

THE JOURNAL  
OF THE  
American Chemical Society

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY  
OF KANSAS].

**THE OCCURRENCE OF HELIUM IN NATURAL GAS AND THE  
COMPOSITION OF NATURAL GAS.**

BY HAMILTON P. CADY AND DAVID F. MCFARLAND.

Received September 10, 1907.

**Historical.**

During the year 1903, a gas well drilled at Dexter, in Cowley County, Kansas, gave a strong flow of gas, which was found very difficult to burn. A sample was sent to the University of Kansas for analysis, and was found to contain only a small proportion of combustible constituents and a very large proportion of incombustible residue, such as is usually reported in gas analyses as nitrogen. The results of the analysis were published in a paper by Haworth and McFarland,<sup>1</sup> and by McFarland.<sup>2</sup> When the nitrogenous residue, mixed with oxygen, was subjected to the action of an electric spark over a strong solution of potassium hydroxide, for a very long time, there was left a residue which refused to combine with the oxygen, and was evidently not nitrogen. This suggested the presence of some of the inert gases of the Argon group.

Further investigation of the Dexter gas by the methods described in this paper, has shown the presence of considerable quantities of helium, and in a paper read for us by Prof. E. H. S. Bailey, at the New Orleans meeting of the American Chemical Society, we reported 1.84 per cent. helium. Since that time the investigation has been extended to many other Kansas natural gases, and also to gases from other fields, and in nearly every case helium has been found.

Moreover, a method has been worked out by which the percentage of helium may be readily determined, and this has been done in the case of all the gases examined.

<sup>1</sup> Science, 21, 191.

<sup>2</sup> Proc. Kans. Acad. Sci., 19, 60.

Along with the determination of helium, an extended analysis of each gas has been made to determine its other more common constituents. In all, over forty gases from the Kansas field and from other fields at widely separated parts of the country, have been worked with and complete results are now available from most of these. It is our purpose, in this paper, to present these results with a description of the methods employed in obtaining them and some general facts brought out by their consideration.

*Collection of Gases.*—Much of the work of collecting the samples of gas for analysis was done by members of the University Geological Survey, and the cost of collection was in most cases borne by the Survey.

Several strong steel and tin cylinders of a variety of shapes and sizes were adapted to the needs of the work. Stop-cocks were put at each end of the cylinder, fitted with caps to prevent leakage. The tin cylinders were shipped in galvanized iron carrying cases, which protected them from injury. At the gas well both ends of the cylinder were opened and one end attached by a secure connection to the source of gas. The gas was then allowed to flow through the cylinder, at a considerable pressure if possible, for several minutes to insure the complete driving out of all air. This was found to be quite effective when properly carried out. Then the stop-cock at the end of the cylinder opposite to that at which the gas was entering was closed tightly and the gas was allowed to accumulate in the cylinder. In the tin cylinders a pressure of fifty pounds was often carried, while in the steel cylinders the entire well pressure of several hundred pounds could be reached. When this maximum pressure had been attained the cylinder was tightly closed and shipped to the laboratory.

When received at the laboratory, enough gas was taken from the cylinder to fill a large glass gasometer in which the gas was confined over distilled water. This constituted the portion for the extraction of helium. At the same time a small flask was filled with gas for the analysis. The determination of helium and the complete analysis were carried out immediately whenever possible, and if any delay was necessitated, it was made as short as possible, and precautions were taken to avoid contamination of the sample or absorption of carbon dioxide.

*Methods of Analysis.*—For the determination of the constituents of the gas other than the rare elements of the argon group, the standard methods of Hempel were used. In a one hundred cubic centimeter portion of the gas, the determinations were made in the following order. Oxygen was absorbed in a phosphorus pipette; carbon dioxide in strong potassium hydroxide solution, ethylene and the olefines in fuming sulphuric acid, followed by potassium hydroxide, and finally, carbon monoxide in ammoniacal cuprous chloride.

After the determination of carbon monoxide, a portion of the residue, usually about 20 cc., was measured off, mixed with pure oxygen and air in such a manner as to give a proper excess of oxygen, and exploded over mercury. The contraction in volume, and the amount of carbon dioxide produced were determined in the usual manner, taking precautions to avoid, as much as possible, the error introduced by the absorption of carbon dioxide in the water produced by the explosion, which error may be considerable if haste is not used in the measurement of the volume after explosion. The residual oxygen was then determined by means of the phosphorus pipette in order to show both its amount and also that of the residual nitrogen. Frequent readings of barometer and thermometer, enabled corrections to be made for changes in temperature and pressure.

