detection of synthetic coloring matters (*U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin* 107, page 136) and none were found that gave any color to the wool from the second bath. It was found preferable, however, to thoroughly wash the wool with a strong soap solution, when taken from the first bath, in order to remove all oil and resin. Samples colored with the ordinary oil-soluble synthetic dyes were readily detected by this test.

The results of the examinations made are tabulated below. It will be noted that paprika produced from the shells alone contains not to exceed 7.50 per cent. of ash, and not to exceed 8.00 per cent. total ether extract, having an iodine number of not less than 127, while paprika made from the whole pods contains not to exceed 7.50 per cent. ash, and not to exceed 13.00 per cent. of total ether extract, having an iodine number of not less than 130.

PERCENTAGE OF SHELL, SEEDS AND STEMS IN WHOLE PODS.

Lab No.	Variety.	Shell.	Seeds and placentae.	Stems.
20......	Hungarian	64.2	26.4	9.4
28......	Hungarian	64.3	27.4	8.3
41......	Hungarian	56.6	40.4	3.0
33......	Spanish	55.0	36.2	8.8

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THE NATURE OF THE VOLATILE MATTER OF COAL AS EVOLVED UNDER DIFFERENT CONDITIONS.[1]

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The experiments described below have been a part of the fuel investigations conducted during the year 1907–1908 by the Technologic Branch, U. S. Geological Survey. The investigation is still in progress along the same and similar lines.

It is a familiar fact to retort coke oven and gas works operators that the volatile products of coal are largely affected both in quantity and character by the conditions of temperature and rapidity of the rise of temperature in the coal, and by the conditions to which the products are subjected after leaving the coal. The laboratory determination of volatile matter serves almost universally as a more or less valuable indication of the coal's adaptability to industrial uses either for combustion, destructive distillation or gasification. The method for this determination is, however, an arbitrary one and does not duplicate closely that of any industrial operation, nor is the character of the volatile matter produced by the laboratory method known with any degree of certainty.

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[1] Presented with the permission of the Director, U. S. Geological Survey.

Furthermore, the results by the laboratory method are very sensitive to varying conditions and the influence of such variation on the character of the volatile products has not heretofore been the subject of extended study.

The importance of the rôle played by the volatile matter in all industrial applications of fuel is generally recognized. There are more heat units in the volatile matter in proportion to its weight than in the fixed residue. Pittsburg coal of 30.0 per cent. volatile matter and 7.0 per cent. ash has 36.0 per cent. of its heat value in its volatile matter, as shown by comparing the heat values of coal and coke. When coal is fired under a boiler either by hand or mechanically, it first undergoes a process of distillation, and both the quantity and quality of the volatile products and the relative ease of their liberation are concerned very largely in the boiler efficiency and the production of smoke.[1] It is reasonable to suppose that coals of different origin may yield volatile gases carrying different percentages of tarry vapors and heavy hydrocarbons and may on that account differ in smoke-producing tendencies. A knowledge of the chemical reasons why coals smoke in varying degree, and why high-volatile coals are hard to burn with maximum efficiency is a necessary preliminary to the taking of intelligent steps toward improvement in these respects.

The gas producer for bituminous and low-grade fuels is coming more and more into favor. Here also the volatile matter in the fuel plays a very important rôle, since at the top of the fuel bed a process of distillation is continually going on. A certain proposed new type of producer will utilize high volatile fuels, such as bituminous coal, lignite, peat and wood, by passing the hot gases from the producer through the raw fuel in a series of preliminary chambers, thus distilling the valuable hydrocarbon gases (as well as ammonia) out of the fuel before it is charged into the producer itself.

Attention need hardly be called to the preeminent importance of the volatile matter of coal in the illuminating gas and by-product coke oven industries. It is of interest, however, to note the increasing favor accorded by the gas industry to the vertical gas retort as most successfully operated by the Bueb system at Dessau, Germany,[2] and to explain that one advantage of this process lies in avoiding the decomposition of certain valuable gases in passing over heated surfaces, as occurs in the ordinary processes, although at the same time a higher gas yield is obtained by using higher temperatures in the retort itself.

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[1] William Kent, "Steam Boiler Economy;" D. T. Randall, *Bull.* 334, *U. S. Geol. Survey*, "The Burning of Coal without Smoke in Boiler Plants," page 11; L. P. Breckenridge, *Bull.* 15, *Univ. of Illinois Engineering Exp't Sta.*, "How to Burn Illinois Coals without Smoke," page 7.

[2] *Amer. Gas Light J.*, **86**, 319; **86**, 361; **86**, 407; **88**, 446; *J. Gas Light*, **96**, 484.

In connection with the by-product coke oven industry there have been many experiments carried out on the industrial scale to determine the yield and quality of by-products from coal, and the composition of the gas at successive stages,[1] and many also of similar nature in connection with illuminating gas manufacture.[2] In very few of these experiments, however, has there been any comparison of the behavior of different types of coal under the same conditions or any study of the effect of varying conditions on the volatile products.

The purpose of the investigation described in this paper has been (1) to throw light on the nature of the volatile products from coal, and on the manner in which they are affected by the conditions prevailing during their formation or to which they are subjected after formation; (2) to contribute, in the interests of smoke abatement, some data on the comparative amount and character of the gases and vapors distilled from different coals at low temperatures, a subject intimately concerned in the production of smoke; (3) to prove experimentally that the volatile product of coal is to some extent incombustible, and that the proportion of inert volatile matter varies in different coals; and finally (4) to show that the oxygen of coal is in many cases evolved in the volatile matter very largely in combination with carbon as CO and CO_2 as well as with hydrogen as water, thereby explaining in great degree the discrepancy found in these cases between the determined calorific value and that calculated by Dulong's formula.

Volatile Matter at Ordinary Temperature.—Parr and Wheeler[3] have noted the accumulation after ten months of combustible gas in tightly sealed glass jars containing samples of Illinois coal. They do not, however, report any determinations of the quantity or composition of these gases. Other investigators have extracted and analyzed gas from coal under reduced pressure at ordinary temperature.[4] But a study of the formation of gas and absorption of oxygen by coal during storage for a long period does not seem to have been attempted heretofore.

In connection with a series of experiments, not yet completed, on the deterioration in heat value of various coals during storage under different conditions, we have found in certain cases a liberation of gas in remarkably large quantities. About 25 lbs. of coal of buckwheat size were stored in a 20-liter glass bottle closed with a rubber stopper, which was provided with glass tubes for removing gas samples. The bottles stood in the

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[1] J. D. Pennock, THIS JOURNAL, 21, 678 (1899); F. Schniewind, *J. Gasbel*, 45, 125, 141 (1902); Short, *J. Soc. Chem. Ind.*, 26, 581 (1907).

[2] Drehschmidt, *J. Gasbel*, 47, 677 (1904); A. H. White, *Amer. Gas. L. J.*, 87, 625 (1907).

[3] *Bull.* 17, *Univ. of Illinois Engineering Exp't Sta.*, 1907, p. 33.

[5] Trowbridge, *J. Soc. Chem. Ind.*, 25, 1129. Bedson, *Chem. News*, 68. 187 (1893).

laboratory at a temperature ranging from 20° to 25°. In some of the bottles the coal was immersed in distilled water and the interstices well filled with water by attaching a partial vacuum for about one hour. About 400 cc. of air remained above the surface of the water. Some of the results on the examination of the gas are given below.

TABLE I.

