The foregoing data obviously furnish evidence from which the heats of vaporization may be computed. Using the Clausius-Clapeyron equation $(L = T \frac{dp}{dt} (V_{\text{gas}} - V_{\text{liquid-solid}})$ and values for the vapor pressures calculated from the logarithmic vapor pressure equations, this has been done for the 3 most volatile substances at various temperatures. The results are expressed in kilogram calories per gram molecule.

TABLE VII.

Heats of Vaporization.

Temperature. ° C.	Chloropicrin.	Cyanogen bromide.	Arsenic trichloride.
100	..	..	6.86
50	..	..	7.29
35	6.77	8.08	..
0	7.10	8.60	7.42

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

STUDIES IN THE ADSORPTION BY CHARCOAL.

I. THE RELATION OF SERVICE TIME TO ADSORPTION AND ABSORPTION.

BY H. H. LOWRY AND G. A. HULETT.

Received March 29, 1920.

Introduction.

Because of the prominence of gas warfare in the recent world war, means of protection against gas had to be developed. Naturally charcoal played a prominent part because of its remarkable properties as an absorbent. Also naturally one sample of charcoal prepared in one way might be better than another for a given use and the test developed to show superiority of one charcoal over another became known as the "service time" test. This method of testing has been described by Lamb, Wilson, and Chaney[1] and was purely an empirical test developed to approximate field conditions. Briefly, it consisted in passing air containing a known concentration of a toxic gas, as chloropicrin, at a definite rate through a sample of charcoal of standard dimensions until the gas could be detected in the effluent air. The test gave the desired data but had no theoretical basis, though many speculations had been made on this point. No known property of a charcoal could, however, lead one to say that it would give a better test than another without actually submitting it to these empirical conditions.

The lack of relation between service time and some physical properties of various charcoals is shown in Table I.

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[1] *J. Ind. Eng. Chem.*, 11, 430 (1919).

TABLE I.[1]

	A909.	Nela.	English.	German.
Density:				
True	1.84	1.89	1.86	1.70
Apparent	0.55	0.46	0.13	0.24
Vol. capillaries per cc.	0.23	0.31	0.39	0.38
Service Time:				
Cal. minutes (accelerated)	17.3	53.5	8.8	60.2[a]
% wt. $C(NO_2)Cl_3$ at break point	14.6	48.7	32.0	110.0[a]

[a] This value was obtained not on the charcoal as taken from the canisters but after having been treated as described later.

Most of the speculations on service time have connected this property with either the well known great adsorptive power of charcoal or with capillary action due to its porous structure. We wished to investigate this relation and decided to measure the adsorptive power of these charcoals for nitrogen, carbon dioxide and water vapor. These were chosen because they were well defined, stable substances not very difficult of preparation in the pure state, and were widely different as to critical temperatures. Attention is called to this fact that at 25°, the temperature chosen for the measurements, water is normally a liquid, carbon dioxide is a gas just below its critical temperature, and nitrogen a gas and far above its critical temperature.

It was also realized that we had an opportunity to obtain adsorption measurements on charcoals which had been prepared in a very definite way and their other characteristics determined in the work on the various charcoals used for gas masks. Previous measurements, as given in the literature, may be considered to have doubtful value because of their non-reproducibility, since no special attention was given to the preparation of the charcoal, to activation, and to the other physical properties of the charcoal. Only in this sense was it intended to supplement the

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[1] NOTE.—The method of determination of these properties follows:

True Density.—Charcoal placed in sample tube and evacuated at 445° and sealed *in vacuo*. Weighed in air, then opened under water and, after the "drift" had disappeared, the weight determined, and volume obtained from weight of water displaced (THIS JOURNAL, 42, 391 (1920)).

Apparent Density.—These figures are calculated on a moisture- and gas-free basis.

Volume of Capillaries.—Values obtained by centrifuging the sample of charcoal opened under water in the density determination for a definite period of time and approximately 1000 r. p. m. The excess weight of the sample over the true weight of the charcoal represented the water retained by the capillaries and is essentially the same as if the external water were removed by filter paper.

Service Time.—These tests were made by Dr. N. K. Chaney, of the National Carbon Co., by the standard accelerated method except that the rate was 500 cc. per minute instead of the usual 1000 cc., *i. e.*, the test is only half as accelerated as the standard. From the actual weight of the chloropicrin absorbed, the minutes service was calculated. We wish to express here our sincere thanks to Dr. Chaney for furnishing us with this data.

enormous amounts of data already collected on the adsorption of gases by charcoal. Special interest, however, was attached to the adsorption of water vapor, first because no accurate measurements of the adsorption of vapors by charcoal, which could normally exist as liquids at the temperature of the measurements, have previously been recorded in the literature, and secondly, because the so-called toxic "gases" of warfare were usually such vapors.

Description of the Charcoals.

A909.—This charcoal was prepared at Astoria in August, 1918, from cocoanut shells. The preliminary carbonization was at 950° for 10 hours. The sample was then steam-activated at 950° for 45 minutes according to a method described in detail elsewhere.[1] The sample used was 18–20 mesh, *i. e.*, that which would pass through an 18-mesh screen but was retained by a 20-mesh screen.