From the explosion data, the quantities of methane and ethane were calculated, assuming that these were the only paraffin hydrocarbons present; an assumption which is not entirely warranted because of the fact that it was found possible to condense higher boiling hydrocarbons along with the methane in a bulb surrounded by liquid air. Some of these remained liquid up to ordinary temperatures and had an odor similar to that of light boiling petroleum distillates. The quantity of this residue varied in the different gases. It has seemed practically impossible to get at the amounts of these substances by explosion methods, and for the present the above assumption will be made. It seems probable, however, that they may be determined by the fractional distillation of the liquefied gas, and work along this line is being carried on in this laboratory.

For the determination of hydrogen, a portion of the residue from the absorption of carbon monoxide was used. It was found that the data from explosions were entirely too unreliable for the calculation of hydrogen, and the combustion of the hydrogen, mixed with air, over palladinized asbestos, was adopted. In order to insure the combustion of only the hydrogen on heating to a constant temperature of  $100^{\circ}$ , the U-tube containing palladinized asbestos was surrounded by a Dewar vacuum jacketed tube containing water which was kept at the boiling point by a platinum coil, heated by the passage of an electric current. Several determinations of hydrogen in mixtures of known composition proved the efficiency of this arrangement. With the electrical heating device, a constant temperature could be maintained, while the vacuum jacket around the bath prevented effectually the heating of the apparatus outside the U-tube.

*Determination of Helium.*—For the determination of helium, use was made of the property of cocoanut charcoal of absorbing all gases except helium, neon and hydrogen, when cooled with liquid air. This prop-

erty was discovered by Dewar<sup>1</sup>. It is our experience that hydrogen is rather freely absorbed, neon much less than hydrogen, and helium so slightly that all but an infinitesimal trace can be removed by pumping with a mercury pump.

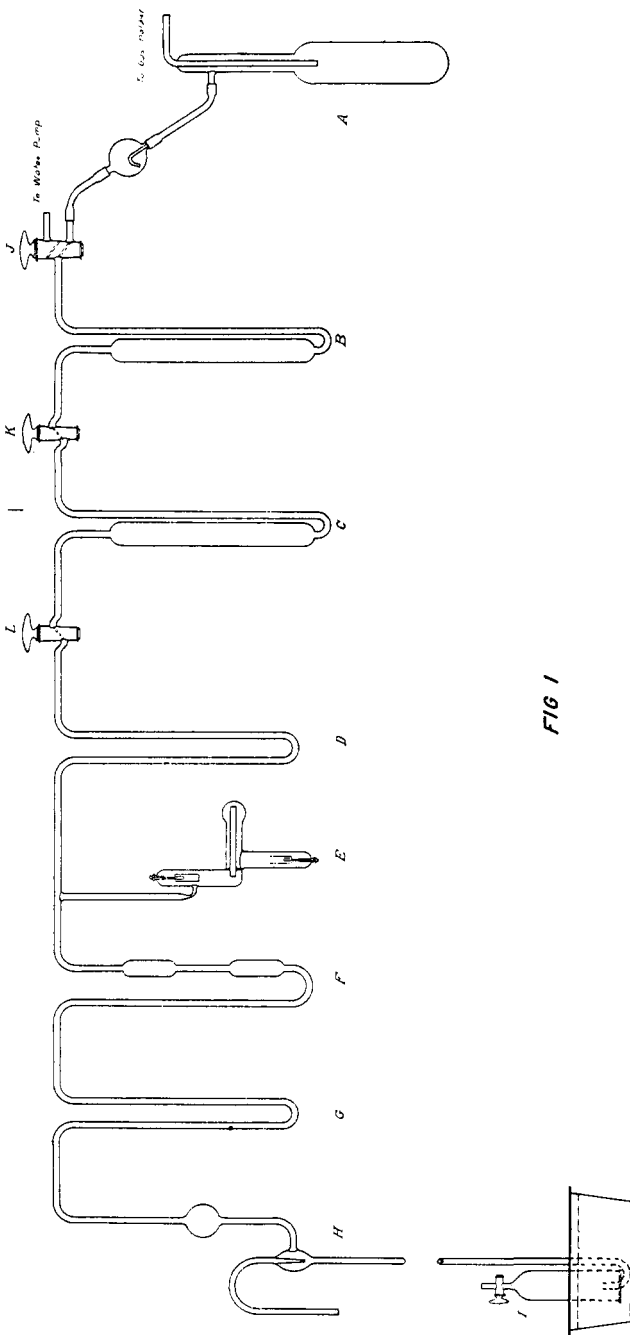
*Apparatus.*—The apparatus used is shown diagrammatically in Fig. 1. (A) is a condensing bulb, in which, when surrounded by liquid air, the greater part of the methane and other hydrocarbons contained in the natural gas can be liquefied. (B) and (C) are bulbs containing 20 grams of cocoanut charcoal each. (D) and (G) are U-shaped glass tubes which when immersed in liquid air, hold back water and mercury vapors. This is by far the simplest and most effective method of preventing the diffusion of mercury vapor into the spectral tubes used. The actual apparatus is so constructed that D and G may both be immersed in the same vacuum tube. (H) is an automatic Sprengel air pump, the mercury being returned to the reservoir in the form of small drops by the suction of a Chapman pump. (I) is the receiver for collecting helium, (F) and (E) are Plücker tubes. (F) is a permanent part of the apparatus; (E) is filled with the gas and sealed off for later examination with a large spectrometer.

