was liberated in all the trials, but in no case was helium detected, even by the use of the highly sensitive spectroscopic method of Soddy, which will detect 2 × 10^{-10} g. of helium. It is found that ordinary spectroscopic methods for the detection of helium are, on the other hand, not at all sensitive. In no case was the amount of heat produced noticeably greater than that to be expected from the condenser discharge alone. However, no actual measurements were made of the heat liberated, since it was found that the spectroscopic method of Soddy is fully as sensitive as the calorimetric method, and is more definite in its significance.

4. The theory of atomic disintegration is discussed, and it is pointed out that the failure of the electrical discharge methods to disintegrate the atom is due to the fact that energy is not transmitted to the nucleus in a sufficiently high concentration. Electrons with velocities of several million volts may prove effective, though thus far only high-speed α-particles have induced disintegration, as in the experiments of Rutherford.

5. The condenser, using the 84,000-volt arrangement, was discharged 100 times through a 500cc. bulb containing very pure hydrogen at 40mm. pressure. This was repeated three times. Tests by the method of Soddy revealed no trace of helium.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY, AND THE WESTERN ELECTRIC COMPANY, INCORPORATED]

THE RELATION BETWEEN THE HYDROGEN CONTENT OF CERTAIN CHARCOALS AND SOME OTHER PROPERTIES

BY H. H. LOWRY

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Investigations of sorption of gases and vapors by charcoals have yielded such varying results that many theories have been advanced to explain the nature of the sorption. While these various theories are usually consistent with the particular data from which they were derived, they are not sufficiently general to enable one to predict correctly the course of the sorption in any specific case. That this should be so is, however, almost to be expected for two main reasons. First, because the process is complex, involving adsorption on the surface, diffusion into fine capillaries, condensation within these capillaries, and possibly solution, the relative effects of these factors varying in different samples of charcoal with the source of the material and the method of preparation. Second, because all charcoals cannot properly be assumed to be the same chemically and to be amorphous carbon. The present investigation shows that charcoals contain a proportion of hydrogen chemically combined with the carbon and that the amount of this combined hydrogen depends upon the previous history of the charcoal. Indeed, we have found a definite correlation between the hydrogen content of charcoals and such properties as apparent density in water and other liquids, gas and moisture content, and porosity as determined by the sorption of water vapor. The chemical composition of the charcoal is, therefore, a factor which must be considered in any attempt to explain the nature of sorption by charcoals.

Source and Preparation of Material

Twenty-three samples of charcoal were prepared from a large supply of anthracite coal selected from a single vein. The raw coal was freed as far as possible from all extraneous material, crushed, washed free from dust, and sieved by machine. The material passing a standard screen of sixty meshes to the linear inch and retained on one of eighty was subsequently carbonized in a gas-fired furnace. The temperature of this furnace was raised uniformly until a definite maximum temperature had been reached and this temperature maintained for about a quarter hour. The samples were allowed to cool in the furnace. No special control of the composition of the atmosphere during the roast was attempted, but since, except for changes in temperature, the same procedure was followed for all the samples, there is no reason to believe that the composition of the atmosphere differed to any considerable degree in the preparation of these samples. Also, since gas furnace atmosphere is generally a reducing atmosphere, no considerable activation of the material caused by oxidation would be expected. As the measurements show, the material may properly be classed as inactive.

Attention should be called to the fact that the material used in the following investigation was not prepared specifically for this purpose, but consisted of small samples taken from each of twenty-three 22-kg. lots prepared over a period of six years. Hence, even though careful records were kept of the rate of heating and the temperatures to which the samples were heated in accordance with the best commercial practice, we do not know just how accurately the data represent the treatment given the small samples on which the following measurements were made. However, careful consideration of these commercial records has indicated that the probable range of maximum temperature attained by the actual samples was from 900° to 1200°, and that this final temperature determined the amount of chemically combined hydrogen in the resulting charcoal. Both these indications have been substantially confirmed by a direct experimental study of the factors determining the hydrogen content of charcoal, in which over a hundred samples of charcoal have been prepared under accurate control of temperature and atmosphere; this study is being continued and the results will soon be ready for publication. By reason of this direct relationship between maximum temperature and hydrogen content, we feel that the previous history of these charcoals is known as accurately as that of any other group of charcoal samples on which data have been published.

Chemical Composition

The chemical composition was ascertained by means of a simple organic combustion, by which carbon was determined as carbon dioxide by absorption by soda lime, hydrogen as water by absorption by phosphorus pentoxide, and the ash directly. In order to bring the charcoals to a condition as nearly uniform as possible with respect to sorbed gas and moisture, the sample was placed in a fused quartz boat, heated at 800° for one hour in a stream of carefully purified hydrogen, which was dried by passing over phosphorus pentoxide, and then allowed to cool in the hydrogen. Experiments had shown that this treatment completely removes the moisture and sorbed gas other than hydrogen. It had also been determined previously that the hydrogen adsorbed by the samples at room temperature prior to this heating was much less than 1.0 cc. per g., as would be expected since at ordinary temperature even highly activated charcoals generally adsorb less than 1 cc. of hydrogen per g., which would be equivalent to 0.009% by weight. Since the preheating was carried out in a reducing atmosphere and since an oxidizing atmosphere has always been found necessary for activation, or increase in sorptive capacity of charcoal, it would not be expected that any of the samples would adsorb more hydrogen after the heating than before they were so treated. The temperature, 800°, was chosen so as to be at least 100° lower than the maximum temperature to which the samples had previously been heated, to insure that it would not affect the amount of chemically combined hydrogen. Experiments on several samples showed that varying the length of this preheating in hydrogen from 45 minutes to 11 hours did not influence the final value obtained for the hydrogen content.

After cooling in hydrogen the boat and sample were quickly transferred to a closed weighing vessel, weighed, and finally transferred to the combustion tube and burned. These two transfers to and from the weighing vessel were made as rapidly as possibly in order to prevent re-sorption of gas and moisture from the air.

Two to five, and sometimes more, analyses of each sample were made. From these determinations the mean values given in Table I were found to have the following precisions: hydrogen, ±0.02%; carbon, ±0.3%; ash, ±0.05%. It will be noticed that the total of these three constituents in the table is generally less than 100%. Analyses of anthracite coal generally show some nitrogen and; since this was not determined here, the lack might be due to undetermined nitrogen. That this is not likely, however, is indicated from a consideration of the probable errors which are involved in the combustion of charcoal. First, and probably the most variable, is the error due to re-sorption of water or carbon dioxide or both from the air during the transfers to and from the weighing vessel. One-ninth of the actual weight of such water would be calculated as hydrogen, and similarly three-elevenths of the weight of carbon dioxide would be calculated as carbon. Second, water of hydration or of composition of the ash, and carbon dioxide from carbonates of the ash, would similarly be calculated as hydrogen and carbon. Also, this error in carbon and hydrogen due to the ash would simultaneously directly affect the weight of the ash, since the ash would be weighed as oxide instead of hydrate or carbonate. Thus the errors in such an analysis all tend to give results too low, and it would be expected that the observed totals would be less than 100%; therefore the small percentages unaccounted for may be directly attributed to errors inherent in the method rather than to un-