A909 Es.—This was the same charcoal as the preceding, the only difference being in the size of the particles. It was prepared by grinding the coarse A909 in a ball mill and collecting by electrical precipitation the dust which was too fine to settle.[2] The maximum diameter of the particles as determined microscopically was one micron, 0.001 mm.

Nela.—This was a mixture of cocoanut charcoals prepared and activated in the C. W. S. Laboratory at Nela Park, Cleveland. The charcoals composing this mixture were very similar but of various degrees of activity. The preliminary carbonization was made at 950° for 10 hours and the charcoals were then activated with steam at 950° for approximately 45 minutes.

English.—This was a mixture of English charcoals which were very similar. These charcoals were made from birch wood in gas retorts, that is, they were really air activated. The method of preparation was the standard adopted for the preparation of British war charcoals.

German.—For the details of the method of preparation of this charcoal, the reader is referred to an article by J. F. Norris.[3] Briefly, the carbonization was affected as follows. The wood in pieces of uniform size was soaked in a hydrochloric acid solution of zinc chloride for about $^1/_2$ hour. The acidified wood was then heated in a closed muffle furnace at a cherry-red for at least 6 to 8 hours. The charcoal obtained was washed with hydrochloric acid until the soluble ash was reduced to a minimum. The finished product contained about 0.01% of zinc. It was finally washed free from acid, drained on a grill, and dried in a vacuum at 70° to 80°. This sample of charcoal was taken from unused canisters which had been captured in September, 1918, and was further treated

[1] *J. Ind. Eng. Chem.*, **11**, 430 (1919).

[2] THIS JOURNAL, **42**, 391 (1920).

[3] Norris, *J. Ind. Eng. Chem.*, **11**, 829 (1919).

before using it in the measurements, including those of the service time, as follows. It was boiled in distilled water for 2 hours, its water decanted and this treatment repeated 7 times. It was then boiled for 3 hours in dil. (1 : 7) hydrochloric acid, the acid decanted and then again treated as at first 3 times with water. It was dried in the air on filter paper, and then for 5 hours at 110–115° in air free from carbon dioxide and water vapor.

Preparation of Nitrogen, Carbon Dioxide, and Water.

Nitrogen.—A mixture of air with hydrogen from a Kipp generator using dil. hydrochloric acid and zinc metal, was forced through a combustion tube in the proper proportions to remove completely the oxygen and hydrogen, using copper-copper oxide as the indicator.[1] The effluent gases, nitrogen and argon, were collected and stored in a large glass gasometer over a dil. alkaline pyrogallate solution in order that they might not be contaminated with the oxygen originally dissolved in the water. Subsequent analysis showed no traces of oxygen, carbon monoxide, carbon dioxide, or hydrogen, Assuming that the air originally contained 78% of nitrogen and 1% of argon, the "nitrogen" used contained 1.25% argon. The gas, as used, was dried by passage over calcium chloride and phosphorus pentoxide.

Carbon Dioxide.—The carbon dioxide was prepared by dropping 1 : 1 sulfuric acid, kept in an atmosphere of carbon dioxide, on a saturated solution of sodium hydrogen carbonate. The sulfuric acid had been previously saturated with carbon dioxide to displace the dissolved gases. The gas was dried over calcium chloride and phosphorus pentoxide. Analysis showed a residue of less than 0.1% of gas not absorbed by a caustic potash solution. The gas was generated as used.

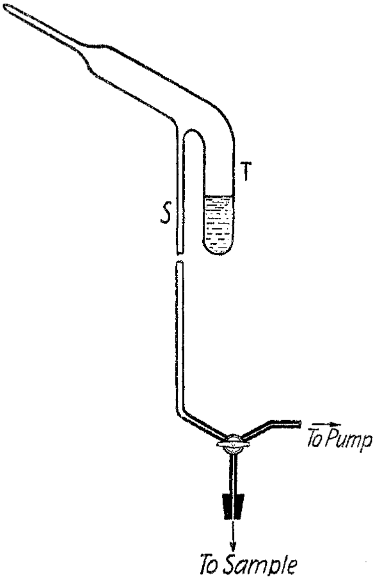

Fig. 1.

Water.—The water used was ordinary distilled water freed from dissolved gases as follows. About 10 cc. of distilled water was placed in the tube T, Fig. 1, and the system partially evacuated through the stopcock M by means of a Töpler pump. The water was then carefully frozen with solid carbon dioxide and ether and the system evacuated to the vapor pressure of water at that temperature. After closing the

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[1] This Journal, 27, 1415 (1905).

stopcock M, the ice was allowed to melt and M opened again momentarily. Any air dissolved in the water would be given up to the vacuum. To remove this air, which was always less than 0.02 cc., the water was again frozen and the system re-evacuated.

Description of Apparatus.