Time in storage.	Composition of gas (taken at surface of coal, if not immersed).						
	CO_2.	Illum.	O_2.	CO.	CH_4.[1]	H_2.	N_2.
Coal No. 23:	(Immersed under water.)						
4 days........	0.3	0	2.5	..	1.3	..	95.9
6 days........	0.0	0	0.5	..	6.8	..	92.7
10 days........	0.3	0	0.2	..	15.9	..	83.6
13 days........	0.3	0	0.3	..	32.0	..	67.4
16 days........	0.4	0	0.3	..	74.9	..	24.4
25 days........	0.3	..	0.2	..	87.3	..	12.2
39 days........	0.5	..	0.3	..	90.5	..	8.7
104 days........	0.8	..	0.0	..	95.7	0[2]	3.5
	Total gas removed in 104 days, 4,930 ccs.						
Coal No. 23:	(Dry in closed bottle.)						
10 days........	0.5	..	0.0	..	18.9	..	80.6
34 days........	0.0	..	0.1	..	73.3	..	26.6
71 days........	0.6	..	0.3	..	72.0	0[2]	27.1
	Total gas removed in 104 days, 770 cc.						
Coal No. 21:	(Dry in closed bottle.)						
35 days........	0.4	..	0	..	51.4	..	48.2
	Gas removed in 104 days, 270 cc.						

Coal No. 23: O'Gara No. 8 Mine, Saline Co., Illinois.
Sample mined 19 days before storing.

Coal No. 21: Herrin, Williamson Co., Illinois.
Sample mined 28 days before storing.

The gas liberated in the above cases consists almost entirely of methane with a very slight amount of CO_2 and no more than doubtful traces of CO and heavy hydrocarbons. No hydrogen could be detected by the palladium fractional combustion method. Whether this gas may properly be considered as volatile matter due to decomposition of the coal or whether it is held in the coal as such by occlusion or adsorption cannot be decided without further study. The fact that the oxygen of the air surrounding the coal is rapidly absorbed without forming CO_2, indicates a change of composition in the coal. By comparison of the analyses at the 10-day period from dry and immersed coal it may be seen that more methane has been formed by the dry coal, since the gas sample in this case represents a larger volume of gas. It is reasonable to sup-

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[1] Hydrogen was determined separately only in the analysis at 104 days; hence the higher hydrocarbons of the paraffin series could not be calculated, except in that analysis and none was found there.

[2] Hydrogen tested for, by palladium method.

pose that a larger quantity of gas escaped between the mining of the coal and the starting of the experiments than was measured during the experiments. The measurement of the quantity of gas formed is therefore of little value. The gas pressure in case of No. 23, immersed, reached at one time 7 inches of mercury.

Volatile Matter at 105°.—A series of experiments conducted primarily for direct weighing of moisture driven off from coal at 105° yielded results incidentally which showed the extent of the loss of substances other than moisture. Ten grams of air-dried, powdered coal in a 20 cm. copper boat were heated at 105° in a current of dry air in a glass tube. The gaseous products passed out of the tube into a train consisting of two $CaCl_2$ U-tubes, a tube of soda lime and a U-tube containing platinized asbestos at 300°, preceded and followed by a bulb of clear lime water. A blank test in which 5 cc. of natural gas (94 per cent. CH_4) mixed with 95 cc. of air were passed through the apparatus gave a very distinct precipitate in the second lime water bulb, while a blank with air alone showed none. The following results were obtained with three typical coals.

TABLE II.

Coal No.	Time of drying.	Loss in weight.	Moisture weighed.	CO_2 weighed.	Hydrocarbons or CO.	Remarks.
16	2 hrs.	0.46	0.62	0.01	None	
16	2 hrs.	0.46	0.60	0.00	Faint trace	
16	4 hrs.	0.45	0.68	0.01	Faint trace	
16	2 hrs.	0.53	0.66	0.02		In nitrogen
23	2 hrs.	2.06	2.44	0.06		
23	2 hrs.	2.15	2.55	0.04	Trace	
23	4 hrs.	2.07	2.69	0.19	Considerable	
23	2 hrs.	2.35	2.52	0.04		In nitrogen
5	2 hrs.	9.14	9.53	0.36		
5	2 hrs.	8.94	9.00	0.30	Faint trace	
5	4 hrs.	9.36	9.93	0.46	Trace	
5	2 hrs.	9.23	9.13	0.27		In nitrogen

Coal No. 16: Pocohontas, W. Va. .... Official moisture. 0.47%
Coal No. 23: O'Gara, Saline Co., Ill. .... Official moisture. 2.30%
Coal No. 5: Sheridan, Wyo. (Sub-bituminous). Official moisture. 9.40%

It may be seen from the above results that a slight amount of carbon dioxide is produced by drying the Illinois and Wyoming coals at 105° for two hours (whether in air or in nitrogen), but only slight traces of hydrocarbons or carbon monoxide. The direct moisture weighings in air and in nitrogen show that oxidation of the coal has occurred to the extent of 0.4–0.5 per cent. (as increase in weight of coal). The direct moisture weighed is greater in almost every case than the official moisture (determined at about the same time).

Volatile Matter at 500°–1100°.—In studying the nature of the volatile matter at the medium and higher temperatures (500°–1100°) two sets of experiments were run, using a different apparatus in each. In one (see Fig. 2) a small sample (10 grams) was heated in a platinum retort suspended in an electric resistance furnace maintained constant at the desired temperature, the gases evolved being collected by displacement of water in a bottle. No attempt was made in this set of experiments to duplicate the methods or results of industrial practice. The apparatus was designed with the idea of maintaining definite and controllable conditions which would yield results comparable with each other in experiments on different coals. The other set of experiments (see Fig. 1) was run on a somewhat larger scale, heating 400 grams of coal in a cast iron retort resting in a cylindrical electric resistance furnace, the tar, water, ammonia, carbon dioxide, hydrogen sulphide, and gas being collected in appropriate absorption apparatus and measured. Owing to the heavy nature of the retort and the large sample of coal the temperature in the coal could not be varied as easily in these experiments as in those using the platinum retort. Accordingly one set of conditions was adopted approximating as nearly as possible those of industrial by-product coke oven practice, and a number of typical coals compared under these conditions. The object was rather to compare the different coals with each other under this set of conditions, than to determine absolutely the industrial by-product yields; and further to determine the composition of the volatile matter from different coals under these conditions.

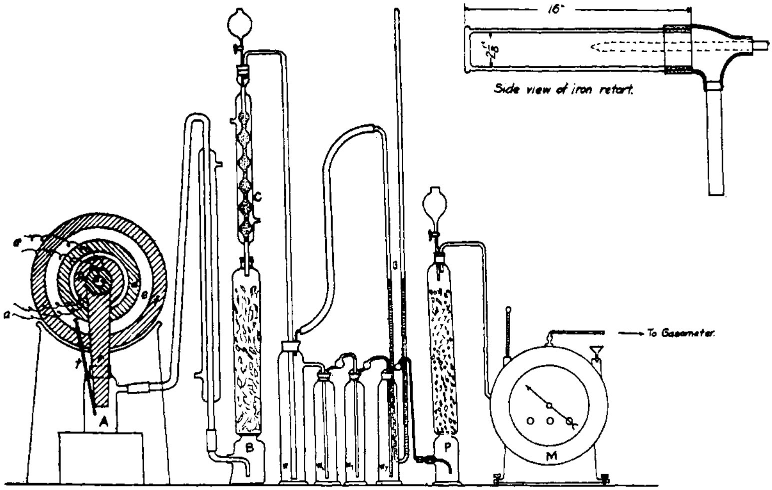

Fig. 1. Apparatus for Collecting By-Products from the Coking of Coal.

The coal, crushed to buckwheat size, was placed in the inner end of the retort, a 10 cm. layer of coke added and the retort made tight. The furnace having been heated to 1050°, the retort was introduced and the by-product apparatus connected. The heating was continued until gas practically ceased to be formed, usually about one and one half hours. The temperature in the interior of the coal rose to 700° in 25–30 minutes.