To prepare the apparatus for an analysis, a good water pump was connected to the charcoal bulbs at (J), and dry air drawn through the apparatus to remove all gases left from the previous analysis. The connection with the outer air was then cut off and the whole exhausted as thoroughly as possible with the water pump, heating the charcoal bulbs strongly at the same time. When exhaustion had been carried to the limit of the water pump, the Sprengel pump was put into operation, and the pumping continued until practically all the air had been removed. The charcoal bulbs were allowed to cool and then immersed in liquid air. The vacuum quickly became so good that a spark would not pass through the Plücker tubes. The apparatus was then ready for use.

*Method of Analysis.*—The gas for analysis was taken from the gasometer containing it and the amount used was determined from the weight of water which displaced it, making all necessary corrections for temperature and pressure. The bulb (A) was first filled with water, inverted, and the water displaced by the gas. It was then surrounded with liquid air and put into connection with the gas holder. If the gas did not contain more than 50 per cent. of nitrogen, from 12 to 15 liters would quickly pass into the bulb. A large amount of nitrogen seems to dissolve in the liquid methane. When the desired amount of gas had passed into (A) the connection with the gas holder was closed and after standing for several minutes the stop-cock leading into (B) was opened for a moment, that between (B) and (C) being closed. The gas was held in B for five

<sup>1</sup> Chem. News, 90 (1904).

HELIUM IN NATURAL GAS



minutes to allow the absorption of everything except the helium. Stop-cock L being closed, the gas was passed into C and allowed to stay there another five minutes, and finally admitted to the Plücker tubes and pump. Here it was examined with the spectroscope, removed by means of the pump, and collected in I. When the pressure in the system became low, stop-cock K was closed and more gas admitted into B from A, allowed to stand, passed into C, and finally after standing there the required time, the connection to the pump was again opened. This entire series of operations was repeated until no more helium could be obtained. It has been repeatedly proven by our experience that practically all the helium may be removed by this process. Towards the end of the operation when the pressure in the entire system was low, the liquid methane solution in A could be made to boil even when surrounded by liquid air, and this insured the removal of all the helium from the bulb. It might be mentioned in passing, that the freezing point of the methane was lowered by the nitrogen, etc., so that only part of it solidified in A.

With care all the helium could be transferred to the charcoal bulb without permitting so much nitrogen to pass over as to saturate the charcoal. The purity of the gas could be insured by watching the spectrum and if there was any suspicion of nitrogen the apparatus was prepared as for a new analysis and the gas run through again. The operation was tedious but not more so than most gravimetric determinations.

By essentially the same method, but using larger charcoal bulbs, considerable quantities of helium have been obtained, and a still larger apparatus is being constructed.

That the gas obtained in these experiments is helium, is proven by the fact that all of the visible lines of helium catalogued have been observed, the wave-lengths agreeing within the limits of error, with the accepted values. This is also established by direct comparison of the spectra with those given by known specimens of helium.

The spectrometer in use for the examination of the gases is a new Pulfrich auto-collimating instrument made by Zeiss. It is very powerful and quite satisfactory. Readings can be taken rapidly and the duplicates agree closely.

