to pull off all of the ethane from the original residue. All the ethane was obtained, there being only small quantities of propane remaining as a residue. The analysis of a portion of the total ethane fraction is given in Table II.

TABLE II.—ANALYSIS OF A PORTION OF THE TOTAL ETHANE FRACTION.

	(1). Cc.	(2). Cc.
Sample taken	25.50	20.30
O_2 added	96.60	99.40
Total volume	122.10	119.70
Volume after combustion	58.30	69.20
Contraction due to combustion	63.80	50.50
Volume after CO_2 absorption	7.20	28.70
CO_2 produced by combustion	51.10	40.50

According to the equation $C_2H_6 + 3.5\ O_2 = 2\ CO_2 + 3\ H_2O$, the contraction should be equal to the $CO_2 \times 1.25$. In Analysis No. 1 the contraction then becomes 51.1 cc. × 1.25 = 63.87 cc. This corresponds well with the contraction actually observed, 63.80 cc. In Analysis No. 2 the contraction is equal to 40.50 cc. × 1.25 = 50.62. The contraction actually observed is 50.50 cc. In calculating the ethane from the carbon dioxide and contraction, use was made of equations that correct for the deviations of carbon dioxide and ethane from the ideal conditions,[1] as follows:

Analysis No. 1.

$0.990\ C_2H_6 + 3.5\ O_2 = 1.992\ CO_2 + 3H_2O$
cc. ethane = 0.396 × contraction = 25.26
cc. ethane = 0.497 × CO_2 = 25.39

Analysis No. 2.

$0.990\ C_2H_6 + 3.5\ O_2 = 1.994\ CO_2 + 3H_2O$
cc. ethane = 0.397 × contraction = 20.05
cc. ethane = 0.496 × CO_2 = 20.09

Third Series of Fractionations.

The final residue from the second series of fractionations then contained propane and higher paraffins.

The ethane-free residue was next liquefied and pumped at a temperature that started at —125° and ended at —110°, the object being to remove practically all of the propane (b. p. —45°) and also some of the butanes (b. p. + 1° and —10°). The residue from this operation was again treated in the same manner to obtain any propane that still remained behind. It was thought that, if a temperature was used that would permit the distillation of an appreciable quantity of butane, practically all of the pro-

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[1] Errors in gas analysis due to assuming that the molecular volumes of all gases are alike. *Technical Paper* 54, U. S. Bureau of Mines, by G. A. Burrell and F. M. Seibert.

pane should come over. The total distillate obtained in this manner was then liquefied and pumped at a temperature ranging from —135° to —120°. There resulted a distillate that consisted of propane only. In other words, propane can be separated from the butanes at a temperature below —135° and —120°.

The analysis of a portion of the total propane fraction is given in Table III.

TABLE III.—ANALYSIS OF A PORTION OF THE TOTAL PROPANE FRACTION.

	Analysis No. 1. Cc.	Analysis No. 2. Cc.
Sample taken	12.60	13.30
O_2 added	93.80	97.20
Total volume	106.40	110.50
Volume after combustion	67.60	70.00
Contraction due to combustion	38.80	40.50
Volume after CO_2 absorption	28.50	29.70
Carbon dioxide produced	39.10	40.30

According to the equation $C_3H_8 + 5\ O_2 = CO_2 + 4\ H_2O$, the contraction — CO_2 = 0.0. In Analysis No. 1 38.8 cc. — 39.1 cc. = —0.3 cc. and in Analysis No. 2 40.5 cc. — 40.3 cc. = 0.2 cc. The propane was calculated from the following corrected equation: $0.986\ C_3H_8 + 5\ O_2 = 2.991\ CO_2 + 4\ H_2O$.

Then, according to Analysis No. 1, the propane, when calculated from the contraction, is $0.329 \times 38.80 = 12.76$ cc. and, when calculated from the CO_2, is $0.329 \times 39.10 = 12.86$ cc.

According to Analysis No. 2 the propane, when calculated from the contraction, is $0.329 \times 40.50 = 13.32$ cc. and, when calculated from the CO_2, is $0.329 \times 40.3 = 13.26$ cc.

In the case of both analyses the cc. of propane as calculated from the CO_2 and the contraction agree closely.

The value 0.986 or the molecular volume of propane at 0° and 760 mm. of mercury was calculated from van der Waals' equation

$$(P + a/V_2)(V - b) = RT$$

or

$$M/d_o(1 + a)(1 - b) = R,$$

where M = molecular weight, d_o = density at 0°.