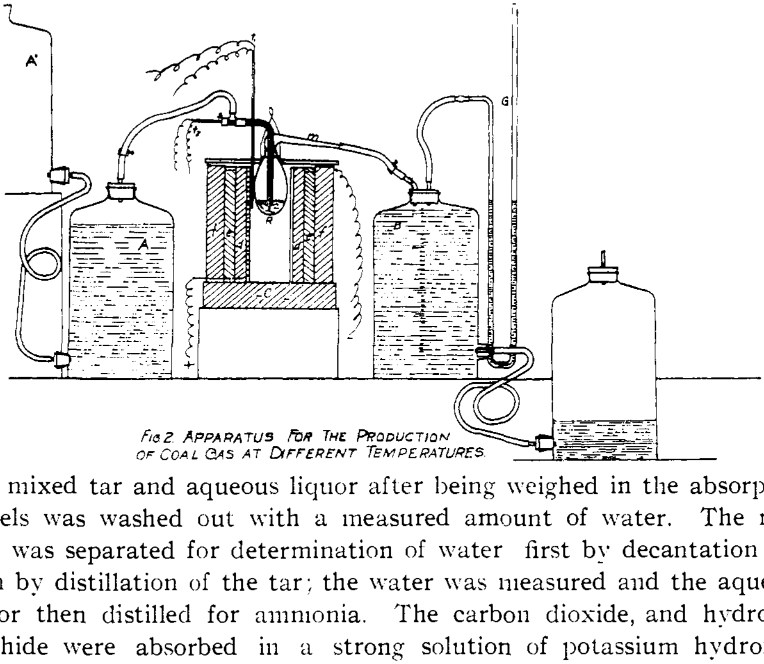

FIG 2. APPARATUS FOR THE PRODUCTION OF COAL GAS AT DIFFERENT TEMPERATURES.

The mixed tar and aqueous liquor after being weighed in the absorption vessels was washed out with a measured amount of water. The mixture was separated for determination of water first by decantation and then by distillation of the tar; the water was measured and the aqueous liquor then distilled for ammonia. The carbon dioxide, and hydrogen sulphide were absorbed in a strong solution of potassium hydroxide on which blank determinations had been run, the carbon dioxide was determined by evolution with acid and the hydrogen sulphide by titration with iodine. The gas after passing through a meter was collected over water and analyzed.

The following results were obtained on four typical coals:

TABLE III.

Test No.	Coal.	Coke %.	Tar %.	Water %.[1]	Ammonia (lbs sulphate per ton).	CO_2.	H_2S.	Gas (cu. ft. per ton at 0° and 760 mm.)
33	No. 16 (Pocahontas)	79.1	7.2	1.0	13.2	0.44	0.08	10180
34	No. 16 (Pocahontas)	79.1	7.2	1.5	12.5	0.43	0.06	9210
15	No. 3 (Connellsville)[2]	70.0	12.5	4.5	18.2	....	....	8070
39	No. 3 (Connellsville)	73.5	14.4		25.0	0.71	0.28	8650
31	No. 23 (O'Gara, Ill.)	63.1	12.3	11.0	26.4	1.20	0.47	8400
32	No. 23 (O'Gara, Ill.)	63.1	11.5	10.3	24.1	1.19	0.44	8400
40	No. 11 (Sheridan, Wyo.)	45.0	6.8	29.0	29.1	8.03	0.10	7740[3]
36	No. 11 (Air-dried)	52.9	5.3	19.0	28.2	8.62	0.12	8540[3]
37	No. 11 (Air-dried)	53.1	5.6	19.0	25.1	8.20	0.10	7790[3]

[1] Includes moisture of coal.

[2] 600 g. coal used in this test; rate of heating slower than in other tests.

[3] Calculated to CO_2-free basis.

TABLE III (*continued*).

Coal analysis.	Moisture.	Volatile matter.	Fixed carbon.	Ash.	Sulphur.	Nitrogen.
16	1.16	20.76	74.90	3.18	0.61	1.07
3	1.18	30.64	60.30	7.88	0.95	1.23
23	7.07	30.37	53.80	8.76	1.48	1.27
11 (Air-dried)	11.45	38.83	44.65	5.07	0.45	1.32
11 (As received)	21.96	34.25	39.22	4.57	0.39	1.18

Analyses of Average Gas from Above Tests. (Calc. to air-free).

Test.	CO_2.	C_6H_6.	C_2H_4.	CO.	CH_4.	H_2.	N_2.
33	0	0.3	1.5	3.1	26.0	69.0	0.1
34	0	0.3	0.7	3.3	26.8	66.5	2.4
15	0.5	1.5	2.0	5.0	28.3	55.4	7.3
39	0	1.8	1.7	5.2	26.4[1]	60.4	4.5
31	0.1	1.7	1.3	7.3	29.7	56.2	3.7
32	0	1.1	1.8	7.5	22.8	57.3	9.5
40	...[2]	1.2	1.4	17.8	18.1[3]	54.0	7.5
36	...[2]	1.2	1.3	21.2	21.4	51.6	3.3
37	...[2]	1.1	1.5	21.6	23.7	47.0	5.1

On the basis of the above results the composition of the volatile products may be stated in the following percentages of the coal as used:

TABLE IV.—BY-PRODUCTS FROM 400 GRAM TESTS.

Coal.	Total volatile.[4]	True volatile (without moisture).	Tar.	Water.	NH_3.	CO_2.	H_2S.	Gas by difference.	Water of constitution.[5]
16	20.9	19.7	7.2	1.3	0.17	0.44	0.07	11.7	0.2
3	28.2	27.0	11.0	4.5	0.28	0.71	0.28	11.4	3.3
23	36.9	29.8	11.9	10.7	0.33	1.20	0.46	12.3	3.6
11	55.0	33.0	6.8	29.0	0.38	8.03	0.10	10.7	7.0
11 (AD)	47.0	35.5	5.5	19.0	0.35	8.41	0.11	13.6	7.5

TABLE V.—RELATIVE PERCENTAGES OF COMBUSTIBLE AND INERT VOLATILE.

Coal No.	16.	3.	23.	11.	11 (AD).
Combustible volatile............	18.9	22.7	24.7	17.6	19.2
Inert volatile[6] (not including moisture).....	0.8	4.3	5.1	15.4	16.3

The inert volatile matter in various types of coal has been calculated by Parr on theoretical considerations as to the behavior of coal.[7] Parr's calculations are based on curves which smooth out the irregularities of

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[1] Includes 20.4 per cent. CH_4 + 6.0 per cent. C_2H_6 calculated as described below under methods of gas analysis.

[2] Calculated to CO_2-free basis.

[3] Includes 14.9 per cent. CH_4 + 3.2 per cent. C_2H_6 calculated as described below under methods of gas analysis.

[4] Difference between average coke yield and 100; therefore includes moisture.

[5] Total water minus moisture.

[6] Does not include moisture or free nitrogen of gas. Values obtained by difference between volatile (without moisture) and tar + gas + H_2S.

[7] THIS JOURNAL, **29**, 585, and *Bull. No.* **3**, *Illinois State Geol. Survey*, 1906.

Dulong's calculation of available hydrogen from analytical data. Parr's values for inert volatile are in most cases considerably higher than those shown by the above experimental results. But the fact remains that the inert constituent of the volatile matter is a considerable quantity, varying in different coals and of importance in the differentiation of coal types.

No definite conclusions as to comparative by-product yields should be drawn from the above tests. They serve rather as indications of differences in behavior which require corroboration by a considerable number of parallel experiments. It may, however, be said that apparently the ammonia yield by this laboratory method is even larger from the low grade coals of the interior and western fields than from the high grade eastern coals. The high yield of gas of thin quality from Pocahontas coal, and its low ammonia and water yields accord with the results of commercial practice. In general the yield of tar is greater and that of gas less in the laboratory tests than in commercial practice, which is due

TABLE VI.—AVERAGE RESULTS ON 10 GRAMS AIR-DRIED COAL.