TABLE I

A. MEAN COMPOSITION OF CHARCOALS AS DETERMINED BY COMBUSTION ANALYSES						B.[b] APPARENT DENSITIES IN		
Sample	% H	% Ash[a]	% C.	Total %	Unaccounted for %	Air	Water	Acetone
1	0.40	3.83	95.6	99.83	−0.17	0.970	1.797 (3)	1.703 (2)
2	.40	4.47	95.0	99.87	− .13	.972	1.745 (2)	1.739 (2)
3	.30	4.20	95.3	99.80	− .20	.974	1.723 (3)	1.723 (2)
4	.38	5.02	94.4	99.80	− .20	.988	1.742 (4)	1.735 (1)
5	.44	5.76	93.8	100.00	.00	1.001	1.815 (3)	1.738 (2)
6	.38	4.43	94.9	99.71	− .29	0.962	1.756 (2)	...
7	.34	3.70	95.8	99.84	− .16	.979	1.757 (1)	...
8	.37	3.82	95.6	99.79	− .21	.976	1.769 (4)	1.746 (2)
9	.23	4.05	95.2	99.48	− .52	.986	1.727 (1)	...
10	.25	4.16	95.2	99.61	− .39	.982	1.729 (2)	...
11	.27	4.25	95.3	99.82	− .18	1.002	1.727 (1)	...
12	.32	4.03	95.8	100.15	+ .15	0.977	1.741 (2)	1.731 (2)
13	.28	4.11	95.5	99.89	− .11	.977	1.730 (3)	1.736 (2)
14	.27	4.00	95.4	99.67	− .33	.972	1.722 (2)	1.724 (2)
15	.29	4.22	95.6	100.11	+ .11	.996	1.728 (1)	...
16	.43	3.88	95.3	99.61	− .39	.970	1.749 (3)	...
17	.34	3.99	95.7	100.03	+ .03	.995	1.710 (1)	...
18	.53	3.12	96.2	99.85	− .15	.898	1.888 (1)	...
19	.35	3.77	95.8	99.92	− .08	.954	1.723 (1)	...
20	.47	2.76	96.2	99.43	− .57	.958	1.845 (1)	...
21	.49	3.23	95.9	99.62	− .38	.910	1.870 (1)	...
22	.28	3.56	96.1	99.94	− .06	.972	1.720 (1)	...
23	.21	4.84	94.8	99.85	− .15	.993	1.724 (2)	1.729 (2)

[a] Analyses of the ash showed that it had the following approximate composition: SiO_2, 42.5–48.0%; Al_2O_3, 36.0–43.0%; Fe_2O_3, 5.8–16.00%; CaO, 2.9–4.7%; with traces of magnesium, sulfur and phosphorus.

[b] Additional density determinations in benzene, ethyl alcohol and tetrabromo-ethane gave for Sample 1, 1.698 (2), 1.707 (2) and 1.696 (1) and for Sample 2, 1.718 (2), 1.717 (2) and 1.723 (1), respectively.

determined constituents. Even if the small percentage unaccounted for were all due to error in the determination of the hydrogen, by including hydrogen due to water, this percentage would be nine times the correction necessary to exclude this error, and hence in almost all cases would be insignificant.

Examination of the data in Table IA shows that the hydrogen content of the charcoals ranges from 0.21 to 0.53%. It may also be observed that there does not appear to be any relation between the ash content and the percentage of hydrogen. This may be considered evidence that the hydrogen was in some way combined directly to the carbon and did not result from dehydration of the ash. Furthermore, if the water weighed had come as such from the ash, the totals of the three constituents, carbon, hydrogen and ash, should be from 1.6 to 4.2% lower than the values tabulated due to calculation of this water as hydrogen. These considerations have led us to believe that the hydrogen determined by the analyses is directly combined with the carbon. The way in which this hydrogen is combined with the carbon is, however, open for speculation. The ratio of carbon to hydrogen atoms in these samples ranges from 15.1 to 37.6. If held by primary valence each hydrogen atom must be held by some one carbon atom. Thus since carbon is also bound to carbon by primary valence it seems reasonable to regard such charcoals as are considered here, not as amorphous carbon nor even as amorphous carbon combined with hydrocarbon, but rather as a continuous series of hydrocarbons, the properties of which vary continuously with composition. This point of view is not inconsistent with the general consensus of opinion on the mechanism of the thermal decomposition of the more complex hydrocarbons.[1] Thus, it has been generally regarded that the complex molecules break down yielding hydrogen, gaseous hydrocarbons containing *few* carbon atoms, free carbon, and residues which tend to polymerize. It has been supposed, furthermore, that the final product of this decomposition is pure, or free, carbon, but it seems doubtful whether pure carbon is obtained until temperatures are reached at which graphitization begins.

The manner in which the hydrogen atoms are held in charcoal and the influence of temperature on the hydrogen content may be pictured as follows. In a charcoal the configuration of carbon atoms, many of which still retain the hydrogen atoms originally attached to them, is somewhat haphazard and is, therefore, a less stable condition than in graphite (graphite being the stable form of carbon) and therefore the atoms tend to arrange themselves as in graphite. Opposing this tendency is the rigidity of the solid, but as the temperature is raised a certain number of the carbon atoms, whose arrangement most closely approximates that of graphite,

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[1] Berthelot, many papers in *Ann. chim. phys.*, **1863–1869**. Haber, *Ber.*, **29**, 2691 (1896). Bone and Coward, *J. Chem. Soc.*, **93**, 1198 (1908).

are able to orient themselves in a graphite lattice, and by so doing transfer the force, which previously had been sufficient to retain a hydrogen atom, to the neighboring carbon atoms. Clearly, as the temperature is raised the mobility of the atoms increases, and therefore hydrogen atoms are continuously given up; but not until the temperature has been raised sufficiently high to allow all the carbon atoms to assume the stable configuration represented by graphite, will the "charcoal" be entirely free from hydrogen. Since in any one piece of charcoal there are a very great number of carbon atoms, it seems probable that the percentage of the atoms at any given temperature which are not able to orient themselves in a graphite lattice will be substantially the same regardless of the source of the charcoal. In other words, the effect is a statistical one. We have experimental evidence, as yet only partially completed, which supports this view.

On this basis, the so-called amorphous carbons, coal, charcoal, etc., would be regarded as polymerized residues resulting from the decomposition of simpler hydrocarbons, the complexity depending on the maximum temperature at which "carbonization" had taken place. It will be shown later that this point of view also offers a logical explanation of the relation between hydrogen content and other properties of the charcoals as determined in this investigation.

Density

The apparent density in air of these samples of charcoal was determined by filling a calibrated tube with a known weight and tamping the tube until constant volume was observed. The values so determined are given in Table IB.

The apparent density in water of all the samples, and of some of the samples in other liquids, was determined by the so-called immersion test. The apparent density of a homogeneous non-porous solid in a liquid is equal to its true density and is independent of the liquid used. This does not appear to be the case with porous solids such as charcoal, and considerable discussion is found in the literature regarding the interpretation of this measurement, especially since the apparent density has been found to be dependent on the liquid used. In view of this situation, and since the value of the true density entered into all the following calculations, it was deemed advisable to use more than one liquid for some of the determinations as a check on the values obtained with water as the liquid. The other liquids chosen were acetone, benzene, ethyl alcohol and tetrabromo-ethane.