The new form of end-on tubes made by Goetze, (See E, Fig. 1) when filled with gases of the argon group give beautifully sharp spectra.

The helium obtained as above practically always shows hydrogen lines and carbon bands, the latter, most likely, from a trace of carbon monoxide, but these two impurities are present in such small quantities that the contraction produced on exploding a mixture of the helium with pure oxygen and electrolytic gas, is too small to measure. During the analysis of the gas, no neon was detected, but later, during the preparation of larger quantities of helium from one of the gases, neon was found, as

will be described in a following paper. The quantity was not determined, but it is certainly small compared to that of helium in the same gas.

*Analytical Results.*—The results of the analyses are given in the following table (Table 1). The analyses are arranged in the order of the quantity of helium contained in the gases. A statement of such data as were obtainable regarding the location, depth and pressure of the wells producing the gases, as well as other matter of interest regarding their occurrence, is appended to the table.

#### Data Concerning Collection of Gases Analyzed.

1. Dexter, Kansas. Original sample. Collected in 1905 from well supplying town. Depth 310 feet. Pressure, 110 lbs. Capacity, 6 million feet.
2. Gas from Kansas Natural Gas Co. pipe-line at Lawrence, Kansas. Comes from near Chanute, Kansas. Composite from several wells. Sample taken Oct. 23, 1905, about one week after gas was first turned on.
3. Pipe Line Gas. Same general source as No. 2. Sample taken at Lawrence, May 16, 1906.
4. Eudora, Kansas. Collected from town mains. Comes from wells in town, 350 feet deep. Pressure, 200 lbs.
6. Dexter, Kansas. Greenwell well. Depth and pressure similar to No. 1. Collected June 12, 1906.
7. Iola, Kansas. City supply. Collected from mains at office of Iola Gas Co. June 10, 1906.
8. Moline, Kansas. Collected June 24, 1906. From wells south, east and west of Moline. Average depth, 1150 feet. Av. pressure, 380 lbs.
9. Fredona, Kansas. Town supply. Wells from 2 to 7 miles, east, south and northwest of town. Depth from 1085 to 1250 feet. Pressure from 300 to 480 lbs.
10. Neodeshia, Kansas. Collected June 27, 1906. Some air in the sample.
11. Lawrence, Kansas. From an old well, about 1200 feet deep. Only slight flow of gas. Collected July 4, 1906.
12. Erie, Kansas. City supply. From wells north and east of town, within two miles. Depth, 510 feet. Pressure 150 lbs. Sample collected July 3, 1906.
14. Bartlesville, Ind. Ter. Received July 8, 1906. Air in the sample.
15. Bonner Springs, Kansas. Collected July 8, 1906. From wells averaging 600 feet in depth, and 190 lbs. pressure belonging to The Bonner Portland Cement Co.
16. Parsons, Kansas. Gas supplied by pipe-line to city of Parsons. Comes from wells in Eson district in southeastern part of Wilson Co., Kan., belonging to the Prairie Oil and Gas Co.

TABLE 1.—COMPOSITION OF NATURAL GASES.  
Analyses Arranged in Order of Magnitude of Helium Content. Kansas Gas.  
(Including Adjacent Missouri and Oklahoma Gases).