(10 Minutes heating.)

					Gas composition (calculated to undiluted gas).						
Coal.	Highest temp. in coal.	Tar. %	Water. %	Gas (cc.).	CO_2.	Illum.	CO.	CH_4.	C_2H_6[1]	H_2.	N_2.
10 Minutes heating at 500°.											
3	335	....	....	8	30.0	0	6.5	6.5	7.0	0	50.0[2]
1	325	....	....	90	14.8	0	5.3	8.0	....	0	71.9[2]
10 Minutes heating at 600°.											
3	441	4.9	3.2	190	6.3	8.2	5.9	36.9	23.7	2.0	17.0[2]
1	440	6.8	13.0	173	15.7	7.0	14.4	19.0	22.2	2.8	18.9[2]
10 Minutes heating at 700°.											
3	562	11.0	3.5	583	3.0	7.2	5.4	44.1	17.7	13.5	9.1
1	545	7.8	14.0	471	8.5	5.1	13.7	59.6	0.0	1.1	12.0
5	580	8.2	18.5	1020	28.8	3.7	20.0	18.6	6.8	15.1	7.0
16	599	4.2	1.9	675	1.9	4.4	3.9	44.4	16.1	28.5	0.8
10 Minutes heating at 800°.											
3	687	12.6	4.5	1375	1.5	5.5	6.9	24.9	12.1	33.1	16.0[2]
1	680	9.3	13.9	1251	3.8	3.8	16.0	27.7	6.1	33.7	8.9[2]
5	...	7.9	19.1	1780	19.8	2.7	21.4	14.1	4.0	30.0	8.0
16	...	6.5	2.4	1590	1.2	3.4	4.8	24.4	11.6	43.2	11.4

COAL ANALYSIS.

	Moisture.	V. M.	F. C.	Ash.	
3	1.10	30.67	60.35	7.88	Connellsville, Pa.
1	7.67	30.38	54.32	7.63	Ziegler, Ill.
5	9.15	39.93	42.92	8.00	Sheridan, Wyo.
16	0.35	20.93	75.51	3.21	Pocahontas, W. Va.

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[1] Includes all higher paraffin hydrocarbons calculated as C_2H_6. See description of gas analysis methods below.

[2] Includes small amount of air.

most probably to the slower distillation in the laboratory method and the unavoidable cooling of the furnace at the start by the cold iron retort.

Particular attention should be drawn to the wide variation in carbon dioxide, carbon monoxide, and water of constitution produced by the destructive distillation of the different coals.

Experiments on 10 Grams of Coal.—The series of tests in a platinum retort on 10 grams of coal at various temperatures is not yet completed but has yielded sufficient results to show their approximate agreement with those obtained on 400 grams of coal and also to indicate the composition of the gas produced from different coals in the early stages of heating at low temperatures. A thermo-couple was inserted in the retort so as to determine the temperature under the surface of the coal itself. The tests were run in an atmosphere of nitrogen which was passed through the retort until the exit gases contained less than 1 per cent. of

TABLE VII.—AVERAGE RESULTS ON TOTAL GAS FROM 10 GRAMS AIR-DRIED COAL.

Coal.	Furnace. temp.	Highest temp. in coal.	Gas (cc.).	Gas composition (calculated to undiluted gas). CO_2.	Illum.	CO.	CH_4.	C_2H_6.[1]	H_2.	N_2.
3	500	390	150	11.2	5.3	5.2	4.5	32.5	0	41.3
1	500	390	130	21.0	5.6	13.3	16.4	14.8	0	28.9
3	600	474	626	3.4	5.7	5.3	41.2	18.9	10.9	14.6
1	600	480	535	6.7	4.3	13.9	34.1	13.6	14.2	13.2
3	700	589	1220	2.7	3.8	5.3	36.2	12.9	27.0	12.1
1	700	585	978	5.7	3.6	19.1	30.0	7.7	24.1	9.8
5	700	604	1300	20.4	3.3	20.2	22.4	5.3	22.4	5.0
16	700	617	1183	1.3	3.2	4.8	42.0	10.0	32.9	5.8
3	800	705	1723	2.0	4.3	7.0	36.0	9.5	38.1	3.1
1	800	685	1550	3.6	3.0	15.7	27.1	5.0	38.5	7.1
3	900	812	2080	1.1	4.7	7.2	25.2	7.1	52.0	2.7
3[2]	900	830	2750	1.3	4.8	7.3	27.1	3.4	52.6	3.5
1	900	811	2335	2.2	3.0	14.5	20.7	6.0	48.7	4.9
1[3]	900	832	2380	2.5	2.6	14.0	21.8	4.7	47.9	5.5
3	1000	922	2900	1.1	4.3	5.9	24.4	3.0	56.0	5.3
1	1000	920	2700	2.5	3.6	14.4	18.1	3.9	52.6	4.9
5	1000	920	3650	9.9	4.3	21.2	11.7	3.8	44.2	4.9
5[4]	1070	990	2700	12.8	1.7	17.7	14.4	4.8	42.1	6.5
16	1000	920	3230	0.4	3.6	4.4	22.5	3.2	61.8	4.1
3	1100	1010	3530	1.0	4.9	7.0	21.5	3.8	58.2	3.6
1	1100	1026	3120	1.7	3.7	14.9	13.9	4.2	54.6	6.0
3[5]	960	845	2750	1.7	4.7	8.2	29.8	3.5	50.5	1.6
1[5]	960	859	2500	3.2	3.8	16.6	20.0	4.8	51.0	0.6

[1] Includes all higher paraffin hydrocarbons calculated as C_2H_6.

[2] Special test, heating neck of retort to redness.

[3] Special test on 10 grams running in air instead of in nitrogen. Gas contains 1.0 per cent. oxygen and very little more CO_2 than in corresponding test run in nitrogen.

[4] Special test, heating gradually during 50 minutes.

[5] Approximation of official volatile determination, heating 1 g for 7 minutes.

oxygen. The tar was collected in two 6-inch tubes of absorbent cotton heated to 100° and also weighed on the neck of the retort. The water was collected in a 5-inch calcium chloride U-tube, and always contained a slight amount of light oil driven over from the tar, causing an error of 1 per cent. or less.

The results given above in Tables VI and VII are in most cases averages of two or more parallel tests at each temperature. The following tabular statements show the detailed results of separate tests, and from these the averages given above were compiled:

TABLE VIII.

Coal No. 3 (Connellsville, Pa.) 10 Minutes Period.

Test No.	66.	70.	72.	75.	64.	65.	67.	80.	86.
Furnace Temperature	500	600	600	600	700	700	700	800	800
Temp. of Coal:									
1 min.	50	65	50	55[2]	75	80	85	125	70
2 "	80	125	130	75	180	175	180	215	250
3 "	140	200	225	150	300	300	300	375	385
4 "	180	255	300	220	380	370	380	445	450
5 "	225	325	345	275	430	415	430	510	520
6 "	260	370	385	315	463	460	460	550	...
7 "	285	405	408	360	590	485	487	610	590
8 "	305	425	430	380	510	510	507	655	650
9 "	325	440	445	400	535	530	540	680	675
10 "	335	455	452	415	565	555	565	695	679
Gas Yield: (cc. per 10 gms.)	8	162	233	176	668	522	560	1400	1350
Gas Composition: [1]									
CO_2	30.0	6.7	5.7	6.4	3.2	2.6	3.3	1.8	1.2
C_6H_6	0.0	5.4	3.1	6.0	4.8	4.9	4.7	3.1	2.7
C_2H_4	0.0	3.4	4.1	2.6	2.5	2.3	2.4	2.8	2.3
CO	6.5	6.1	5.3	6.4	4.6	6.9	7.6	7.1	6.6
CH_4	6.5	17.2	56.4	37.0	69.0	27.0	36.3	30.0	19.8
C_2H_6[3]	7.0	32.4	14.0	24.6	4.5	27.5	21.2	10.2	14.0
H_2	0.0	5.4	0.6	0	3.5	20.8	16.1	30.8	35.3
N_2		17.8	1.9	11.0	14.0	8.0	8.4	10.3	16.4
Air	50.0	5.6	8.9	6.0	1.9	....	....	3.9	1.7
Tar %[4]		4.83	4.98		12.0	10.1		12.9	12.4
Water %[4]		3.44	3.03		3.8	3.2		4.4	4.7

Smoke Formation and the Composition of Low Temperature Gases during Early Stages of Heating.—Börnstein[5] has examined the gases and tars

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[1] Calculated to undiluted gas. Oxygen assumed to be present entirely as air.