The experimental procedure was to put 3–5 g. of material in a tube which was then attached to a vacuum system and evacuated at 400° by means of a mercury condensation pump until a pressure of $<10^{-4}$ mm. was attained, allowed to cool sufficiently to handle and sealed off while the vacuum was being maintained. The tube was then weighed in air, immersed in the freshly distilled liquid, which was held close to its boiling point, and opened below the surface. The tube was then weighed in the liquid, suspended by a fine platinum wire from one arm of a sensitive balance. Weighings were repeated at definite intervals, the tube remaining open to the liquid in which it was immersed, until substantially constant weight was attained. All the samples showed an increase in weight with time. During this period the liquid in which the sample was immersed was kept out of contact with air to avoid sorption of water vapor by the liquid accompanied by increase in density. When constant weight had been reached the tubes were broken and the weights of glass and charcoal obtained. All weights were corrected to a vacuum and the density, S, was derived by means of the following formula,

$$S = \frac{(A-B)}{(A-B)-(C-D)}, \qquad (1)$$

where A is the weight of glass and charcoal in a vacuum; B is the weight of glass in a vacuum; C is the weight of glass and charcoal in liquid corrected from temperature and density of liquid to weight if immersed in water at 4°, that is, $C = A - \frac{A-C'}{d_{t^\circ}}$ where C' is the observed weight in the liquid at t° and density d_{t°; and D is the weight of glass in liquid corrected as C.

The precision of this measurement was found to be ±0.005 by making from two to four independent determinations for several of the samples. The number of determinations made on each sample is given in Table IB in brackets following the mean value for the apparent density.

There appear to be two groups of investigators with conflicting data and ideas regarding the influence of different liquids on the observed apparent density. According to the first group[2] the final value of the apparent density in any liquid depends on the penetrability of the liquid, that is, the ratio of the surface tension, σ, to the viscosity, η. It is evident that the driving force of a liquid entering a capillary is measured by the surface tension, while the retarding force is the viscosity, and that therefore the speed of penetration should vary as the ratio σ/η. That this relation follows from Poiseuille's law for the rate at which a liquid penetrates a small cylindrical capillary has been shown by Washburn.[3] It should be pointed out that this relation does not hold unless the liquids all wet the surface to the same degree. According to Harkins and Ewing,[4] the compressibility of the liquid at 12,000 atmospheres' pressure determines the final value of the apparent density, and they found that the density of one charcoal sample ranged from 1.843 in water to 2.129 in pentane with nine intermediate values in as many liquids arranged in the order of their compressibility at this pressure, in cases where the compressibility data were available. This viewpoint is qualitatively supported by the work of Lamb and Coolidge[5] on the heat of sorption of eleven liquids by charcoal which was interpreted to indicate a compression of

[2] (a) Cude and Hulett, THIS JOURNAL, **42**, 391 (1920). (b) Rose, *J. Ind. Eng. Chem.*, **14**, 1047 (1922).

[3] Washburn, *Phys. Rev.*, **17**, 374 (1921).

[4] Harkins and Ewing, THIS JOURNAL, **43**, 1787 (1921).

[5] Lamb and Coolidge, *ibid.*, **42**, 1146 (1920).

the sorbed liquids amounting to 37,000 atmospheres. From density determinations in chloroform and water, Williams[6] also concluded that the liquid in the capillaries was under a pressure of 11,000 to 12,000 atmospheres. Similarly, Briggs[7] from measurements of sorption of nitrogen at —190° was led to believe that the density 1.88 observed in water was 0.55 too high due to compression of the water, giving a corrected value of 1.33. Harkins and Ewing[4] believe the correct value for the true density of charcoal to be about 1.60.

Due to the fact that the capillaries in charcoal have been shown to be of molecular dimensions (10^{-8} cm.) in diameter, both Cude and Hulett and Harkins and Ewing considered a possible effect of the molecular size of the liquids used, but no definite influence could be detected.

The physical properties of the liquids used in this investigation which have been regarded as influencing the observed values of the apparent density are given in Table II.

TABLE II[a]

PROPERTIES OF LIQUIDS USED IN DENSITY DETERMINATIONS AT 25°

Liquid	Surface tension Dynes per cm. (σ)	Viscosity in abs. units (η)	Penetrability σ/η	Coefficient of compressibility $\beta \times 10^6$, 100–500 Megabars, 20°	van der Waals' "b" $\times 10^4$
Water	72.8	0.0089	8180	42.7	14
Acetone	23.5	.0035	6720	90.1	44
Benzene	28.9	.0064	4510	72.1	54
Ethyl alcohol	22.1	.0108	2050	81.6	38
Tetrabromo-ethane	47.8	.0164 (calcd.)	3430	..	about 80

[a] The values, with the exception of the coefficient of compressibility, for water, acetone, benzene and ethyl alcohol were obtained from Landolt-Börnstein-Roth "Tabellen." The coefficients of compressibility are from Richards and others in THIS JOURNAL, **34**, 972 (1912) and **38**, 989 (1916). The values for tetrabromo-ethane were obtained as follows. Surface tension in International Tables for **1921**; viscosity calculated according to Thorpe and Rodgers [*Phil. Trans.*, **185A**, 397 (1894)]; van der Waals' "*b*" calculated from Landolt-Börnstein-Roth "Tabellen."

While no single constant can be given for the coefficient of compressibility for all ranges of pressure, since this varies with the degree of compression, the values given in the table probably represent the order of the compressibility of the liquids at all pressures.

Now it is evident from Table IB that the values of density observed are almost independent of the liquid used. Notable exceptions are Samples 1, 5 and 8. Sample 1 showed in the peculiar character of its increase in weight with time in water the probable existence of an influence lacking in the other determinations. A rapid increase in weight was observed for about two weeks and then a continued, almost constant, rate of increase for another two months, at the end of which time the experiment

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[6] Williams, *Proc. Roy. Soc. London*, **98**, 223 (1920).

[7] Briggs, *ibid.*, **100**, 88 (1921).

was stopped. Similarly, Sample 5 contains the greatest amount of ash. These facts seem to indicate a possibility of a hydration of the ash which would be lacking with the other liquids. It is also evident from this table that in general the value of the density tends to be higher in water than in the other liquids, which is directly opposed to the idea of an influence of the compressibilities of the liquids since the compressibility of all the other liquids is greater than that of water. On the other hand, the data are insufficient to afford any support to the idea that the penetrability is a main factor in determining the final value. Likewise, no effect of molecular size, which is roughly given by van der Waals' "*b*" in Table II, is noticeable.

Attention should again be called to the fact that these samples of charcoal were inactive. It would be expected that, in case compressibility did influence the observed density value, this effect would be greater the greater the sorptive capacity of the sample of charcoal. As will be shown later, the sorptive capacity of these samples varied over a range of fifty to one, from which it is evident that over this range, for the small capacities observed, any compressibility effect does not parallel the sorptive capacity.

Certain other considerations render the acceptance of the compressibility hypothesis questionable. The calculated pressures are those which would cause the pore volume, as derived from experiments with different liquids, to be independent of the liquid. Since the compression is calculated from the total volume of liquid in the capillaries, the volume of which is made up almost exclusively of pores with diameters greater than ten molecular diameters, while the range of molecular attraction, effective in adsorption, is of the order of one molecular diameter,[8] it is obvious that this calculated pressure is much too low, and that an almost inconceivably great pressure is required to produce the calculated effects.[9] Also, it is difficult to understand the penetration of benzene into the capillaries of the charcoal, if such pressure effects exist, since benzene solidifies at 25° under a pressure of 600 atmospheres. Furthermore, if the liquids were already under a pressure of 12,000 atmospheres, it is difficult to explain how the application of an additional external pressure of 500 atmospheres could cause the apparent density of a charcoal in water to increase from 1.85 to 1.90, which is equivalent to increasing the volume of liquid in the pores 100%, as was observed by Cude and Hulett.[2a]

The main objection to the penetration theory is expressed by Harkins and Ewing, whose determined values of apparent densities in different

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[8] See discussion on this point in Gustaver, *Kolloidchem. Beihefte*, **15**, 184 (1922).