A diagram of the apparatus is shown in Fig. 2. This consisted of a quartz tube, NP, 15 mm. inside diameter, and about 25 cm. in length. The sample of charcoal was placed in the lower 8 to 10 cm. of the tube and above this, in order to reduce the amount of dead space as much as possible, there was placed another quartz Tube, O, sealed at both ends and fitting tightly in NP. A ground glass, vacuum-tight joint at N joined the quartz tube containing the sample to a 3-way Stopcock, M. By means of this stopcock, the charcoal could be directly opened to the reservoir holding the gas to be absorbed or to a manometer S and through the stopcock R to a Töpler mercury pump, by which the evacuation of the system was effected. Pressures from a fraction of a millimeter to 400 mm. could be read from the manometer by means of a cathetometer and a scale placed between the 2 arms of the manometer. The pressure was read to the nearest 0.1 mm. The volume of the apparatus enclosed by the stopcock R and the quartz tube NP was measured directly by putting the quartz tube and filler, O, in place empty, with R closed and the system evacuated to R, and subsequent opening of R and evacuation of the rest of the apparatus, the gas being collected at the delivery of the pump and measured in a gas buret to the nearest 0.01 cc. Since the inside diameter of the manometer was previously measured and was of uniform bore, the volume of the apparatus at 0 mm. pressure could be calculated, as also the increase in volume with each millimeter pressure. For determining the free space in the apparatus when the charcoal was in place, the volume of the charcoal, calculated from the weight of the gas- and moisture-free sample and its previously determined true density, was subtracted from these values.

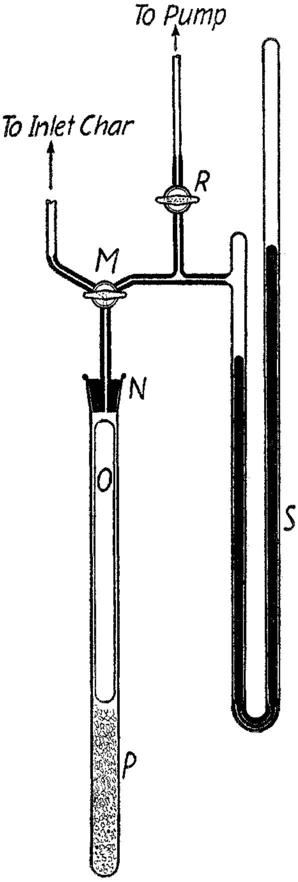

Fig. 2.

Method.

In practice, a sample of charcoal, containing an unknown weight of gas and moisture, was weighed directly into the quartz tube NP. The weight of the sample used depended on the apparent density of the charcoal since the volume of the charcoal used was a constant—about 14 cc. In the line between the pump and the stopcock R was sealed a small glass condenser (Fig. 2*a*), which was immersed in solid carbon dioxide and ether after the system had been completely evacuated to the stopcock M. This stopcock was then opened and simultaneously an electric heater was placed around the quartz tube, the ground glass connection at N being cooled by a lead coil through which cold water was passing. The heater had been calibrated and sufficient current was passed through to raise the sample of charcoal to 750° and this temperature was maintained until, with continual evacuation by means of the Töpler pump, less than 0.1 cc. was given off in each 10-minute interval. This condition was usually obtained only after 5 to 7 hours heating. Previous experience had shown that until such a temperature had been reached the effluent gases contained fairly large percentages of the oxides of carbon. The gas as given off was collected at the delivery of the pump and stored in a large gas buret over mercury, in which the total volume of gas was measured. An analysis of a sample of this allowed easy calculation of the weight of gas given up by the charcoal during the treatment. This varied with the charcoals used from 1% to 10% of the original weight of the charcoal. The moisture in the charcoal, having been retained in the condenser by freezing, was determined directly by cutting the condenser out of the line, the stopcock R being closed, and weighing the condenser with the water and then empty. This moisture varied from 1% to 13% of the original weight of the charcoal. After the quartz tube had cooled, it was kept immersed in a thermostat at 25° ± 0.2°, while the pressure concentration measurements were being made. Fairly close adjustment of the temperature was necessary because of the large though undetermined temperature coefficient of pressure with temperature. After the measurements with one gas were obtained, the charcoal was re-evacuated at 184° (aniline b. p.) to remove the last traces of the adsorbed gas.

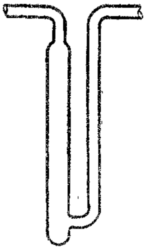
Fig. 2*a*.

Admission of Nitrogen and Carbon Dioxide.

Since both these substances are gases, their pressures and concentrations were measured similarly, though necessarily differently from the method followed with water, a description of which will be given later.

For the admission of nitrogen, the apparatus shown in Fig. 3 was sealed to the stopcock M (Fig. 2). This apparatus consisted essentially of a small gasometer, R, of known volume, kept immersed in a jacket of water NP, the temperature of which was recorded by the thermometer, T. The rest of the apparatus was the large gasometer in which the nitrogen was stored, and drying tubes containing calcium chloride and phosphorus pentoxide. By opening the stopcock, M, this apparatus, including the small gasometer R, could be completely evacuated to J. The line was then "washed out" several times with nitrogen from the large gasometer. When this was accomplished, the small gasometer was opened to the nitrogen supply and simultaneously the line to the gasometer from the pump closed by turning the 3-way stopcock K. The stopcock J being opened, the gasometer R was filled with nitrogen to the zero mark at atmospheric pressure by means of the leveling bulb L. The temperature and pressure of this volume being known, it was readily reduced to N. T. P. The volume of the gasometer was 94.62 cc. Now the stopcocks K and M were so turned as to connect the sample of charcoal with the nitrogen in the gasometer and the levels of mercury in L and R kept approximately level while the gas was being adsorbed. Equlibrium was very rapidly reached and the 2 levels carefully adjusted. The stopcock M was then turned so the line