[2] Thermocouple accidentally placed somewhat higher than usual.

[3] Includes all higher paraffin hydrocarbons calculated as C_2H_6.

[4] Separate tests from above gas tests.

[5] *J. Soc. Chem. Ind.*, **25**, 583, 213 (1906); *J. Gasbel*, **49**, 627, 648, 667 (1906); *Z. angew. Chem.*, **17**, 1520 (1904).

TABLE IX.

Coal No. 1 (Illinois) 10 Minutes Period.

Test No.	59.	69.	73.	62.	63.	76.	83.
Furnace Temperature.	500	600	600	700	700	800	800
Temp. of Coal:							
1 Min.	70	70	60	....	95	75	....
2 "	85	85	....	160	150	150	180
3 "	125	170	135	250	230	305	....
4 "	165	220	....	335	315	410	435
5 "	215	290	290	390	380	505	570
6 "	345	340	330	440	450	550	590
7 "	270	380	370	470	480	610	625
8 "	290	405	395	505	510	635	660
9 "	315	430	420	535	530	655	678
10 "	325	445	435	550	540	670	689
Gas Yield: (cc. per 10 g.)	90	175	171	485	456	1224	1280
Gas Composition: [1]							
CO_2	14.8	15.6	15.7	8.7	8.3	3.7	3.9
C_6H_6	0.0	4.0	1.3	3.0	3.0	2.1	1.0
C_2H_4	0.0	2.8	5.9	2.3	1.9	1.6	2.8
CO	5.3	12.6	16.2	14.1	13.2	16.7	15.3
CH_4	8.0	23.6	14.3	60.2	59.0	....	27.7
C_2H_6[2]	...	21.6	22.9	0.0	0.0	....	6.1
H_2	0.0	4.6	0.9	0.9	1.3	....	33.7
N_2	34.9	6.2	19.7	4.7	7.9	....	7.8
Air	37.0	9.0	3.1	6.1	5.4	1.2	1.7
Tar %[3]	.....	6.84	.....	7.5	8.1	9.3	....
Water %[3]	.....	12.96	.....	14.3	13.7	13.9	....

obtained by distilling German bituminous and brown coals at low temperatures (up to 450°). The gas he finds high in carbon dioxide and in the *homologues of methane*; the tar carries no solid aromatic hydrocarbons.

From our results given in Table VI and in different form in Table XIV it may be seen that the low temperature gases are high in illuminants and the higher homologues of methane, and low in hydrogen. Comparing the four coals at 700° (565° in the coal) where the gas begins to be formed in considerable amount, the Connellsville is the richest of the four coals in illuminants and heavy hydrocarbons and the Pocahontas the highest in hydrogen. The high carbon dioxide and carbon monoxide from the Illinois and Wyoming coals accords with other experiments on these coals. The tar at 700° is greater also in the Connells-

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[1] Calculated to undiluted gas. Oxygen assumed to be due to air.

[2] Includes all higher paraffin hydrocarbons.

[3] Separate tests from above gas tests.

Table X.

10 Minutes Period: Coals No. 5 and 16.

	Coal No. 5 (Sheridan, Wyo.)				Coal No. 16 (Pocahontas, W. Va.)			
Test No.	105.		114.		103.		115.	
Furnace Temperature	700	700	800	800	700	700	800	800
Temp. in Coal:								
1 Min.	90	......	......	......	140	......	......	......
2 "	190	......	......	......	310	......	......	......
3 "	300	......	......	......	430	......	......	......
4 "	360	......	......	......	495	......	......	......
5 "	430	......	......	......	530	......	......	......
6 "	480	......	......	......	550	......	......	......
7 "	530	......	......	......	570	......	......	......
8 "	550	......	......	......	565	......	......	......
9 "	568	......	......	......	585	......	......	......
10 "	580	......	......	......	599	......	......	......
Gas Yield:								
(cc. per 10 g.)	1020	......	1780	......	675	......	1590	......
Gas Composition:[1]								
CO_2	28.8	......	19.8	......	1.9	......	1.2	......
C_6H_6	2.3	......	1.7	......	2.8	......	2.1	......
C_2H_4	1.4	......	1.0	......	1.6	......	1.3	......
CO	20.0	......	21.4	......	3.9	......	4.8	......
CH_4	18.6	......	14.1	......	44.4	......	24.4	......
C_2H_6[2]	6.8	......	4.0	......	16.1	......	11.6	......
H_2	15.1	......	30.0	......	28.5	......	43.2	......
N_2	7.0	......	8.0	......	0.8	......	11.4	......
Tar %	8.50	7.83	7.80	7.95	....	4.19	6.15	6.74
Water %	18.0	18.9	19.4	18.8	....	1.93	2.58	2.19

ville coal. The smokeless character of the Pocahontas coal may be connected more or less with the presence of considerable hydrogen in its gas at low temperatures, since the low ignition point of hydrogen tends to assist in the burning of other gases present.

From Table XIV and the curves in Fig. 3 the bearing of these results on smoke formation may be seen. The smoke-producing constituents of the volatile matter are here considered as including tar, and the heavier hydrocarbon gases: benzene, ethylene and homologues of methane (calculated as C_2H_6). While at 440° (in the coal) the Illinois coal (and probably also the Wyoming) has produced more smoky gases than the Eastern coals, at 565° and higher the Connellsville produces much more. This accords with the finding in practice of greater difficulty in burning coals of the Connellsville type without smoke.

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[1] Calculated to undiluted gas; oxygen assumed to be present entirely as air.

[2] Includes all higher paraffin hydrocarbons calculated as C_2H_6.

TABLE XI.—TOTAL GAS FROM 10 GRAMS AIR-DRIED COAL.

Coal No. 1. (Ziegler, Illinois.)

Test No.	60.	71.	78.	68.	81.	85.	93.	88.	97.[1]	90.	99.
Furnace Temperature.	500	600	600	700	700	800	800	900	900	1000	1100
Temp. of Coal:											
2 Min.	85	115	85	155	150	...	230	340	450	570	840
4 "	175	280	175	320	360	500	470	660	700	820	970
6 "	220	390	300	445	470	600	600	755	807	905	1025
8 "	265	435	370	520	520	650	660	790	832	920	1025
10 "	330	462	410	550	550	670	681	797	825	915	1026
15 "	375	487	457	578	572	675	689	789	822	912	1020
20 "	390	490	469	580	575	679	689	785	820	910	....
30 "	390	490	470	582	579	676	691	788	821	900	....
40 "	390	485	470	583	578	672	690	785	810	....	....
50 "	390	485	469	588	580	679	689	....	815	....	....
60 "	390	490	468	588	575	679	690	....	....	....	....
70 "	...	...	...	590	579	....	....	....	....	....	....
Gas Yield (cc. per 10 gms.)	130	570	500.0	965	990	1500	1600	2290	2380	2700	3120
Gas Composition:[2]											
CO_2	21.0	6.4	7.0	5.1	6.2	3.4	3.7	2.2	2.5	2.5	1.7
C_6H_6	.....	2.0	3.0	2.2	2.4	1.6	1.5	2.0	1.3	1.2	1.0
C_2H_4	5.6	2.0	1.6	9	1.7	1.8	1.2	1.5	1.3	2.4	2.7
CO	13.3	14.3	13.4	22.0	16.0	16.0	15.3	14.8	14.1	14.4	14.9
CH_4	16.4	39.2	29.0	34.4	25.5	23.8	30.3	19.3	22.0	18.1	13.9
C_2H_6[3]	14.8	10.6	16.5	7.7	7.6	4.8	5.1	6.9	4.8	3.9	4.2
H_2	0	11.9	16.3	21.9	26.0	40.4	36.6	49.1	48.4	52.6	54.6
N_2	28.9	13.6	13.2	5.8	14.5	8.2	6.3	4.2	5.6	4.9	6.0

[1] Test run in air instead of in nitrogen.