[9] Attention should be called to the fact that this pressure could not be exerted by the capillaries, since the liquid would be under tension in the capillaries. The tension in capillaries of 50 × 10^{-8} cm. may be calculated as equivalent to a negative pressure of —1000 atmospheres and in capillaries of 10 × 10^{-8} cm. to a negative pressure of —5000 atmospheres. (Ref. 8, p. 206.)

liquids are not in the order of the penetrability ratio, σ/η. This does not seem a valid objection if the different liquids do not wet the charcoal to the same degree,[10] and this is tacitly assumed by Harkins and Ewing in their statement that "mercury penetrates neither the capillaries nor the micropores" where micropores are considered to be less than 10^{-5} cm. in diameter. Now it has been shown by Gustaver[11] that other liquids do not wet charcoal to the same degree and so no rigid parallelism between the penetrability ratio and the observed value of the apparent density in a liquid should be necessarily expected.

If, as is assumed in the previous discussion on the hydrogen content, charcoals are to be regarded as hydrocarbons rather than as amorphous carbon and such hydrocarbons gradually approach graphite in properties as the percentage of hydrogen decreases, it becomes necessary to assume that the observed apparent densities in the different liquids are all too low rather than too high and that the true density is not far different from that of graphite,[12] 2.25. In a porous material such as charcoal there must be pores ranging from zero to some indefinite maximum. Therefore, there must also be a certain impenetrable volume of capillaries into which no liquid can penetrate.[13] The highest apparent density would, therefore, be obtained in that liquid in which this impenetrable volume was a minimum. From this point of view it is very interesting that the maximum values of apparent density in different liquids approach but never equal that of graphite. The highest value obtained by Harkins and Ewing is 2.129 in pentane. Also, this point of view can readily explain the effect of external pressure observed by Cude and Hulett and cited above as due to increasing the penetration of the water molecules into previously unfilled capillaries.

Gas and Moisture Content

Since the samples under investigation were inactive or, in other words, sorbed little gas or moisture, and since it was desired to determine the quantities of all the commonly occurring gases, the usual methods of gas analysis could not be used. Therefore, a method of refinement was developed[14] for determining carbon dioxide, water (vapor), oxygen, carbon monoxide, hydrogen and nitrogen in the small quantities in which they existed on the samples. It is recognized that the information gained

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[10] See Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m.b.H., Leipzig, 2nd ed., **1922**, pp. 211 and following. Langmuir, *Gen. Elec. Rev.*, **24**, 1025 (1921).

[11] Ref. 8, p. 323.

[12] This is qualitatively supported by the failure of X-ray methods to determine any essential difference between amorphous carbons and graphite; see p. 843.

[13] Compare the "ultraporosity" of Herbst, *Biochem. Z.*, **115**, 204 (1921).

[14] The application of the principles involved in this method was first suggested by Mr. J. B. Ferguson.

by such an analysis of the gas on the sample probably has less value from a strictly scientific viewpoint than might be gained from measurements of sorption capacity for any one gas, since little is known of the sorption of mixtures of gases. However, since it was necessary to make these measurements for another purpose, they are given here, especially since it is felt that the measurements do offer a useful indication of the relative sorptive capacity of the different samples.

The apparatus assembled for the determination of these gases is shown diagrammatically in Fig. 1. It consists primarily of a sample tube, S; mercury cut-outs, M_{1-8}; liquid air traps, T_{1-6}; mercury condensation pumps for producing high vacua, P and P_3; a Töpler pump, P_2, for the transfer of gas; McLeod gages, G_2, capable of reading pressures from 2 mm. to 10^{-6} mm.; two manometers, G_1; a measuring buret, B; and two tubes in a furnace, F_2, maintained at 320°, and containing copper and copper oxide, respectively. Preliminary to a determination, 5 to 7 g. of carbon was carefully weighed into Tube S and the air washed out with a stream of chemically pure dry nitrogen, prepared by warming a solution of sodium nitrite and ammonium chloride, and drying over phosphorus pentoxide. In order that the change in the equilibrium of the gas sorbed by the sample might be about the same in each case the stream of nitrogen was passed through a capillary tube at constant rate for 90 seconds in each determination. The stopcock to the tube was then closed, the room temperature and barometric pressure recorded, the tube attached to the apparatus and the whole system evacuated to $<10^{-5}$ mm. When the furnace, F_2, had reached 320°, the mercury was raised in M_6, making the apparatus a closed system from the sample tube to that point. Liquid air was placed around the traps T_{1-5}, and the stopcock of the tube containing the sample opened. On raising the temperature of the furnace, F_1, over a period of 24 hours to 360°, the gas on the sample was given up to the high vacuum maintained by the pumps, P_1 and P_2. On passing through the trap, T_1, all carbon dioxide and water vapor were removed from the gas. The residual gas, consisting of oxygen, hydrogen, carbon monoxide, nitrogen and possibly some methane, next passed over the hot metallic copper which removed the oxygen as oxide. Advantage was here taken of the fact that the charcoal samples were all prepared in a reducing atmosphere and always contained an excess of reducing over oxidizing gases, so that the oxide was immediately reduced

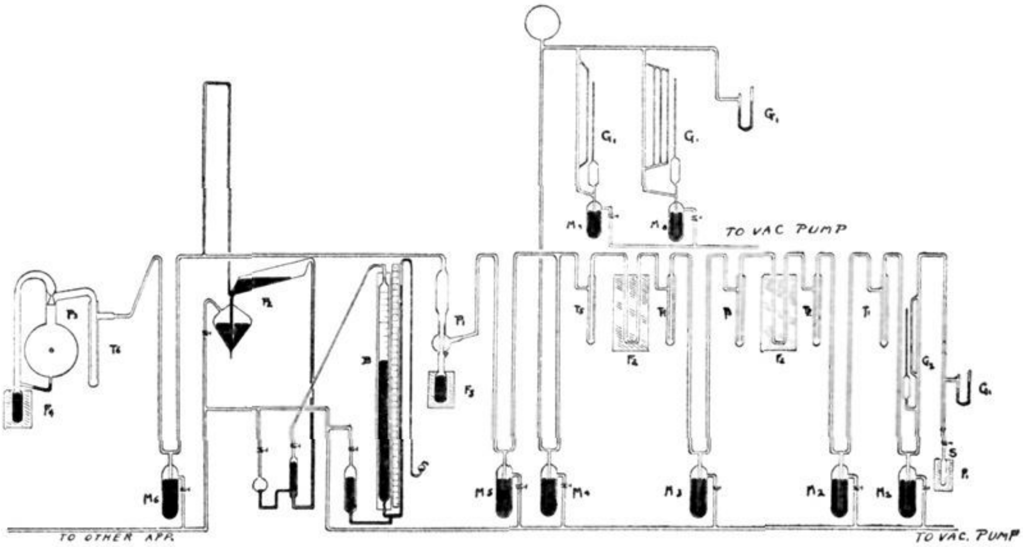

Fig. 1.—Apparatus.

by some carbon monoxide or hydrogen and collected in the traps T_2 and T_3 as water vapor and carbon dioxide. The remainder of the hydrogen and carbon monoxide was collected in traps T_4 and T_5 as water vapor and carbon dioxide, after passing over the copper oxide. The nitrogen, together with whatever methane might be present, was collected by means of the transfer pump and measured directly in the buret B. When the pressure over the sample was determined to be $<10^{-5}$ mm., the mercury was allowed to rise in the cut-outs M_1, M_2, M_3 and M_5. The volume between M_3 and M_5 was held constant and was previously determined to be 1229 cc. with a probable accuracy of 1–2%. It was, therefore, possible to determine by fractionation the amount of carbon dioxide and water vapor resulting from the oxidation of the carbon monoxide and hydrogen from the samples. Carbon dioxide snow was used as the bath for the fractionation. After each pressure was determined, the residual gas was pumped out. By a series of three fractionations, the total amounts of carbon monoxide, hydrogen, oxygen, carbon dioxide and water vapor were determined. All volumes of gas were reduced for purposes of comparison to standard conditions of temperature and pressure. The amount of nitrogen sorbed was equal to the amount obtained less the volume of the Tube S corrected for the volume occupied by the sample.