No.	Locality	Oxy- gen O <sub>2</sub>	Car- bon Diox- ide CO <sub>2</sub>	Olef- ines C <sub>2</sub> H <sub>4</sub> etc.	Car- bon Mon- oxide CO	Meth- ane CH <sub>4</sub>	Eth- ane C <sub>2</sub> H <sub>6</sub>	Hydro- gen H <sub>2</sub>	Hel- ium He	Nitro- gen N <sub>2</sub>
1	Dexter	0.20	0.00	....	0.00	14.85	0.41	trace	1.84	82.70
6	Dexter (Green- well well)	0.10	0.00	0.00	0.00	14.33	1.06	trace	1.64	82.87
41	Eureka new field	0.10	0.20	0.00	0.00	51.80	0.00	0.00	1.50	46.40
42	Eureka town supply	0.50	0.20	0.00	0.00	51.40	0.00	0.00	1.50	46.40
9	Fredonia	trace	0.61	0.12	0.00	82.25	0.00	0.00	0.616	16.40
40	Elmdale	0.30	0.15	0.55	0.00	78.60	7.71	0.00	0.56	12.13
8	Moline	0.00	0.54	....	0.00	74.10	0.00	trace	0.51	24.85
36	Burlington	0.00	0.00	0.20	0.00	85.50	3.20	0.00	0.495	10.60
27	New Albany	0.00	0.20	0.25	0.00	89.10	0.00	0.12	0.49	9.84
11	Lawrence Deep Well	trace	0.92	0.00	0.00	81.40	0.00	0.00	0.46	17.22
34	Olathe	trace	0.00	0.10	0.00	84.40	0.00	0.00	0.40	15.10
33	Garnett	trace	0.20	0.16	0.00	94.30	0.36	0.00	0.37	4.61
4	Eudora	0.31	0.62	0.00	0.00	88.60	0.00	0.00	0.27	10.20
16	Parsons (Wilson Co.)	trace	0.72	0.00	0.00	91.90	3.37	0.00	0.27	3.74
31	Buffalo	trace	0.00	0.00	0.11	96.20	0.78	0.18	0.27	2.46
28	Altoona	0.00	0.92	0.00	0.00	92.00	2.85	0.00	0.263	3.97
37	Augusta	0.00	0.00	0.77	0.00	79.10	7.44	0.00	0.25	12.44
25	Chanute	0.10	0.00	0.00	0.00	94.70	0.00	0.00	0.24	4.96
20	Moran	0.20	0.30	0.35	0.20	92.00	0.00	0.39	0.214	6.35
23	Peru	0.10	0.51	0.51	0.00	81.70	7.60	0.00	0.19	9.39
7	Iola	0.23	0.00	0.00	0.00	94.50	0.00	trace	0.183	5.08
3	Lawrence Pipe Line Kans. Nat. May 16, '06	trace	0.20	....	0.00	98.06	0.00	trace	0.17	1.57
2	Pipe Line Oct. 23, '05	0.12	0.00	....	0.00	98.00	0.00	0.00	....	1.88
45	Pipe Line Dec. 12, '06	0.24	1.94	0.00	0.00	94.30	0.75	0.00	0.17	2.60
17	Arkansas City	0.20	0.10	0.10	0.00	81.10	11.95	0.00	0.159	6.39
32	Blackwell, Okla.	0.00	0.00	0.61	0.00	83.40	10.31	0.33	0.16	5.19
26	Humbolt	0.10	0.00	0.81	0.00	94.00	1.97	0.00	0.14	2.98
21	Iola	0.40	0.70	0.00	0.30	91.50	0.00	0.00	0.132	6.97
12	Erie	0.22	0.33	0.30	0.00	90.30	4.26	0.00	0.13	4.45
10	Neodesha	No complete analyses								0.106
15	Bonner Springs	0.10	0.00	0.00	0.00	97.18	0.00	0.25	0.104	2.36
18	Altamont Pipe Line Liberty and Coffeyville	0.00	0.92	0.61	0.00	95.70	0.00	0.00	0.080	2.69
22	Cuney	0.15	0.81	0.10	0.00	92.40	0.00	0.00	0.08	6.46
44	Sheffield, Mo.	0.20	0.83	0.50	0.10	92.90	0.00	0.00	0.041	5.43
43	Kansas City, Mo. 2416 Tracy Ave.	0.10	0.60	1.20	0.20	87.20	7.03	0.00	0.013	3.65
35	Paola	0.40	0.70	0.00	0.00	98.00	0.00	0.00	0.0093	0.88
14	Bartlesville, Ind. Ter.	No complete analysis.								He present but not det.
<i>Gases from Other Fields.</i>										
24	Butler, Ohio	0.05	0.00	0.40	0.00	70.00	16.75	0.27	0.15	12.38
38	Marion, Ind.	0.00	0.73	0.86	0.00	77.40	14.18	0.00	0.167	6.66
39	Morgantown, West Va.	0.00	0.24	0.65	0.00	88.10	7.37	0.25	0.09	3.60
46	Jennings, La. Some air in sample	1.81	1.80	0.80	0.40	88.40	1.03	....	trace	5.76
47	Los Angeles, Cal. Some air in sample	2.86	6.68	0.20	0.25	83.70	0.00	....	0.00	6.31



17. Arkansas City, Kansas. City supply. From well 750 feet deep, with pressure of 355 lbs. and capacity of 5-6 million feet.