[2] Calculated to undiluted gas. Oxygen assumed to be present entirely as air.

[3] Includes all higher paraffin hydrocarbons calculated as C_2H_6.

TABLE XII.—COAL NO. 3 (CONNELLSVILLE, PA.) TOTAL GAS.

Test No.	61.	74.	79.	84.	77.	82.	87.	94.	89.	92.	106.
Furnace Temperature.	500	600	600	600	700	700	800	800	900	1000	1100
Temp. of Coal:											
2 Min.	105	130	100	75	140	155	285	385	450	600	600
4 "	210	290	240	260	340	370	460	535	630	740	880
6 "	280	385	360	360	440	455	550	...	720	905	1010
8 "	320	415	410	405	490	498	655	...	800	922	1005
10 "	347	435	438	435	555	550	685	708	812	918	999
15 "	375	470	483	478	579	572	692	711	803	913	1000
20 "	384	465	477	472	582	578	692	714	801	905	...
30 "	392	460	473	474	580	575	691	714	...	914	...
40 "	390	462	475	475	590	575	690	719	...	...	...
50 "	390	462	475	477	578	588	688	...	...	...	...
60 "	390	465	479	479	590	580	692	...	...	...	...
70 "	.....	.....	476	.....	......	......	690	...	...	...	...
Gas Yield: (cc. per 10 gms.)	150	443	730	705	1280	1160	1685	1760	2080	2900	3530
Gas Composition: [1]											
CO_2	11.2	3.0	3.7	3.4	3.2	2.2	1.7	2.2	1.1	1.1	1.0
C_6H_6	4.1	.....	3.7	1.8	2.8	...	2.5	2.1	2.3	1.5	1.3
C_2H_4	1.2	5.6	2.0	4.0	1.1	3.6	2.0	1.9	2.4	2.8	3.6
CO	5.2	6.0	6.0	4.0	4.8	5.8	6.9	7.1	7.2	5.9	7.0
CH_4	4.5	56.4	35.3	32.0	32.9	39.5	35.0	37.0	25.2	24.4	21.5
C_2H_6[2]	32.5	17.0	22.8	17.0	14.4	11.4	11.0	8.0	7.1	3.0	3.8
H_2	0.0	2.3	17.2	13.3	26.9	27.0	38.5	37.6	52.0	56.0	58.2
N_2	41.3	9.7	9.3	24.5	13.9	10.5	2.4	4.1	2.7	5.3	3.6

[1] Calculated to undiluted gas. Oxygen assumed to be present entirely as air.

[2] Includes all higher paraffin hydrocarbons calculated as C_2H_6.

TABLE XIII.—MISCELLANEOUS TESTS UNDER VARIED CONDITIONS (TOTAL GAS).

	Coal No. 1.		Coal No. 3.			Coal No. 5 (Wyo.).			Coal No. 16 (Poca.).		
Test No.	91.	98.	95.	108[3].	89.	101.	104.	102.	96.	100.	107.
Furnace Temperature......	[1]	[2]	[2]	900°	900°	700°	1000°	1070°[4]	700°	700°	1000°
Temperature of Coal:											
1 min............	650	600	500	....	....	130	.....	110	125	170	420
2 “	865	830	790	440	450	240	600	170	240	280	620
3 “	865	850	835	560	...	360	790	240	380	445	690
4 “	850	859	845	630	630	430	900	300	440	492	740
5 “	848	850	843	690	...	495	...	370	490	532	830
6 “	842	849	...	760	720	530	...	410	510	552	892
7 “	840	849	840	820	...	560	...	460	532	552	912
10 “				830	812	600	920	550	590	600	920
15 “				814	803	600	915	609	614	615	...
20 “				811	801	604	903	680	610	620	908
40 “				...	...	604	912	990	650	619	915
60 “				...	...	...	...	...	...	...	...
Gas Yield:											
(cc. per 10 grams)..	2600	2500	2750	2750	2080	1300	3650	2700	1190	1175	3230
Gas Composition:[5]											
CO_2...............	3.1	3.2	1.7	1.3	1.1	20.4	9.9	12.8	1.1	1.4	0.4
C_6H_6..............	1.3	1.8	1.7	1.9	2.3	2.0	2.1	1.1	1.4	1.8	1.1
C_2H_4..............	4.1	2.0	3.0	2.9	2.4	1.3	2.2	0.6	1.8	1.4	2.5
CO...............	15.6	16.6	8.2	7.3	7.2	20.2	21.2	17.7	4.9	4.7	4.4
CH_4...............	18.0	20.0	29.8	27.1	25.2	22.4	11.7	14.4	43.6	40.5	22.5
C_2H_6[6]............	4.4	4.8	3.5	3.4	7.1	5.3	3.8	4.8	8.9	11.1	3.2
H_2................	52.0	51.0	50.5	52.6	52.0	22.4	44.2	42.1	32.1	33.6	61.8
N_2................	1.5	0.6	1.6	3.5	2.7	5.0	4.9	6.5	6.2	5.5	4.1

[1] Approximation of Official Volatile Method, 1 gram coal, 7 min.

[2] Ditto, slightly lower temperature.

[3] Top and delivery tube of retort heated to redness for 2″ space.

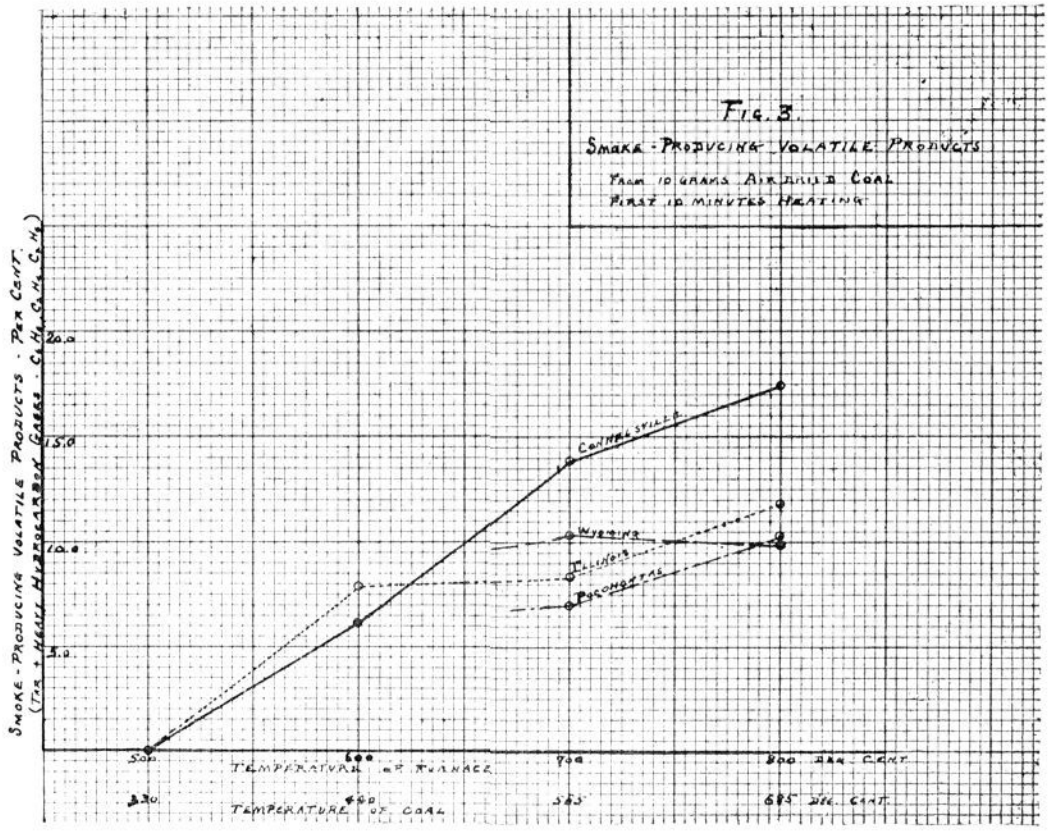
[4] Slow elevation of temperature, approximating Somermeier's modified method for volatile.