By the procedure described above, a series of five determinations was made on one sample and two on each of four other samples, from which the precision of the measurements was determined. Only one determination was made on each of the remaining 18 samples. The results of the

TABLE III

THE OBSERVED GAS AND MOISTURE CONTENT OF CHARCOALS EXPRESSED IN CC., N. T. P., PER GRAM

	1	2	3	4	5	6	7
Sample	±0.01 H_2O vapor	N_2 ±0.05	CO_2 ±0.003	CO ±0.003	O_2 ±0.003	H_2 ±0.003	Σ(2–6)
1	4.82	0.73	0.565	0.043	0.013	0.048	1.40
2	6.48	.84	.616	.002	.001	.000	1.46
3	1.12	.17	.128	.003	.001	.001	0.30
4	2.45	.33	.199	.006	.001	.001	0.54
5	4.07	.78	.502	.007	.001	.007	1.29
6	7.10	.59	.446	.006	.001	.001	1.04
7	5.20	.62	.405	.007	.002	.062	1.10
8	3.55	.68	.413	.020	.001	.024	1.14
9	1.97	.06	.558	.027	.002	.001	0.65
10	5.09	.12	.142	.020	.000	.002	.28
11	2.32	.01	.123	.012	.002	.003	.15
12	8.22	.25	.401	.035	.005	.007	.70
13	4.83	.06	.186	.022	.003	.046	.26
14	0.66	.09	.087	.010	.002	.004	.19
15	3.32	.06	.077	.018	.007	.074	.24
16	5.35	1.00	.668	.050	.020	.030	1.77
17	3.83	0.08	.394	.043	.016	.024	0.56
18	19.76	2.60	2.61	.151	.056	.043	5.46
19	2.42	0.15	0.165	.025	.008	.031	0.38
20	14.67	0.57	2.13	.112	.030	.033	2.89
21	14.34	1.83	2.52	.110	.028	.058	4.55
22	3.79	0.09	0.156	.024	.004	.005	0.28
23	0.89	0.00	0.035	.013	.005	.055	0.11

analyses together with their determined precisions are given in Table III. The volumes given are calculated per gram of charcoal free from gas and moisture.

Undoubtedly the total gas sorbed, as given in Col. 7, is less than if no water vapor were present, since the water must render some of the surface inaccessible for gas sorption. However, it is of interest to determine how the data accord with a monomolecular theory of adsorption. For simplifying the calculations, it was assumed that the water present occupied the smallest capillaries, which would be true if equilibrium were established, and that no gas was dissolved in this water, which probably is not true. These calculations showed that, with three exceptions, the thickness of the sorbed layer was less than 3×10^{-8} cm. or, in other words, the extents of the surfaces[15] were more than enough to hold the gas in a monomolecular layer.

The table shows that the gases consisted mainly of carbon dioxide and nitrogen which, with few exceptions, were present in approximately equivalent amounts. The exceptions occur generally when the nitrogen was present in amounts less than or equal to the experimental error of its determination. This circumstance is fortunate in that a comparison of the total amounts sorbed by the differents amples does, therefore, have greater significance. Since it is generally stated in the literature that oxygen is sorbed by charcoal to a greater extent than nitrogen, the presence of such small quantities of oxygen must be interpreted to mean that the greater portion of oxygen was removed by the preliminary "washing-out" of a sample with nitrogen, and was replaced by nitrogen.

Porosity

It has been shown[16] that not only does the sorption of water vapor by charcoal consist in filling the fine pores in accordance with the known laws of capillarity, but also that the sorption isotherm gives directly the distribution of the capillaries according to diameter, since the lowering of the vapor pressure is greater, the smaller the diameter. Since both the diameters and volumes of the capillaries may thus be determined by measuring the sorption isotherms for water and assuming the capillaries to be cylindrical in structure, it therefore becomes possible to calculate the surface of the charcoal within the pores. While these values probably do not give any exact measure of the extent of surface in the samples, nevertheless, they are comparative. Accordingly, sorption isotherms for water of all 23 samples were determined.

The apparatus used for this determination is shown in Fig. 2. It consisted of sample tubes, S_{1-3}; a tube containing water, A; a McLeod gage, G_1; a closed-arm manometer,

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[15] For the method of calculation of surface see the next section.

[16] (a) Lowry and Hulett, This Journal, 42, 1393 (1920). (b) See also Ref. 8, p. 306.

P. G.; a mercury condensation pump, P; and mercury cut-outs, M_{1+2}. The volume enclosed by M_1 and M_2 was known. Samples of about 3 g. were weighed into the tubes, the tubes then attached to the apparatus and evacuated at 250° to $<10^{-5}$ mm. The stopcocks were closed and the tube was immersed in a thermostat kept at 20° ±0.03, in which there was also immersed the water tube, A. The entire system was then evacuated again to remove all the air admitted during the transfer of the tubes to the thermostat. Water vapor was then admitted to the known volume and its pressure read on the manometer by a depth gage to ±0.04 mm., as described by J. B. Ferguson.[17] One tube was then opened and the decrease in pressure measured until equilibrium was established. By application of the gas laws, the amount of water vapor sorbed was calculated and reduced to cubic millimeters of liquid at 20°. Five or more points were determined on each isotherm in this way. The volume of liquid sorbed at the saturation point, which had to be determined by a short extrapolation, represented the total volume of the capillaries. By a series of measurements on one sample the precision was found to be better than ±3%. The relatively low order of the precision was found to be due largely to the fact that equilibrium is very slowly reached, especially as the sample nears saturation, requiring at times at least 24 hours.

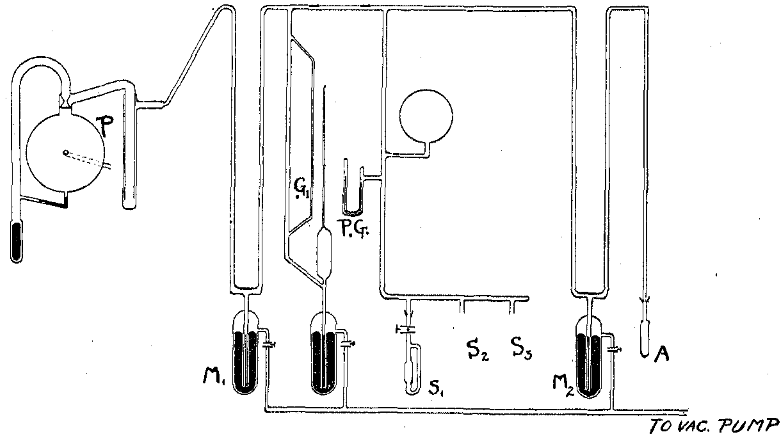

Fig. 2.—Apparatus.