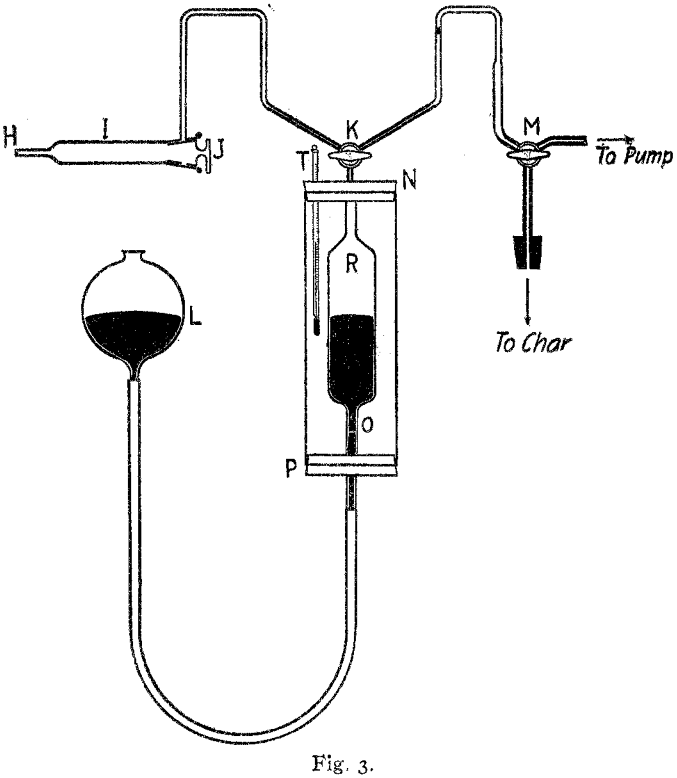

Fig. 3.

between K and M and the gasometer R could be evacuated. In this way the excess of gas remaining in the gasometer could be measured by collecting it as pumped off at the delivery of the Töpler pump and its volume determined in a gas buret. By subtracting this volume, corrected to N. T. P., the amount of nitrogen in the quartz tube NP, Fig. 2, was known, and by subtracting from this value the nitrogen in the previously determined free space of the tube, also corrected to N. T. P., the amount of nitrogen in cc. N. T. P. adsorbed at 25° and atmospheric pressure was determined. By a series of evacuations, and collecting and measuring each volume of gas as pumped off, and subtracting this from the previous volume of gas in the system, the amount of nitrogen in the system at several pressures could be measured. Since the volume of the system was known for each pressure, the volume of nitrogen adsorbed on the charcoal could be easily calculated. The nitrogen could be completely pumped off at 25°. A typical table is given in Table 2 as an example of the method of recording results. Fig. 4 represents the concentration

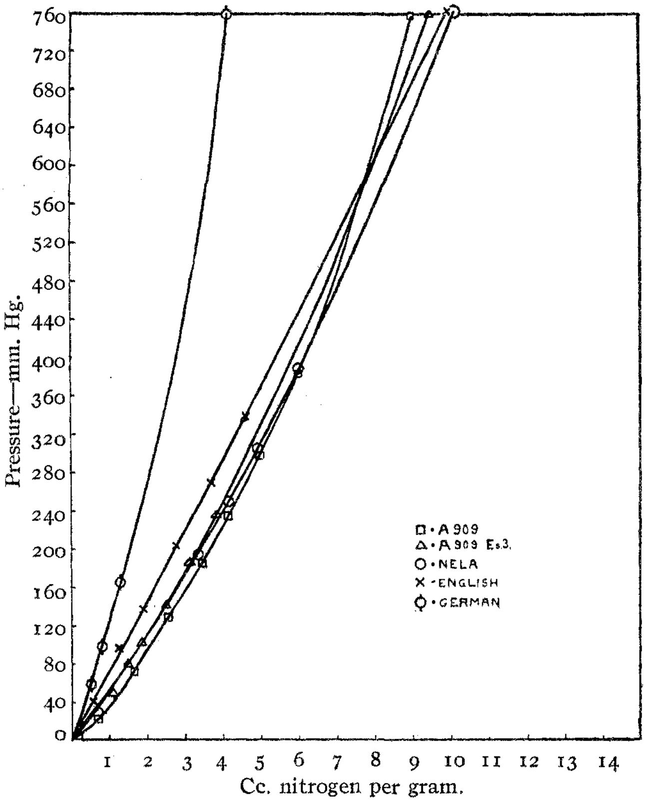

Fig. 4.—Adsorption isotherms for nitrogen on charcoals at 25°.

pressure curves for nitrogen as plotted from the data obtained with the various charcoals.

Table II.

Adsorption of Nitrogen by A909 Es. 3.