[5] Calculated to undiluted gas.

[6] Includes all higher paraffins calculated as C_2H_6.

TABLE XIV.—ABSOLUTE QUANTITIES OF SMOKING AND NON-SMOKING PRODUCTS IN 10 MINUTES HEATING. 10 g. COAL.[1]

	Temperature.		Smoking products.				Non-smoking gases (cc.).				
				Gas (cc.).							
Coal No.	Furnace.	Coal.	Tar Per cent.	Illum.	Ethane, etc.	Total.	CO_2.	CO.	CH_4.	H_2.	Total.
3	500	335	....	0	0.6	0.6	2.4	0.5	0.5	0	3.4
1	500	325	....	0	0.0	0.0	13.5	4.7	7.2	0	25.4
3	600	441	4.9	16	46.0	61.0	12.0	11.0	71.0	4	98.0
1	600	440	6.8	12	39.0	51.0	28.0	25.0	33.0	5	91.0
3	700	562	11.0	42	103.0	145.0	18.0	31.0	256.0	78	383.0
1	700	545	7.8	24	0.0	24.0	40.0	64.0	281.0	5	391.0
5	700	580	8.2	38	69.0	107.0	294.0	204.0	190.0	154	842.0
16	700	599	4.2	30	109.0	138.0	13.0	27.0	300.0	192.0	532.0
3	800	687	12.6	76	166.0	242.0	21.0	95.0	343.0	458	917.0
1	800	680	9.3	47	76.0	123.0	47.0	200.0	346.0	420	1013.0
5	800	...	7.9	48	72.0	120.0	355.0	381.0	254.0	534	1524.0
16	800	...	6.5	54	186.0	240.0	19.0	77.0	390.0	691	1177.0



Methods of Gas Analysis.

For the determination of CO_2, C_6H_6, C_2H_4, O_2 and CO the well-known apparatus of Hempel was used. For benzene, sulphuric acid (specific gravity 1.84) was the reagent used, as recommended by Morton.[2] For ethylene (or total illuminants) fuming sulphuric acid (specific gravity

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[1] Compiled from results given in Table VI.

[2] THIS JOURNAL, 28, 1728 (1906).

1.53) was used in a double pipette provided with glass beads; and for carbon monoxide, an ammoniacal solution of cuprous chloride (according to Winkler's formula[1]) for which three double pipettes were used successively on each sample.

Hydrogen was determined in most cases separately by fractional combustion over palladium asbestos as recommended by F. C. Phillips.[2] Palladium black was precipitated upon acid-washed, ignited asbestos, by the action of alkaline sodium formate upon palladium chloride solution, and the product then washed, dried and ignited at a moderate red heat. A mixture of the gas residue and air, equivalent to a hydrogen-oxygen ratio of not more than 1:2 by volume, was passed slowly over the palladium in a small U-tube maintained at about 50° by a water bath, and the contraction measured. According to Prof. Phillips, hydrogen is completely burned under these conditions and hydrocarbons are not affected. We have verified this statement by tests with pure electrolytic hydrogen and with natural gas (testing for CO_2 formation).

Methane and its higher homologues were determined by the slow combustion method of Winkler as modified by Dennis and Hopkins.[3] The combustion pipette was of glass, the platinum spiral was heated by a direct current of 120 v. 6–8 amp. and in order to assist in the combustion and reduce the necessary temperature a few threads of platinized asbestos were inserted in the platinum spiral. The contraction and carbon dioxide formed were measured.

Hydrogen having been separately determined, the contraction due to its combustion is known and may be subtracted from the total contraction obtained by the complete burning in the Winkler pipette. The remainder is contraction due to the burning of hydrocarbons. If we assume only two hydrocarbons present, *viz.*, methane and ethane, and know the contraction and carbon dioxide formed from their combustion we can calculate their amount as follows:

1 volume CH_4 gives, on burning, 1 volume CO_2 and 2 volumes contraction.

1 volume C_2H_6 gives 2 volumes CO_2 and $2\frac{1}{2}$ volumes contraction.

Therefore,

$$\text{contraction found} \mathrel{=\!\!\Diamond\!\!=} 2CH_4 + 2\tfrac{1}{2}\, C_2H_6.$$

$$CO_2 \text{ found} \mathrel{=\!\!\Diamond\!\!=} CH_4 + 2C_2H_6.$$

Solving for CH_4 and C_2H_6:

$$CH_4 = 1/3\ (4 \text{ contraction} - 5CO_2).$$

$$C_2H_6 = 1/3\ (4CO_2 - 2 \text{ contraction}).$$

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[1] Winkler, Technical Gas Analysis.

[2] *Amer. Chem. J.*, **16**, 164–168.

[3] Hempel, Gas Analysis (*Transl. of 3rd German Ed.*), p. 138.

Values thus obtained for the higher homologues of methane must be considered as merely approximate since several compounds are probably present whose average composition is uncertain. In case the higher homologues include others beside ethane (C_2H_6) their total percentage will be less than the above calculation shows:

Composition of Gas Formed in the Official Volatile Determination.—By means of a thermocouple inserted through the lid of the crucible until it rested under the surface of the coal, a measurement of temperature in the coal was obtained during the official volatile determination in a platinum crucible.

TABLE XV.—TEMPERATURE DURING OFFICIAL VOLATILE DETERMINATION.

	Time in minutes.										
Coal.	½.	1.	1½.	2.	2½.	3.	3½.	4.	5.	6.	7.
Empty	300	500	670	750	770	780	790	795	799	800	800
No. 1	200	530	720	800	825	830	832	832	832	830	830
No. 3	180	420	570	750	820	835	...	837	839	840	839

In order to determine the composition of the gas formed during the official volatile determination, two tests were run in the platinum retort on 1 g. of coal for 7 minutes at temperatures corresponding as nearly as practicable with the above. The retort was filled with nitrogen. The results are given at the end of Table VII.

An attempt was made also to measure the tar and water formed in the official volatile determination, but on account of the analytical difficulties in collecting these products from so small a sample of coal (1 gram) concordant results have not as yet been obtained.

There are given also in Table VII the results of a special test on Wyoming sub-bituminous coal (No. 5) in which the heating was very gradual. A smaller gas yield by 25 per cent. was obtained and a gas of higher carbon dioxide but lower illuminants than in case of rapid heating to the same temperature.

Calculation of the Heat Value of Coal from its Ultimate Analysis.

The experimental results given in the preceding pages show conclusively that in the process of breaking down under the influence of heat the coal substance gives up its oxygen partly in the form of carbon-oxygen compounds and partly as the hydrogen-oxygen compound water. Some recent work by Vignon in Europe supports this conclusion.[1] The figures demonstrating this point are given again below in more compact form.