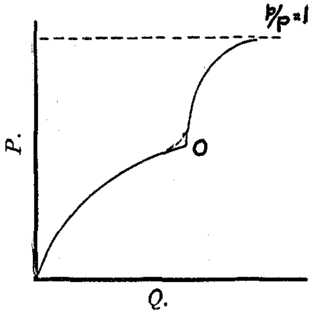

Fig. 3.—Sorption isotherm of water vapor by charcoal, typifying results obtained on over 80 isotherms.

The form of the curve in all cases was that shown in Fig. 3, having a break at 0. Later, more detailed curves have shown that the break at 0 is not sharp but curved as shown by the dotted line. The significance of the break is not known definitely, but can probably be best explained as representing the point where the walls of the capillaries are completely wetted and the menisci begin to flatten out.[18] In such a case the maxi-

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[17] Ferguson, *J. Wash. Acad. Sci.*, **10**, 285 (1920).

[18] Compare Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

mum diameters of the capillaries are represented by this point, and can be calculated by means of the equation given by Anderson.[19]

$$r = \frac{2T \cdot S_0 \cdot 0.4343}{d\ p_0 \log p_0/p_1}, \quad (2)$$

where r is the capillary radius; T the surface tension in dynes per cm. = 72.8; S_0 the vapor density = 1.723×10^{-5}; d the density of liquid = 0.9982; p_0 the maximum vapor pressure at 20° = 2.32×10^4 dynes per cm.; and p_1 is observed pressure.

The surfaces were calculated from the isotherms as follows. From the smoothed curve of the isotherm the value of Q, the quantity sorbed for each mm. pressure was read. These values of Q were used then in calculating the aggregate surface of the capillaries of diameters corresponding to the given pressures; that is, Q_1 from 0 to 1 mm. represented the volume of capillaries of diameter corresponding to $p_1 = 1$; Q_2, the volume between 1 and 2 mm., corresponding to $p_1 = 2$; etc., to the saturation point. The area corresponding to Q assuming the capillaries to be cylindrical is $a_1 = 2\pi r h_1$, where $h_1 = \frac{Q_1}{\pi r^2}$ and r is calculated according to Equation 2 with

TABLE IV

PROPERTIES OF CHARCOALS AS DERIVED FROM MEASUREMENTS OF SORPTION OF WATER VAPOR

Sample	Position of break p/P	Position of break Q (cu. mm.)	Pore volume vol. sorbed at $p/P = 1$ (cu. mm.)	Diameter of largest capillaries by Equation 2 (10^{-8} cm.)	Total surface m^2/g.
1	0.72	11.1	11.7	66	5.8
2	.57	15.3	17.9	38	13.8
3	.78	3.7	4.6	86	2.5
4	.62	5.9	7.8	45	5.5
5	.59	11.2	14.9	42	8.8
6	.48	13.5	19.0	29	15.4
7	.49	15.3	19.2	30	15.3
8	.56	13.9	16.2	38	11.6
9	.59	2.8	3.9	42	2.1
10	.69	4.7	5.1	59	4.1
11	.68	4.1	4.6	55	3.8
12	.57	7.2	9.6	39	7.2
13	.54	4.8	6.6	36	5.1
14	.86	1.6	1.9	150	1.0
15	.68	3.5	4.5	57	3.5
16	.69	15.8	18.2	58	8.9
17	.57	3.7	4.9	38	3.4
18	.57	40.0	44.8	38	32.2
19	.42	2.8	4.9	25	3.4
20	.61	17.5	19.8	44	15.9
21	.64	24.7	26.8	48	17.8
22	.39	2.9	4.8	23	3.8
23	..	..	0.9	...	0.6

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[19] Cobb and Greenwood, *Gas Journal*, **158**, 37 (1922).

$p_1 = 1$; similarly for Q_2, etc. The total area then is $A = \Sigma 2\pi rh$ where $\Sigma 2\pi rh$ is the sum of the individual areas a_1, a_2, etc.

In Table IV is given a summary of the values of some of the properties which can be determined by a study of the sorption of water vapor. The pore volumes varied from 0.9 cu. mm. per gram to 44.8 cu. mm., as compared with pore volumes of 273 cu. mm. to 854 cu. mm. for gas mask charcoals, which have been activated,[16a] while the surfaces were also proportionately smaller, varying from 0.6 to 32.2 square meters per gram. The calculated diameters of the largest capillaries are seen to range from about ten to about one hundred times atomic dimensions.

Discussion

As can be seen from the curves in Fig. 4, the data obtained in this investigation show that there is a definite correlation of such properties as porosity, sorptive capacity and density, with the chemical composition of so-called charcoal sorbents, with particular reference to the hydrogen content of the charcoal. It will be noticed that the points show consider-

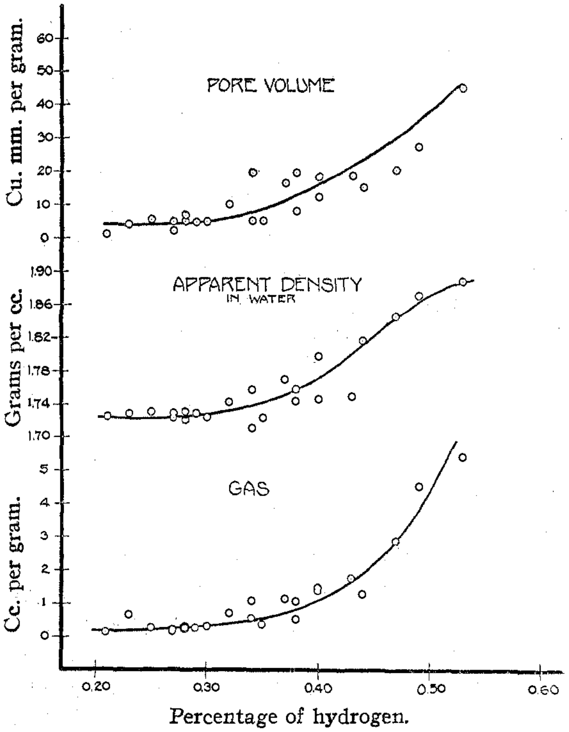

Fig. 4.—Relation of the total gas sorbed, the apparent density in water, and the pore volume to the percentage of chemically combined hydrogen of certain charcoals.

able deviation from the curves drawn in Fig. 4. However, since the samples were taken from material prepared under manufacturing conditions on a large scale without the accurate control of conditions possible in a laboratory, and since certain indeterminate errors are involved in the measurement of the properties considered, as pointed out in the discussion of each measurement, it seems quite remarkable that such good agreement between the curves relating the properties and the experimental data was attained.

Relation of Pore Volume to Hydrogen Content of Charcoals.—It was pointed out earlier that these 23 samples of charcoal were all from the same source and that they differed primarily in the maximum temperature to which they had been heated. Also, the data available on their preparation indicated qualitatively that those samples with the highest hydrogen content were heated at the lower temperatures (about 900°) and, conversely, that those samples with the smallest hydrogen content were heated at the higher temperatures (about 1200°). Resistance measurements made on these samples support this conclusion, although these data are not included in this report. Cobb and Greenwood[19] have shown that there is a definite shrinkage in coal when heated at temperatures above 850°, and this is in harmony with the results presented in this paper, which show that the pore volume decreases with decreasing hydrogen content, or, from the above considerations, with increasing temperature. This must mean that shrinkage is taking place and closing off the pores or decreasing their diameters and that the total shrinkage of the charcoal increases with increasing temperature. Furthermore, if the viewpoint is correct, that the elimination of hydrogen from charcoals by heat is accompanied by a union of two or more carbon atoms which previously were not so united, it follows directly that the decrease in hydrogen content would effect shrinkage of the charcoal, thereby decreasing the volume of capillaries into which water could penetrate as in our measurements of pore volume.