18. Altamont. Gas collected from Kansas Natural Gas Company's pipe-line supplying Joplin district. Comes from near Liberty and Coffeyville in Montgomery Co. Coffeyville wells are about 950 feet deep and have a pressure of 450 lbs. Sample is a composite, representing the district.

20. Moran, Kansas. Collected July 13, 1906. No data.

21. Iola, Kansas. City supply. A composite sample from several wells. Collected July 13, 1906. from mains at city gas office.

22. Caney, Kansas. From a well two miles east of Caney. Pressure, 620 lbs. Depth is 1550 feet. Belongs to Caney Gas and Mining Co. Collected July 14, 1906.

24. Butler, Ohio. Richland Co. Collected July 19, 1906, from well belonging to Frank O. Levering. Well pressure is 1200 lbs.

23. Peru, Kansas. Collected July 20, 1906. No data.

25. Chanute, Kansas. City supply. From wells east of city. Composite sample. Depth, 850 feet. Pressure averages 200 lbs. Collected July 24, 1906.

26. Humboldt, Kansas. Composite sample from low pressure mains of city supply. Collected July 23, 1906.

27. New Albany, Kansas. Received July 25, 1906. No data.

28. Altoona. Received July 25, 1906. No data.

31. Buffalo, Kansas. Sample from well inside of town. Collected July 28, 1906.

32. Blackwell, Okla. Received from J. W. Beatty, July 31, 1906. Taken from well No. 2, of Union Gas and Oil Co. Depth 640 feet. Pressure, 185 lbs. Capacity is one million feet.

33. Garnet, Kansas. Sample collected Aug. 1, 1906, from mains bringing in town supply from wells east of town. Av. depth, 600 feet. Av. pressure, 200 lbs.

34. Olathe, Kansas. Sample from city supply. Aug. 2, 1906. Comes from Spring Hill, Kansas (ten miles south of Olathe). Av. depth is 580 feet. Pressure, 184 pounds.

35. Paola, Kansas. City supply. No data. Received Aug. 3, 1906.

36. Burlington, Kansas. Collected Aug. 4, 1906, from high pressure supply pipe bringing in gas for city supply from wells several miles south.

37. Augusta, Kansas. Sample received Aug. 4, 1906. City supply from wells averaging 1440 feet in depth with producing strata at 1200, 1325 and 1420 feet. Av. pressure about 650 lbs.

38. Marion, Indiana. Sample collected by B. A. Kinney, State Supervisor of Natural Gas for Indiana. Received Aug. 25, 1906.

39. Morgantown, West Virginia. Collected by B. H. Hite, of West Va. Agricult. Exp. Sta., under direction of Dr. I. D. White, State Geologist. From Bowlby well No. 1, 10 miles west of Morgantown. Depth 1800 feet. Pressure, 160 lbs. Collected Aug. 18, 1906.

40. Elmdale, Kansas. Collected Oct. 6, 1906. Wells 150 to 154 feet deep. Pressure, 45 lbs. Capacity nearly one million feet.

41. Eureka, Kansas. City supply. Received Oct. 25, 1906. No data.

42. Eureka, Kansas. City supply. Received Oct. 25, 1906. No data.

43. Kansas City, Mo. No. 2416 Tracy Ave. Well about 300 feet deep. Very low pressure. Yields only gas enough to light one house.

44. Sheffield, Missouri. Composite sample from several shallow wells at the Sheffield Nut and Bolt Works. Initial pressure about 40 lbs. Aggregate production about 1600 cubic feet per day. Used to run gas engine.

45. Pipe Line Gas. Collected from mains of Kansas Natural Gas Co. at Lawrence, Kansas, Dec. 12, 1906. Composite sample coming from various wells, mostly in Allen and Neosho Co.

46. Jennings, Louisiana. Collected by L. Reinecke, Asst. Geologist on La. Geol. Survey, from gas-producing oil well. Received February, 1907. A little air in sample.

47. Los Angeles, Cal. Collected from gas-producing oil well by Chas. R. Fletcher, 534 Stimson Building, Los Angeles. Sample had some air in it.

#### Discussion of Results.

An inspection of the above table shows that in all cases save one, the Los Angeles gas, helium was found, and it seems very probable that it might have been found in this also if a sufficiently large quantity of gas were taken for analysis. It will be noticed that gas was examined not only from the Kansas field and the adjoining Oklahoma and Missouri fields which are really continuations of the former, but also representative samples from five other gas fields at rather widely separated positions in the country; from West Virginia, Ohio, Indiana, Louisiana, and California.