Dulong's calculation of heat value from ultimate analysis assumes that all of the oxygen of the coal combines with hydrogen of the coal during combustion, thereby neutralizing, so to speak, the calorific value of hydrogen equal to O/8. Dulong's calculation, as is well known, gives

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[1] *Bull. soc. chim.* [4], 3, 109.

in many cases less calories than are shown by experimental determination. These cases of discrepancy are usually medium and low grade coals, high in oxygen, which we have shown above give up their oxygen in large part combined with carbon instead of with hydrogen.

TABLE XVI.—(All figures are percentages of air-dried coal).

	Oxygen relations in volatile matter.					
	Oxygen compounds in volatile matter.[1]					
Coal.	CO_2.	CO.	Water of constitution.	Oxygen in CO and CO_2.	Oxygen in water of constitution.	Oxygen in dry coal.
No. 16 (Pocahontas):						
400 g. tests.......	0.44	1.21	0.2	1.01	0.09	3.18
10 g. tests.......	0.26	1.76	...	1.21	....	....
No. 3 (Connellsville):						
400 g. tests.......	0.71	1.47	3.3	2.01	2.93	5.23
10 g. tests.......	0.64	2.14	...	1.55	....	....
No. 23 (O'Gara, Ill.):						
400 g. tests.......	1.24	2.88	3.6	2.55	3.20	8.60[2]
No. 1 (Ziegler, Ill.):						
400 g. tests.......	2.72	4.26	...	4.41	....	9.12
10 g tests.......	1.35	4.86	...	3.75	....	....
No. 11 (Sheridan, Wyo.): (Air-dried)						
400 g. tests.......	8.60	6.90	7.5	10.19	6.67	16.63
10 g. tests.......	7.28	9.67	...	10.81	....	....

By combining with carbon instead of with hydrogen in the coal the oxygen exercises less of an anti-calorific influence on the efficiency of the coal since one gram of oxygen in combining with carbon to CO_2 neutralizes $^3/_8$ gram of carbon or 3030 potential calories; with carbon to CO it partly neutralizes $^3/_4$ gram of carbon thus neutralizing $^3/_4$ (2490) = 1870 calories; while one gram of oxygen in combining with hydrogen to H_2O neutralizes $^1/_8$ gram of hydrogen or $^1/_8$ (34460) = 4313 calories. The anti-calorific influence of a unit of oxygen in forming CO_2 or CO is therefore approximately either 70 per cent. or 43 per cent., respectively, of its influence when forming water.

In a paper before the Geological Society of Washington (*Science*, **27**, 537, Apr. 3, 1908) David White has recently called attention to the uniform anti-calorific value of oxygen in coal and has based partly on this factor a scheme for the classification of coals. He states that the negative value of 1 per cent. of oxygen in "ordinary bituminous coals" is probably 70–80 calories, or "about twice as great as has been supposed." It is not clear to what supposition he refers, for Dulong's calculation assigns a negative value to 1 per cent. oxygen of $^1/_8 \times 1$ per cent. of 34460

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[1] There is a possibility of the formation of CO_2 in slight amount from the oxygen of air in contact with the coal at the beginning of a test; assuming 500 cc. of air in contact with the coal, there could be formed, if all its oxygen entered into CO_2, only 0.28 gram CO_2 or 0.07 per cent. on 400 grams of coal.

[2] From analysis of Ill. 34 (U. S. Fuel Testing Plant), a similar coal.

or 43 calories plus the diluent effect of 1 per cent. of the coal or approximately 65 calories, making a total of 108 calories, 50 per cent. greater than the value which White finds from experimental results. This excessive anticalorific value for oxygen in Dulong's method we propose to explain in some degree by the distribution of oxygen between carbon and hydrogen as set forth above.

If we calculate the heat value of an Illinois coal (Ill. No. 19)[1] and of a Wyoming coal No. 11[2] by Dulong's formula and by formulas based on the distribution of oxygen between H_2O, CO and CO_2 according to our experimental results, the following values are found:

	Ill. No. 19.	Wyo. No. 11.
Composition (*Water Free*):		
Ash	6.16	5.56
Carbon	76.96	68.90
Hydrogen	4.49	4.56
Nitrogen	1.52	1.51
Sulphur	0.52	0.51
Oxygen	10.35	18.96
Calorific Value:		
Dulong's calculation	7322	6333 cal.
Modified calculation	7453	6524 cal.
Determined	7536	6582 cal.

The formulas used for the modified calculation are the following:

Illinois Type: W (calor. value) = $8080\ (C - 0.1200 \times O) + 34460\ (H - 0.063 \times O) + 2250\ S$.

Wyoming Type: W (calor. value) = $8080\ (C - 0.182 \times O) + 34460\ (H - 0.050 \times O) + 2250\ S$.

Summary.

1. It is shown that some coals liberate gas during storage, of a composition similar to that of natural gas, and that some coals rapidly absorb oxygen from the air during storage without forming carbon dioxide.

2. During drying in air at 105° C. some coals lose appreciable amounts of carbon dioxide, and most coals take up oxygen to a considerable extent, but none of those tested showed any considerable formation of combustible gases.

3. The nature of the volatile products distilled from several coals at low temperatures in the early stages of heating is shown to vary in different coals in accordance with their smoke-producing tendencies.

4. It is shown experimentally that the volatile matter of coal comprises a considerable proportion of non-combustible matter, varying with the type of coal.

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[1] From Ziegler, Franklin Co., Illinois.

[2] From Dietz, near Sheridan, Wyoming (sub-bituminous).

5. The temperature in the coal during an official volatile determination was measured and the composition of the official volatile matter determined.

6. A modification is suggested of Dulong's heat value calculation for coal based on experimental results showing the distribution of oxygen between hydrogen and carbon.

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NOTES.

A Characteristic Test for Hippuric Acid.—Hitherto no easily-applied, characteristic test for hippuric acid in urine has been at hand. For the reason that its detection in urine is of little or no clinical value, the lack of a convenient practical method for its detection has not been felt. On the other hand, for purely scientific purposes, the methods now in use involve inconveniences that are surprisingly great when compared with the methods available for the detection of other constituents of urine. As a matter of fact, the detection of hippuric acid has necessitated the concentration of the urine, the extraction with organic solvents and either a melting point determination of the residue or its transformation into more easily recognized nitro or benzaldehyde derivative.[1]

The following test for hippuric acid can not only be applied directly to urine but it yields definite results in solutions so dilute even as hundredth-normal. A few cubic centimeters of the urine in a test tube are first treated with a quantity of sodium hypobromite solution, just sufficient to decompose the urea and to impart to the mixture a permanent yellow color. The solution is then heated to boiling; an orange or brown-red precipitate is formed, if hippuric acid is present. When present only as a trace the solution appears smoky and faintly red in color; when present in larger quantities the solution is rendered opaque and orange or brown-red in color. In either case after standing for some time the solution clears up and a light, finely divided precipitate settles. It consists of white "earthy phosphates" intermixed with the amorphous orange or brown-red solid[2] about to be described.

When a 0.1 *N* solution of hippuric acid is boiled with the sodium hypobromite solution, a deep brown-red color is formed at once and on standing settles to the bottom of the tube as an opaque, red, closely-adhering

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[1] Spiro, *Z. physiol. Chem.*, 28, 117. For quantitative methods, vide, Wiener, *Arch. exp. Path Pharm.*, 40, 314; Blumenthal, *Chem. Centr.*, 1900, II, 447.

[2] Application of the hypobromite test to aqueous solutions of other constituents of urine gave no color effects. The following were tested: uric, benzoic, oxalic and fatty acids, creatinine, acetone, acetacetic ester, glucose, glycogen and leucine.