Relation of Apparent Density in Water to Hydrogen Content, Pore Volume and Gas Content of Charcoals.—The apparent density in water, when plotted against the hydrogen content as in Fig. 4, gives an S-shaped curve which has a minimum at about 0.2 to 0.3% of hydrogen and which tends to reach a maximum between 0.5 and 0.6%; between these two there is a region of apparent instability between 0.3 and 0.5% in which the density rises quite rapidly with increasing hydrogen content. That the indicated maximum is real is suggested by the fact that this value of the apparent density in water is the same as that which is obtained generally for all types of porous charcoals. Direct evidence has recently been obtained on a sample of activated coconut charcoal which has an apparent density in water of 1.815 and a hydrogen content of about 0.8%. The fact that the apparent density in water decreases with decreasing hydrogen content appears at first a contradiction of the hypothesis that the samples with the least hydrogen content most closely approach graphite in properties. The following considerations will show that such contradiction is not real. As has been pointed out several times previously, the hydrogen content of the charcoals decreases as the maximum temperature to which they have been heated increases, while simultaneously the shrinkage increases. The assumption was also made that the diameters of the capillaries have zero as their lower limit and that hence there must be a certain volume of capillaries of diameters less than the diameter of the molecules of the entering liquids. The observed relationship between the apparent densities in water and the hydrogen content of the charcoals is a logical consequence of these assumptions. Thus, in the case of the charcoals which have not been heated very high, and hence have high hydrogen content, the volume of the impenetrable space is relatively small, but as the temperature is raised and the material begins to shrink this impenetrable volume becomes relatively larger. Thus it follows that the apparent densities in water of the samples of low-hydrogen content should be lower than those of high-hydrogen content, as was observed.

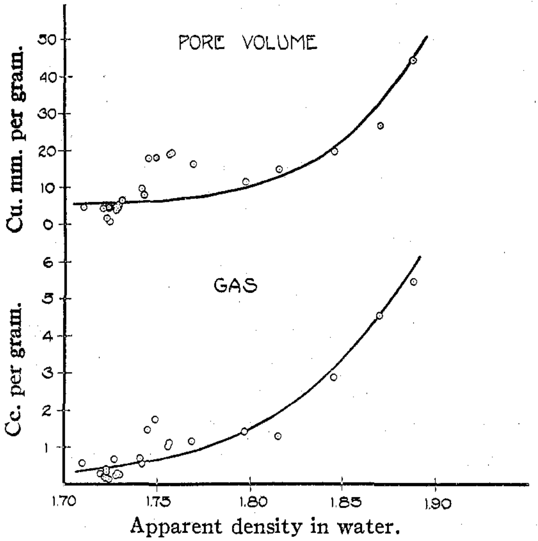

Fig. 5.—Relation of total gas sorbed and pore volume to the apparent density in water of certain charcoals.

While it is believed that the above explanation of the relation of the apparent density in water of the charcoals to the hydrogen content is correct, proponents of the theory that the compressibility of the immersion liquid determines the apparent density may emphasize the relation of the apparent density either to the pore volume or to the gas content, as shown in Fig. 5, rather than to the hydrogen content. The fact that the increase in pore volume, and therefore the surface available for gas sorption, does parallel the increase in the apparent density in water might mean to them that the compressive effects become more noticeable in the samples of larger pore volume and hence give the larger value of the apparent density as observed. As may be recalled, however, it was pointed out in the discussion on the influence of the immersion liquid on the determined value of the apparent density (p. 832) that no indication of compressive effects was obtained for these samples. It would seem, therefore, that the observed relationship between the apparent density in water and the pore volume and gas content of the charcoals is significant only of their mutual relationship to the hydrogen content, which is an indication of the previous heat treatment of the samples.

Relation of the Gas Content of the Charcoal to the Hydrogen Content.—The experimental data, presented in Fig. 4, show that the charcoal which contains the most hydrogen has the largest sorptive capacity. It is of interest that the sorptive capacity of a sample of activated coconut charcoal having a hydrogen content of about 0.8% was found to be about five times that of the highest of the 23 samples under consideration, which, by a long extrapolation, is what might be expected from Fig. 4. This relationship, together with those previously discussed, has led to a picture of the make-up of charcoals which, so far as is known, is in accord with all existing published data on charcoal. The data here presented do not, however, seem altogether compatible with the theory relating sorptive capacity to methods of preparation given by Lamb, Wilson and Chaney[20] and later more fully developed by Chaney.[21]

It has been suggested[22] that the so-called amorphous carbons prepared from hydrocarbons, coal, etc., and the various charcoals are not pure carbons but either highly complex hydrocarbons high in carbon and low in hydrogen content, or mixtures of such hydrocarbons. This point of view is supported by the experimental data presented in this paper, since it has been shown that charcoal prepared by heating anthracite coal retains measurable quantities of combined hydrogen at all temperatures up to 1200°, that the hydrogen content is a function of the maximum temperature to which the charcoal was heated, and would not be zero until above 1500°.[23] That the element, carbon, does not exist as such in any crystalline form

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[20] Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, **11**, 420 (1919).

[21] Chaney, *Trans. Am. Electrochem. Soc.*, **36**, 91 (1919).

[22] For instance, see Bancroft, *J. Phys. Chem.*, **24**, 127 (1920); Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., **1923**, p. 569.

[23] This is further supported by the data of Lowry and Hulett, Ref. 16a, p. 1415, Table I.

other than graphite and diamond is supported by the results of X-ray analysis.[24] Amorphous carbon is regarded by Debye and Scherrer as differing from graphite only in the size of the crystals. The essential identity of graphite and amorphous carbon was established by Asahara by the X-ray analysis of 34 different types of carbon, including those from the thermal decomposition of such gases as carbon monoxide, acetylene, and carbon disulfide, and he likewise suggests that the word "amorphous" be replaced by "extremely minutely crystalline." In accordance with the view presented previously, it would be expected that the samples having the larger amount of combined hydrogen would have smaller groups of carbon atoms in regular array (that is, smaller "crystals" of carbon), and that the average size of these regular groups would increase with decreasing hydrogen content until, when the latter has been reduced to zero, growth of these smaller "crystals" to the structure characteristic of natural graphite is possible.

In accordance with this viewpoint we might expect that as the hydrocarbon decomposition proceeds with rise of temperature there would be a progressive increase in what might be termed the degree of unsaturation of the complex, and that this degree of unsaturation would reach a maximum and subsequently fall off to zero as one approaches graphite. The fact that charcoals prepared at lower temperatures, and having higher hydrogen contents, have higher sorptive capacities would indicate that this maximum in the degree of unsaturation is reached at a temperature lower than those to which any of the twenty-three samples studied were heated. Heating above this temperature would cause a decrease in hydrogen content accompanied by a "doubling up" of the unsaturated groups, thus decreasing the amount of unsaturation. This offers an explanation for the gradual transition of low to high sorptive capacity shown in Fig. 4 and by charcoals in general. That the degree of unsaturation should thus influence the sorptive capacity is consistent with modern ideas of sorption, in which the effective forces are regarded as those unsatisfied by the primary valences.