Lebeau gives for a the value 0.01727 and for b 0.003770, from which

$$M/d_o = 22.41/1.0133 = 22.116$$

$$22.116/22.412 = 0.986$$

This value, as far as the authors are aware, has never been determined experimentally as in the case of oxygen, methane, ethane, and carbon dioxide.

The same procedure was followed in the case of the propane separation as in the case of the ethane and methane separations. Distillates and residues were liquefied and pumped until no propane could be obtained.

The analysis of a portion of the final residue is given in Table IV. This should consist of butane only, providing no vapors of the liquid paraffins were present.

TABLE IV.—ANALYSIS OF A PORTION OF THE TOTAL BUTANE FRACTION.

	Cc.
Sample taken	9.30
O_2 added	100.00
Total volume	109.30
Volume after combustion	76.30
Contraction due to combustion	33.00
Volume after CO_2 absorption	39.30
CO_2 produced by combustion	37.00

From the equation $C_4H_{10} + 6.5\ O_2 = 4\ CO_2 + 5\ H_2O$, the contraction $\times\ 1.14 = CO_2$. From the above analysis, $33.0 \times 1.14 = 37.62$ cc. $37.62 - 37.00 = 0.62$ cc. difference.

The above analysis was calculated to butane only, and appears to be almost entirely this gas, but undoubtedly a very small proportion of the vapors of the liquid paraffins were contained in the mixture.

Vapor pressures obtained by means of a manometer attached to the pump furnished evidence which indicated when a separation had been accomplished. For instance, at the temperature of liquid air that had stood for some time (about —185°) the vapor pressure of the original hydrocarbon mixture was 63 mm. This vapor pressure was not the pressure of methane at that temperature; it remained near this value throughout the pumping until near the end, when it suddenly dropped to 0.0 mm. Then the pumping was stopped and the residue allowed to volatilize and again liquefied and pumping continued until no more distillate was obtained.

Three liquefactions of the residues were usually necessary for the removal of all the methane.

When the methane- and nitrogen-free residue was liquefied for the removal of the ethane, the vapor pressure of the mixture was about 2 mm. at —155° and about 4 mm. at —145°. When nearly all the ethane was removed and pressure dropped off suddenly to 0.0 mm., the pumping was stopped. The residue was again liquefied and treated in the same manner until all the ethane was removed. Three successive treatments of the residues were usually sufficient.

After the removal of the nitrogen, methane, and ethane from the mixture had been accomplished, it became necessary to separate the propane from the butanes, etc. This was accomplished at —130° to —120°. The vapor pressure at —130° was about 0.5 mm., and about 1 mm. at —125°. The pressure dropped suddenly to 0.0 mm. after nearly all the propane had been removed. The residues were then treated as previously described, until all the propane had been removed. The final residue consisted of the butanes and any vapors of the liquid hydrocarbons that were present. There follows a list of the constituents found by the foregoing method.

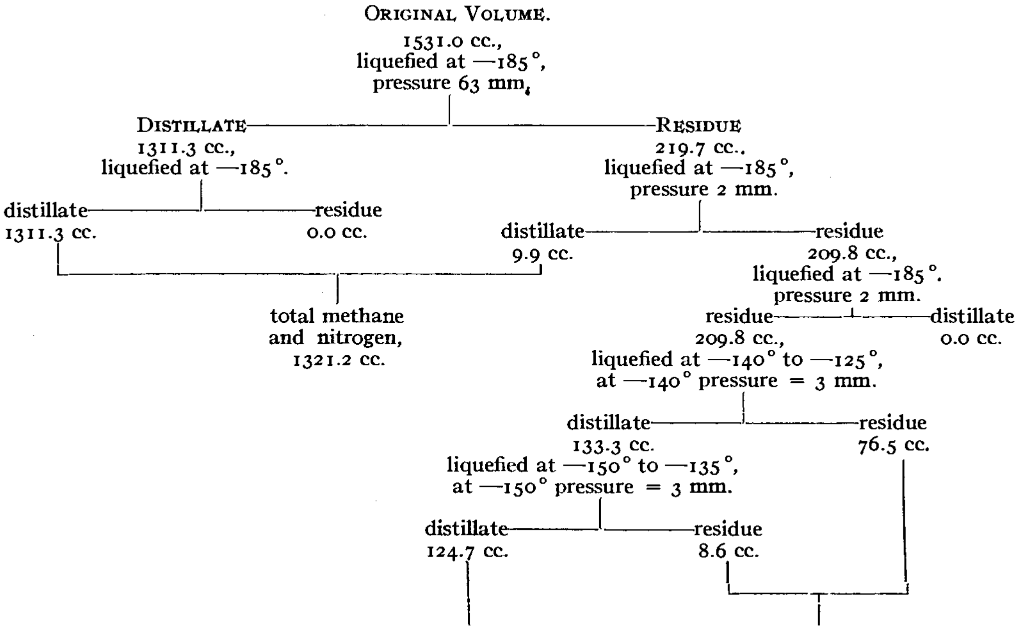
Constituents.	Cc.	Per cent.
Nitrogen	23.8	1.6
Methane	1297.4	84.7
Ethane	144.5	9.4
Propane	46.1	3.0
Chiefly Butanes	19.2	1.3
Total	1531.0	100.0