	Cc. admitted.		Cc.	Press.	Room	Vol. system.		Gas in	Gas on	Cc. gas
	T.	*P.*	N. T. P.	Mm. Hg.	temp.	Bulb.	Line.	Sys. N.T.P.	char.	per g.
75.89	19.0	760	70.99	760.0	....	10.66	....	10.66	60.33	9.46
32.38	19.5	760	30.21	235.8	19.8	3.32	2.58	5.90	24.31	3.84
26.06	19.5	760	24.32	186.0	19.8	2.67	1.83	4.50	19.82	3.11
20.38	19.5	760	19.01	142.0	20.0	1.99	1.26	3.25	15.76	2.48
14.97	19.5	760	13.97	101.5	20.0	1.42	0.80	2.22	11.75	1.84
11.96	19.7	760	11.16	80.0	19.7	1.12	0.60	1.72	9.44	1.48
8.62	20.0	760	8.03	48.9	20.3	0.69	0.34	1.03	7.00	1.10
4.66	20.2	760	4.34	21.7	20.6	0.30	0.13	0.43	3.91	0.61
1.98	20.2	760	1.84	5.1	20.3	0.07	0.03	0.10	1.74	0.27
0.18	20.3	760	0.17	0.2	20.6	...	....	...	0.17	0.03

The measurements of the concentration pressure relation with carbon dioxide were made in exactly the same way as those with the nitrogen except for the necessary modifications due to the much larger amounts

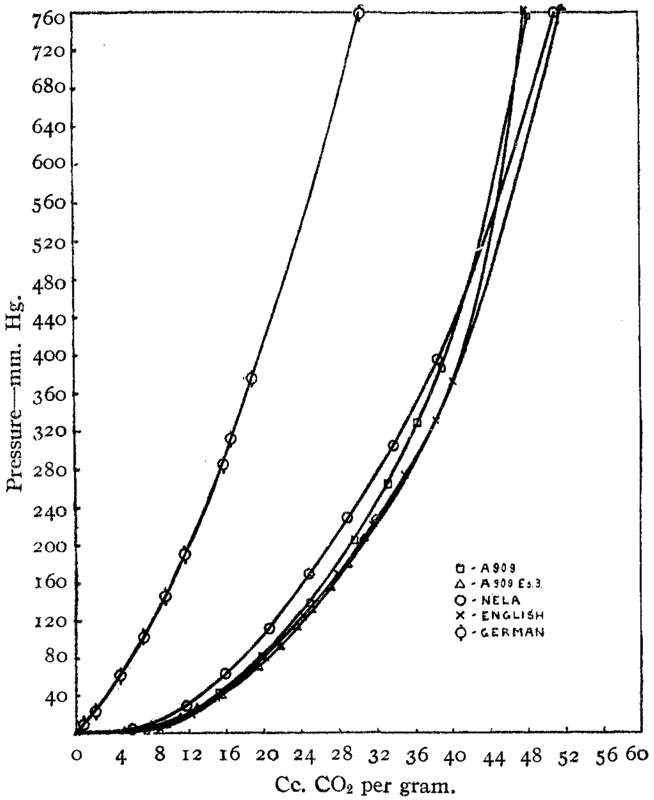

Fig. 5.—Adsorption isotherms for carbon dioxide on charcoals at 25°.

adsorbed. This necessitated several fillings of the gasometer R. For the admission of carbon dioxide, the generator was sealed to the apparatus shown in Fig. 3 at H. The generator was furnished with a mercury valve immediately before a stopcock which separated it from the rest of the system. Carbon dioxide was generated and allowed to escape through this valve until tests showed that the gas was completely adsorbed by a caustic potash solution. The concentration pressure curves obtained for carbon dioxide on the different charcoals are shown in Fig. 5. It was found that the complete removal of the carbon dioxide from the charcoal *at the temperature of adsorption* was a slow and tedious process. The gas came off very slowly at the lowest pressures, as much as 8 cc. per g. of charcoal being retained by one of the charcoals at a pressure of 1.4 mm. Hg. The only exception to this was in the case of the German charcoal, with which the amount adsorbed per g. was about half that of the amount adsorbed by the other charcoals, and where the carbon dioxide was readily pumped off at 25°. In order, therefore, to free the surface from adsorbed gas, the tube was immersed in a tube of boiling aniline vapor. It was very readily possible at this temperature, 184°, to recover completely the amount of carbon dioxide originally admitted.

Admission of Water.

To admit water to the charcoal, the apparatus shown in Fig. 1 was sealed to the stopcock M, Fig. 2, in place of the apparatus used for the admission of the gases. The preparation of the water for use has been described previously. After the last freezing in the preparation, the ice in T was allowed to melt and a beaker of warm water was placed around the bulb containing the water. Since the apparatus was filled only with water vapor, the water distilled and filled the tube S, which had been calibrated with a thread of mercury (0.123 cc. per cm. tube) completely to the stopcock M. A scale—one division = 0.581 mm., was fastened to the tube S and in this way the amounts of water admitted to the charcoal could be directly read to 0.007 cc. and estimated one place farther. Since the adsorption was to be measured at 25°, which is several degrees higher than ordinary room temperature, means had to be provided to prevent distillation from the charcoal to the line which was in the air above the thermostat. At first, heating by means of a Nichrome wire wound around that part of the line was tried, a small current, which was sufficient to keep the line at about 30° as determined experimentally, being passed through the wire. Later it was found to be more convenient to raise the room temperature to 27–30°, thereby removing this difficulty. This necessitated the cooling of the thermostat by means of ice. It was customary to cool the bulb to 10–15°, causing more rapid distillation from the line to the charcoal, and then allowing the temperature to slowly rise. The pressure was read when the temperature reached 25°. As this pressure approached that of water at 25°, 23.5 mm., it was sometimes necessary to repeat this cooling before the pressure would remain constant. It frequently required 3 to 5 hours for equilibrium to be reached. The curves of concentration pressure of water on the various charcoals are shown in Fig. 6. A typical table of experimental data is also appended in Table III:

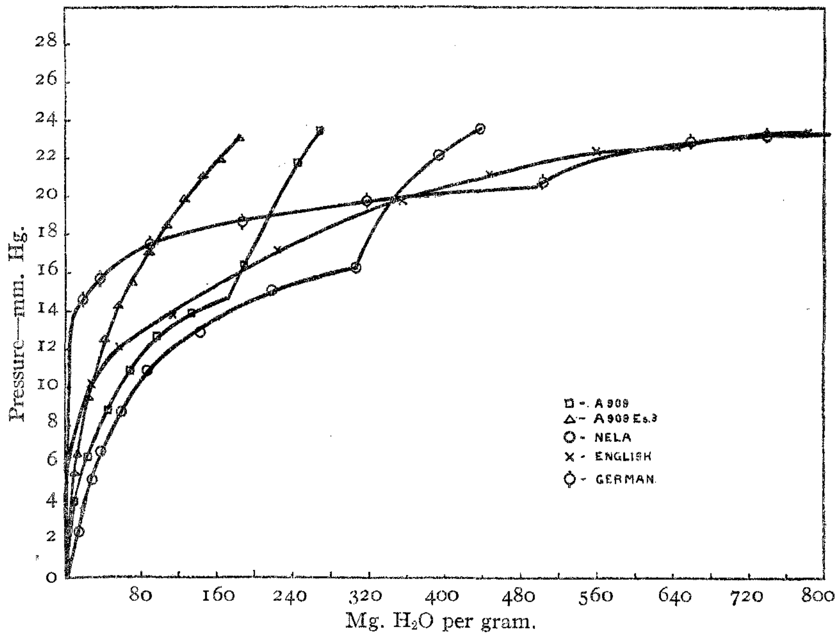

Fig. 6.—Adsorption isotherms for water vapor on charcoals at 25°.

TABLE III.

Adsorption of Water by English Charcoal at 25°.

Cc. of water admitted.	Pressure mm. Hg.	Room temp.	Cc. of water in system.	Cc. of water on charcoal.	G. of water on charcoal.	G. of water per g. of charcoal.
0.0357	10.2	27.8	0.00015	0.0355	0.0354	0.0277
0.0743	12.1	29.2	0.00015	0.0741	0.0738	0.0577
0.1458	13.8	29.6	0.00017	0.1456	0.1449	0.1133
0.2886	17.2	30.4	0.00026	0.2883	0.2872	0.2247
0.4314	19.8	29.4	0.00030	0.4311	0.4295	0.3360
0.5742	21.2	29.6	0.00032	0.5739	0.5720	0.4473
0.7184	22.4	30.2	0.00034	0.7181	0.7156	0.5595
0.8262	22.6	30.3	0.00034	0.8259	0.8230	0.6441
1.0047	23.4	29.9	0.00036	1.0043	1.0009	0.7831

Discussion.

A consideration of these data on adsorption shows that the isotherms obtained for nitrogen and carbon dioxide on the various charcoals are of the same general form as previously obtained by other investigators, *i. e.*, Homfray,[1] Titoff,[2] Travers,[3] Baerwald.[4] Furthermore, the quantities adsorbed do not vary much among themselves for equal weights of the various charcoals, except for the specially treated German charcoal. A slightly larger adsorptive capacity for nitrogen and carbon dioxide was noticed for the finely divided A909 than for the large grained sample. This is taken to indicate that the increase in surface due to pulverizing the charcoal was small, less than 8%, in comparison with the total available surface present in the larger grained material.

In Table IV there are given the amounts of nitrogen and carbon dioxide adsorbed by one cc. of the different charcoals, at 25° and 760 mm., together with their service times. It is necessary to use equal volumes of the charcoals for this comparison with the service time, as this latter test is made on a constant volume of charcoal. This can be obtained by multiplying the volume adsorbed per gram charcoal by the apparent density of the charcoal. It is very readily seen from this table that there is no relation between the capacity for a charcoal to adsorb a gas, as nitrogen or carbon dioxide, and its service time.

TABLE IV.

	Cc. N. T. P. per cc. of charcoal.		Minutes service.
	N_2.	CO_2.	
A909	4.97	26.53	17.3
Nela	4.89	25.04	53.5
English	1.29	6.21	8.8
German	1.01	7.35	60.2

In the exponential formula, $q = a.p^{1/n}$, for adsorption isotherms, Titoff[5] found that the value of n is very close to unity for gases which at ordinary temperatures may be called "perfect gases" and that it increases in value for gases of increasingly high critical temperatures. This would give approximately a straight line to the isotherms of the perfect gases and the curves would become more and more concave to the pressure axis for gases with increasingly higher critical temperatures. If this generality could be applied even to cases where the measurements were made on a vapor which could exist normally as a liquid under the conditions of the measurements, as water in our experiments, we should expect that the isotherm for water would be very much more concave to the pressure axis than that for carbon dioxide. However, the curves obtained for water are of a form exactly opposite, that is, they are concave to the concentration axis.