The action of oxidizing agents on charcoals to increase their sorptive capacity might then be considered as due to an increase in the extent of surface by the production of capillaries and, simultaneously, a splitting up of the solid polymerized residues, increasing the degree of unsaturation. Briggs[25] has already suggested that "activation" is the effect of disrupting the "solid polymers" which he regards as the ultimate structure of charcoal, which idea is supported here. Hence, it is likely that different

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[24] Debye and Scherrer, *Physik Z.*, **18**, 291 (1917). Kohlschütter, *Z. anorg. Chem.*, **105**, 35 (1918). G. Asahara, *Japan J. Chem.*, **1**, 35 (1922). Also, data from these Laboratories, as yet unpublished.

[25] Briggs, *Proc. Roy. Soc. London*, **100**, 88 (1921).

surfaces may have different degrees of unsaturation and be capable of holding different amounts of gas per unit area. This is in accord with the data obtained in this investigation, as may be seen from Fig. 6. In this figure is plotted the amount of gas held by the samples against their extent of surface. It may be observed that the amount of gas sorbed by a charcoal was not strictly proportional to the extent of surface, but that some surfaces were capable of holding more gas per unit area than others. These surfaces, therefore, would be regarded as having a higher degree of unsaturation per unit area than the others. In the terminology used by Langmuir[26] in his theory of adsorption, the degree of unsaturation would be a measure of the number of "elementary spaces" per unit area.

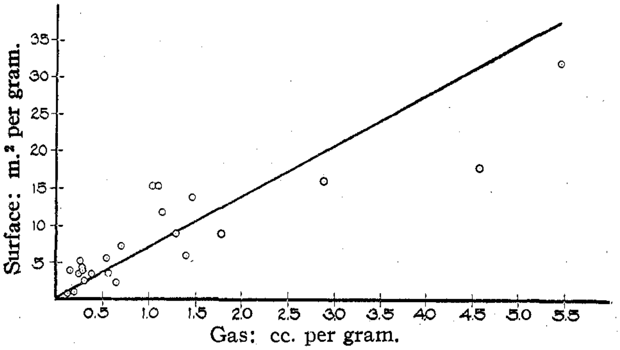

Fig. 6.—Relation of total gas sorbed to extent of surface of certain charcoals.

It has been observed that charcoals lose their sorptive capacity when heated to high temperatures.[27] Such deactivation may be ascribed either simply to a repolymerization or to a repolymerization together with a decrease in surface by shrinkage and closing off of pores. If the temperature is kept low enough to avoid shrinkage, it seems probable that the number of times the cycle of activation-deactivation can take place is limited only by the fact that the mass of the material is decreased each time the sample is activated.

It is not inconsistent with this point of view that graphite itself can be activated. It is unlikely, however, that the ratio of surface to mass can by ordinary means ever be made as large as in the porous carbons, and hence its maximum sorptive capacity would be less. Isotherms of carbon dioxide, nitrogen and hydrogen on graphite from graphitic acid at temperatures from —180° to 100° and pressures to one atmosphere show a sorptive capacity of about one-third that of a commercial activated coconut charcoal. Similarly, if pure carbon could be made from carbon

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[26] Langmuir, This Journal, **40**, 1361 (1918).

[27] See experiments of H. B. Lemon, *Phys. Rev.*, **9**, 336 (1917); *Proc. Nat. Acad. Sci.*, **5**, 291 (1919).

monoxide, it should have a very high sorptive capacity, due to less polymerization than takes place in hydrocarbons.

I take great pleasure in acknowledging my gratitude to Dr. John Johnston for the interest with which he has followed this work and the many helpful suggestions he has offered in the preparation of this paper.

Summary

1. Measurements of chemical composition, apparent density in air and different liquids, sorptive capacity, and porosity, as determined by sorption of water vapor, have been made on 23 samples of nonactivated charcoal prepared from anthracite coal.

2. It was found that charcoal so prepared retained 0.21 to 0.53% of chemically combined hydrogen even after being heated at temperatures from 900° to 1200°. Indications were that the hydrogen content was a function of the maximum temperature at which the samples were heated, the higher the temperature the lower the hydrogen content, and that carbon free from hydrogen would not be obtained until temperatures at which graphitization occurs. It was pointed out that this is in accord with the viewpoint previously expressed in the literature that amorphous carbons are not pure carbon but are hydrocarbons, high in carbon and low in hydrogen.

3. Apparent density measurements of these samples of charcoal in different liquids showed that the values obtained were practically independent of the liquid used as the immersion fluid. These data were considered from the point of view of the penetrability hypothesis of Cude and Hulett and the compressibility hypothesis of Harkins and Ewing. The data supported neither theory. A consideration of the values of these apparent density measurements in different liquids was undertaken, assuming that the charcoals were complex hydrocarbons approaching graphite in properties as the hydrogen content decreased. This indicated that the observed apparent densities were all too low, due to incomplete penetration of the capillary volumes. It was pointed out that this required a modification of Cude and Hulett's penetrability hypothesis to include the influence of different degrees of wetting of the charcoal by the different liquids.

4. It was observed that the pore volumes decreased with decreasing hydrogen content of the charcoals. This was interpreted as indicating that shrinkage of the charcoals occurred at the temperatures at which the samples were heated and that the shrinkage was greater at the higher temperatures as indicated by the lower hydrogen content.

5. The observed relationship between the apparent density in water and the hydrogen content of the charcoals was taken as confirmation of the modified penetration hypothesis. The apparent densities of the

charcoals gave an S-shaped curve when plotted against their hydrogen contents, increasing with the hydrogen content to a maximum value. The maximum value was assumed to be given by charcoal heated below temperatures at which shrinkage occurs, the observed values being low by an approximately constant value because of a relatively small volume of impenetrable capillary space. As the hydrogen content decreased, or as the temperature to which the samples had been heated increased, shrinkage occurred and this impenetrable volume became relatively larger, thereby giving a lower apparent density.

6. That the sorptive capacity of the samples increased with increasing hydrogen content was shown to be in accordance with the view, which is consistent with all known available evidence, that so-called amorphous carbons are hydrocarbons of low hydrogen content built up of polymerized residues from the thermal decomposition of hydrocarbons of greater hydrogen content, and that any treatment which tends to increase the unsaturation of these residues will increase the sorptive capacity of the charcoal.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY AND THE WESTERN ELECTRIC COMPANY, INCORPORATED]

A STUDY OF THE RATE OF OXIDATION OF CERTAIN CHARCOALS

BY H. H. LOWRY AND S. O. MORGAN

RECEIVED OCTOBER 17, 1923

In connection with the work on "The Relation between the Hydrogen Content of Certain Charcoals and Some Other Properties," described in the preceding paper, a study of the rate of oxidation of some of these charcoals was undertaken. This work was nearing completion before the relation between the maximum temperature of roast and the hydrogen content was discovered, and hence the temperatures chosen for this work were unfortunately not those which would now appear best suited for the purpose. Ten of the 23 samples used in the previous investigation were chosen for the present study. These were all non-activated charcoals prepared by heating granular anthracite coal in a gas-fired furnace in the manner described in the previous paper. These ten samples were selected primarily with a consideration of their extent of surface since, from theoretical considerations, if the surfaces were all of the same material, the rate of oxidation should be proportional to the surface exposed to the oxygen, analogous to rate of solution phenomena. However, no strict proportionality need exist between the extent of surface as determined and the surface exposed to the oxygen, available for oxidation, since the distribution of the surface within the capillaries of the various samples most probably is not the same.