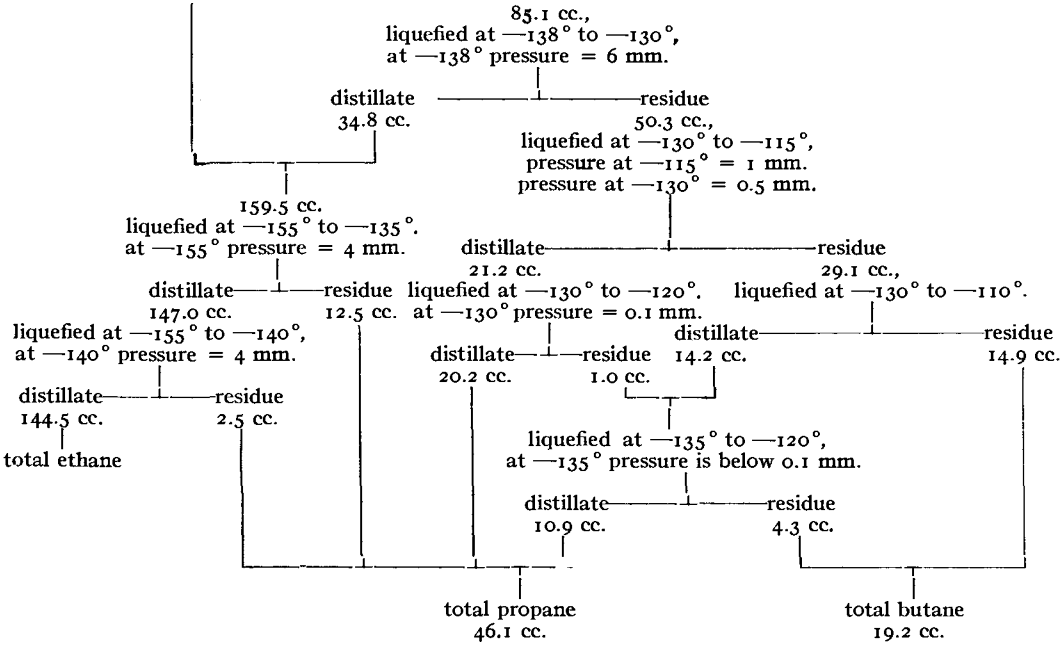
In Table V is given a diagram of the various steps in the separation of a natural gas into its constituents by means of fractional distillation at low temperatures. It will be noted that the original volume of the sample was 1531.0 cc. The sample was first liquefied with liquid air and a distillate of 1311.3 cc. obtained with the mercury pump. A residue of 219.7 cc. was left behind. Both the residue and distillate were again treated at the temperature of liquid air. From the residue there was obtained 9.9 cc. more of methane, but no residue remained behind upon treating the distillate of 1311.3 cc. The sum total of 9.9 cc. and 1311.3 cc. represented practically all of the methane and nitrogen in the natural gas sample. The distillate from the reliquefaction of the residue contained no methane, as determined by a further treatment at the temperature of liquid air.