Since our work has been more particularly with the gases of Kansas we may discuss these at length.

It is at once seen that the composition of these gases varies widely, frequently in places which are but a few miles apart. A case of this kind is found in the gases from Arkansas City and from Dexter, towns only about 20 miles apart, (See Table No. 1). The same phenomenon has been noticed with the oils of Kansas; oil from one side of a town is sometimes of very different composition and properties from that on the other

side. This is said to be due to the fact that the porous sandstone which carries the oil and gas is not laid down in continuous layers, but in lenticular masses of irregular size and distribution.

In general, the helium content increases with the nitrogen, although a direct proportionality does not appear to exist. Of course the percentage of both decreases as the percentage of total paraffin hydrocarbons increases, although the ratio of helium to nitrogen may increase.

While there is such a wide variation in the composition of the different gases, there is a marked tendency toward regularity in percentage of helium and of total paraffin hydrocarbons, along lines running across the state from northeast to southwest, as may be seen from the two accompanying maps. Figure 2 shows these lines of nearly equal helium con-

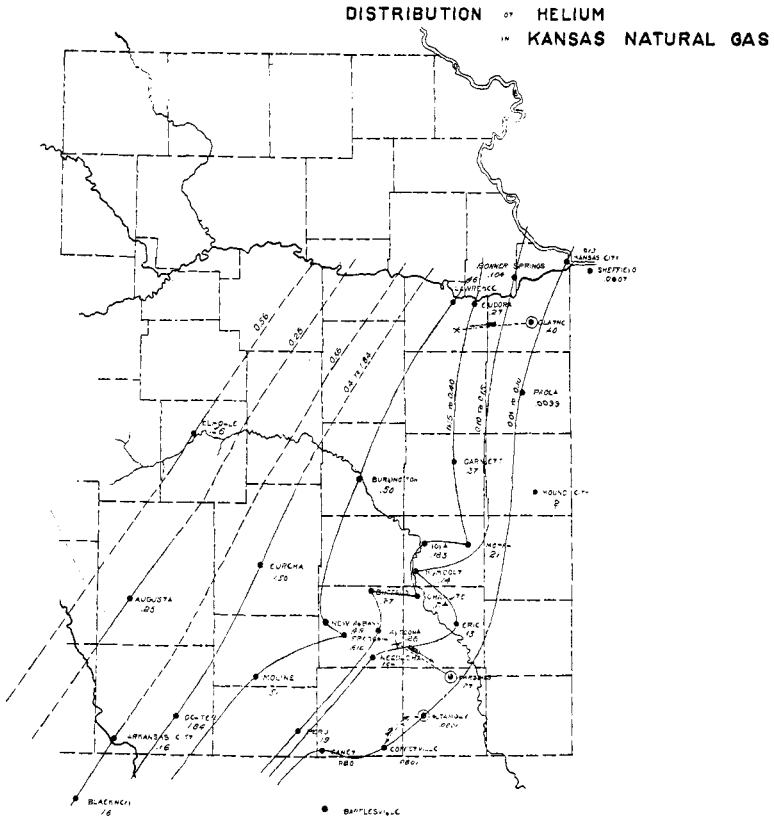


FIGURE 2

tent and Figure 3 shows the lines of nearly equal paraffin content. These lines, which may be called iso-helium and iso-paraffin lines are suggestively similar to the lines showing the outcrop of the various geological



The fact that our analyses have shown helium in all but one of the gases examined from various parts of the United States, together with numerous reports of helium having been found in the gases from mineral waters<sup>1</sup> lead us to believe that helium may be found in greater or less quantities in all gases issuing from the earth, and that like many other so-called rare elements, it is really of very wide distribution.

Since Ramsey and Soddy's demonstration of the transformation of radium emanation into helium<sup>2</sup> and Strutt's work<sup>3</sup> showing the very wide distribution of minute percentages of radium in various rocks and soils, it would, of course, occur to everyone that perhaps the helium in natural gases came from the transformation of the emanation derived from the radium. While the percentage of radium is exceedingly small, the aggregate amount is sufficient, granting the transformation, to account for all the helium, provided that sufficient time is given.