Charcoal, being of a porous nature, besides presenting enormous sur-

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[1] Homfray, *Z. physik. Chem.*, 74, 129 (1910).

[2] Titoff, *ibid.*, 74, 641 (1910).

[3] Travers, *Proc. Roy. Soc.*, 78, 9 (1907).

[4] Baerwald, *Ann. Physik.*, 23, 90 (1907).

[5] *Loc. cit.*

face and accordingly having high adsorptive capacity, also offers the opportunity of capillary action, especially to the vapor of a liquid which has as high a surface tension as water. The isotherms for water must, therefore, be taken to show that in this case the capillary action is greater than the surface attraction of adsorption, since they are just what would be expected from the assumption that water was taken up predominatingly by capillary action. In this case, the smaller capillaries would be filled first since they would give the lower vapor pressures. The smaller the diameter of the capillaries, the more rapidly would they be filled by a given amount of water and so the pressure would increase more rapidly at first in relation to the concentration than when the capillaries were of a larger diameter. This would satisfactorily explain the concavity to the concentration axis obtained for the isotherms for water.

A further indication that water vapor is not *ad*sorbed, but *ab*sorbed, by charcoal is given by the comparison of the ratios of nitrogen, carbon dioxide, and water taken up per g. of the various charcoals. These ratios are for A909, Nela, English and German charcoals, respectively, 1 : 5.3 : 29.9; 1 : 5.0 : 54.2; 1 : 4.8 : 98.1; and 1 : 7.4 : 226.4. It is seen that while there is more or less regularity between the ratios of nitrogen and carbon dioxide, the water varies between the wide limits of 29.9 and 226.4. This must surely mean that if charcoal adsorbs gases, it does not *ad*sorb water vapor, but that this is a different phenomenon, which may be called *ab*sorption.

A quite pronounced break can be seen in the isotherms for water on the different charcoals, with the exception of the finely divided A909. In a study on the "adsorption" of water by silica gel, Anderson[1] obtained a similar break. He seems justified, from his later work on the study of the velocity of adsorption, to conclude that this break marks the intersection of 2 phenomena, the first smooth part of the curve represents the taking up of water vapor by capillary action, the break occurs only when the capillaries have filled up and the further increase in vapor pressure is due merely to the flattening of the meniscus at the ends of the capillaries.

Anderson developed in his paper a formula which can be used for the calculation of the diameters of the capillaries from the vapor pressure measurements. By means of this formula, it is also possible to calculate the surface of the charcoal since the volume of each size capillary can be obtained directly by reference to the concentration axis. The formula is

$$r = \frac{2T.s_0.0.4343}{d.p_0.\log(p_0/p_1)}$$

where r = radius of the capillary; T = surface tension in dynes per cm.

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

at 25° = 72.1; s_0 = vapor density of water vapor above water at 25° = 22.75×10^{-6}; d = density of water at 25° = 0.99707; p_0 = vapor pressure in dynes of water at 25° = $23.517 \times 13.534 \times 980.1 = 31.20 \times 10^4$; and p_1 = the vapor pressure in the capillary.

The lowest pressure measured in our experiments was 2.3 mm. on the Nela charcoal when 16 mg. of water had been absorbed per g. of charcoal. This corresponds to a capillary diameter of 9.1×10^{-8} cm. A vapor pressure of one mm. represents a pore with a diameter of 6.7×10^{-8} cm. In Table V are listed the smallest, largest and mean diameters of the capillaries in each charcoal, as calculated from this equation, together with the surface as calculated by applying this formula as indicated above.

TABLE V.

	Capillary diameters.			Cal. surface.	
	Smallest. Cm.	Largest. Cm.	Mean. Cm.	Per g. M.	Per cc. M.
A909........	6.7×10^{-8}	4.1×10^{-7}	2.8×10^{-7}	230^{-2}	130^{-2}
Nela........	6.7×10	5.5×10	3.7×10	440	200
English......	1.6×10	1.9×10	8.3×10	300	40
German......	2.0×10	1.3×10	9.5×10	160	40

Lamb, Wilson, and Chaney[1] have estimated that the surface of one g. of an activated charcoal is about 1000 square meters, which from our data would appear to be too great. Recently A. M. Williams,[2] in developing a new interpolation formula for the adsorption of gases, was able to calculate that the surface of the charcoal used by Dr. Ida F. Homfray[3] was 131 square meters, which agrees well with the values we have obtained, especially when one considers that this was a pre-war product and not activated. With a surface of the magnitude given by our calculations, adsorption of nitrogen and carbon dioxide at ordinary temperatures and to pressures as high as atmospheric could well be in a monomolecular layer, such as is characterized as true adsorption by Langmuir,[4] since 50 cc. of carbon dioxide at N. T. P. would occupy in a monomolecular layer a surface of less than 150 square meters. Also the fact that, while the differences in the calculated surfaces of A909, Nela, and English charcoals is considerable, there is not a corresponding difference in the adsorption of the gases, this would make the concept of "elementary spaces" postulated by Langmuir[3] necessary. The difference in the adsorptive capacity of a given charcoal for nitrogen and carbon dioxide would then depend solely on the difference in "time-lag" of the condensation evaporation process of adsorption.