After the methane had been separated, there remained a residue of 209.8 cc., consisting of ethane and higher paraffin hydrocarbons. This residue was cooled at temperatures ranging from —140° to —125° and as much gas removed with the pump as possible. Ethane and some propane were obtained (133.3 cc.) and a residue of 76.5 cc. remained behind. The distillate was then cooled to temperatures ranging from —150° to —135° and a distillate of 124.7 cc. obtained, and a residue of 8.6 cc. This 8.6 cc. residue was added to the 76.5 cc. residue and the total, 85.1 cc., cooled from —138° to —130° and pumped. The distillate of 34.8 cc. obtained was added to the 124.7 cc. distillate previously obtained and the total 159.5 cc. were cooled and pumped at a temperature that did not rise above —135°. There was obtained a distillate of 147.0 cc. and a residue of 12.5 cc. The 147.0 cc. distillate was then cooled and pumped at a temperature not higher than —140°. The distillate, 144.5 cc., was found to be pure ethane. The residue from this last treatment, 2.5 cc., was added to the rest of the methane- and ethane-free gas for the propane treatment. The separation of the propane and butane was carried on in a manner similar to the methane and ethane separations except for the use of lower temperatures.

Temperature measurements were made with two pentane thermometers. They agreed closely with each other and gave for the melting

TABLE V.—DIAGRAM SHOWING THE VARIOUS STEPS IN THE SEPARATION OF THE CONSTITUENTS IN NATURAL GAS BY MEANS OF FRACTIONAL DISTILLATION AT LOW TEMPERATURES.




85.1 cc.,
liquefied at —138° to —130°,
at —138° pressure = 6 mm.
distillate
34.8 cc.
residue
50.3 cc.,
liquefied at —130° to —115°,
pressure at —115° = 1 mm.
pressure at —130° = 0.5 mm.
159.5 cc.
liquefied at —155° to —135°.
at —155° pressure = 4 mm.
distillate
147.0 cc.
liquefied at —155° to —140°,
at —140° pressure = 4 mm.
residue
12.5 cc.
distillate
144.5 cc.
total ethane
residue
2.5 cc.
distillate
21.2 cc.
liquefied at —130° to —120°.
at —130° pressure = 0.1 mm.
residue
29.1 cc.,
liquefied at —130° to —110°.
distillate
20.2 cc.
residue
1.0 cc.
distillate
14.2 cc.
residue
14.9 cc.
liquefied at —135° to —120°,
at —135° pressure is below 0.1 mm.
distillate
10.9 cc.
residue
4.3 cc.
total propane
46.1 cc.
total butane
19.2 cc.

point of chloroform —62°, of carbon disulfide —111°, and boiling point of fresh liquid air —193°. The true melting point of chloroform is —63.7°, and of carbon disulfide —111.6°. All temperatures are in degrees centigrade.

Summary.

A method of separation of a natural gas into its paraffin hydrocarbons is shown. At a temperature of —185° to —190° the methane can be removed. The separation of the methane from the propane, butane, etc., is conducted at temperatures ranging from —150° to —140°. The propane is separated from the butanes, etc., at temperatures ranging from —135° to —120°.

This method of separating a gaseous mixture into its constituents while somewhat involved is the only known method in the case of some hydrocarbons. It can be extended to the separation of other gaseous mixtures. The authors have separated other natural gases but the example given herein is sufficient to describe the method.

[From the Chemical Laboratory of the Hospital of the Rockefeller Institute for Medical Research.]

DETERMINATION OF ARSENIC IN ORGANIC MATTER.

By Mariam Vinograd.

Received April 22, 1914.

Oxidation of the Tissue for the Determination of Arsenic.—The use of minimum quantities of reagents in oxidizing tissues for the Marsh test is important, because it is very difficult to get certain reagents, such as nitric acid, absolutely free from arsenic. Another important consideration is the prevention of the escape of the arsenic at the moment of carbonization of the tissue, since, as is well known, arsenic is volatile at the temperature of the oxidation. Both of these difficulties were avoided by Bertrand[1], who showed that dried substance could be conveniently burned in a Bertholet bomb with pure oxygen under 25 to 30 atmospheres pressure. The only disadvantage of Bertrand's method for general use is that analytical laboratories are not ordinarily equipped with the Berthelot apparatus.

Because of this fact, apparently, investigators have continued experimenting with methods of oxidation which could be carried out with the facilities usually available.

Chittenden and Donaldson, in 1880, published a paper describing in detail a simple method for partial oxidation of tissue with relatively small amounts of nitric and sulfuric acids, the carbonaceous residue being extracted with water and used for the Marsh test.[2] This method added

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[1] Bertrand, *Ann. de l'Inst. Pasteur,* 1903, 581.

[2] *Am. Chem. J.,* 2, 255.