If the helium comes from the radium, the percentage of helium in the gas should be proportional to the age of the gas, the radium content of the contributing strata, and inversely proportional to the total quantity of gas. Of course, many other factors would enter into the consideration of this question, such as the rate of diffusion of helium and the accompanying gases, and the fact that the age of the gas cannot always be judged by the age of the strata in which it is found, its position being largely determined by the presence of a sufficiently porous stratum in which it could be stored, and of a difficultly penetrable cap over this stratum.

All of these things make it very difficult to test this hypothesis quantitatively, and at present we wish only to state our belief in its possibility.

#### Conclusions.

In this paper the results of the examination of 41 samples of natural gas from several widely separated parts of the country are given.

These lead to the following conclusions:

First—That helium is present in all cases except possibly one. It is inferred from this that it is present in all or nearly all of the gases issuing from the earth.

<sup>1</sup> Rayleigh, *Chem. News*, 72, 223 (1895); 73, 247 (1896); *Zentralblatt*, 1895, [2] 1112; 1896, [2] 147. H. Kayser, *Chem. News*, 72, 89 (1895); *Chem.-Ztg.*, 19, 1549 (1905). Bouchard and Troost, *Compt. rend.*, 121, 392 (1895); *Zentralblatt*, 1895, [2] 710. Moureu, *Compt. rend.*, 121, 819 (1895); 135, 1335 (1902). F. Pesendorfer, *Chem.-Ztg.*, 29, 359 (1905). R. Nasini, *Atti accad. Lincei* (5) 13, 1, 217, 367 (1904); *Zentralblatt*, 1904, [1] 1190; [2] 77. Prytz and Thorkelsson, *Kgl. Danske Videnski Selsk Forh.* 1905, 317; *Zentralblatt*, 1905, [2] 1570. Ewers, *Physik. Z.*, 7, 224 (1906); *Zentralblatt*, 1906, [1] 1319. Moureu and Biquard, *Compt. rend.*, 143, 795 (1906); *Zentralblatt*, 1907, [1] 500. Moureu, *Compt. rend.*, 142, 1155 (1906); *Zentralblatt*, 1906, [2] 156.

<sup>2</sup> *Pr. Roy. Soc. London*, 72, 204 (1903); 73, 346 (1904).

<sup>3</sup> *Chem. News*, 93, 235 (1906).

Second—The helium content of the gas tends to increase as the nitrogen increases, though no direct relation is observed.

Third—In Kansas, lines of iso-helium and iso-paraffin content can be traced across the state and these follow approximately the lines of outcrop of the various geological strata.

Fourth—A very wide variation in composition is noted in the gases examined; hydrocarbons varying from 15.00 per cent. to 98.00 per cent., and helium from a trace up to 1.84 per cent.

LAWRENCE, KANSAS.  
August 25, 1907.

---

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 145.]

## THE IGNITION TEMPERATURES OF GASEOUS MIXTURES.

SECOND PAPER.

BY K. GEORGE FALK.

Received July 20, 1907.

### Introduction.

In a paper published about a year ago<sup>1</sup> a new method was described for determining the ignition temperatures of gaseous mixtures and the results obtained for mixtures of hydrogen and oxygen were given in detail. The ignition temperature was defined as the temperature at which a gaseous mass would ignite if left entirely to itself for some time, the catalytic action of the walls of the vessel in which the gas was enclosed being eliminated. The new method for determining these temperatures consisted of instantaneously compressing the mixtures enclosed in a suitable vessel. This compression raises the temperature of the gas, and, if carried out with sufficient rapidity, is adiabatic, no heat being lost by radiation or conduction. The rise in temperature of the mixture may then be calculated from the initial and final volumes of the gas, its initial temperature, and the ratio of the specific heats of the gas at constant pressure and constant volume. In compressing the mixtures, as soon as the temperature of ignition is reached there is a sudden reaction (explosion), enough force being developed by the reaction to make the determination of the final volume of the mixture a comparatively simple matter as was shown in the first paper.

In the present paper, the results obtained by this method for mixtures made up of carbon monoxide and oxygen; hydrogen, oxygen and nitrogen; carbon monoxide, oxygen and nitrogen; and carbon monoxide, oxygen and hydrogen are given, and the results obtained before for mixtures of hydrogen and oxygen confirmed. In the results given for mixtures of hydrogen and oxygen in the first paper a small correction was overlooked, but this has been introduced here and will be discussed later.

<sup>1</sup> This Journal, 28, 1517.