Since it has been shown that the taking up of water vapor is a different

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[1] Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, 11, 430 (1919).

[2] Williams, *Proc. Roy. Soc.*, **96A,** 287 (1919).

[3] *Loc. cit.*

[4] Langmuir, THIS JOURNAL, 40, 1361 (1918).

phenomenon from adsorption, it is interesting to see whether there is any relation between this phenomenon, absorption, and service time. The necessary data for this comparison is collected in Table VI. In this table the per cent. weight of chloropicrin held by the charcoal at the break point, the saturation point, and the "retentivity" point are calculated to volume of chloropicrin. The retentivity signifies the amount of chloropicrin left in the charcoal on reversing the test until no trace of chloropicrin can be detected in the effluent air. The density of chloropicrin at 25° has been taken to be 1.651, the density determined at the American University being $d_4^{20} = 1.6539$.

TABLE VI.

	Vol. chloropicrin in cc. at.			Vol. capillaries per g.	
	Break.	Saturation.	Retentivity.	Total.	At break in curve.
A909........	0.0884	0.1762	0.0806	0.2728	0.1735
Nela.........	0.2948	....	....	0.4406	0.3083
English......	01.938	0.3967	0.0696	0.7828	0.6435
German......	0.6561	0.8174	0.1726	0.8543	0.4948

Here, also, we see no relation between service time and capillary action. Further, there does not appear to be any relation between the volume of the capillaries and retentivity or saturation, except as might be expected the saturation occurs in each case before the capillaries were completely filled, due to the fact that the lower layers of charcoal had not yet reached saturation.

This complete lack of quantitative relation between service time with the phenomena of adsorption and absorption is not startling. The test, as developed, was only empirical and such factors as size of mesh of the sample and resistance to the passage of air were known to have a marked influence on the service time. It is this "sieve effect" of removing the vapors from the air that is the uncertain and indeterminate factor in the minutes service that a charcoal can give. We know of no other phenomena, however, which can explain the mechanism of this removal of gases, or vapors, of high critical temperature from those of much lower, than adsorption and absorption. We must conclude, therefore, that both of these phenomena are probably involved in the determination of service time, and, from our work on the absorption of water vapor, that capillary action predominates over the influence of unmodified surface action or adsorption.

Conclusions.

1. No relation between service time and adsorption of a gas, as nitrogen or carbon dioxide, by various charcoals has been found to exist.

2. Measurements of the adsorption of these gases by charcoals have shown that, according to the original preparation of the charcoal, the adsorptive capacity per gram of charcoal at 25° and 760 mm. may vary as much as 100%.

3. It has been shown that the adsorption of nitrogen and carbon dioxide by charcoal may be considered to be in a condensed layer one molecule deep.

4. Measurements of the isothermal adsorption of water vapor by charcoal at 25° show that water is not *ad*sorbed by charcoal but is held by capillary action, *i. e.*, is *ab*sorbed.

5. Using Anderson's formula connecting the radius of a capillary with vapor pressure, the mean diameters of the capillaries of the 4 charcoals used have been calculated and have been found to vary between 2.8×10^{-7} cm. and 9.2×10^{-7} cm. The maximum diameter in any of the charcoals was determined to be 1.3×10^{-6} cm.

6. By means of this same formula and the isothermals for water, the surfaces of the various charcoals were found to vary from 160 square meters to 436 square meters per gram of charcoal.

7. It was pointed out that this variation in surface was not always accompanied by a corresponding variation in adsorptive capacity. This makes the concept of "elementary spaces" as postulated by Langmuir necessary.

8. No relation between the service time of the different charcoals with the volume of the capillaries was found. The same was true for the saturation point and the retentivity of these charcoals. This lack of relation must indicate that other indeterminate factors must influence largely the minute service of a charcoal; *i. e.*, the 2 phenomena, adsorption and capillary action are insufficient in themselves to explain this test.

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STUDIES IN THE ADSORPTION BY CHARCOAL.

II. RELATION OF OXYGEN TO CHARCOAL.

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De Saussure,[1] in one of the first quantitative measurements of adsorption by charcoal, was unable to obtain results for oxygen because it alone of the gases would not apparently come to equilibrium even after a year. This anomalous behavior in the adsorption of oxygen by charcoal has been largely overlooked by recent investigators though previously recognized and recorded by R. Angus Smith,[2] who found that the adsorption of oxygen continued for at least a month, though this was not true for hydrogen, nitrogen or carbon dioxide; and that, when it was sought to remove the oxygen by heat, carbon dioxide was given off in place of

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[1] De Saussure, *Gilb. Ann.*, 47, 113 (1814).

[2] R. A. Smith, *Proc. Roy. Soc.*, 12, 424 (1863).