ADSORPTION AND PORE-SIZE MEASUREMENTS ON CHARCOALS AND WHETLERITES[1,2]

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[1] This article has been approved for publication by the Public Information Division, Department of the Army.

[2] The term "whetlerite" was adopted during World War I for certain chemically treated charcoals which are especially effective for the removal of some of the poison gases. This name is used in a similar way throughout the present paper without, however, making any implications as to the nature of the materials that are added to the charcoal in preparing the modern whetlerites.

The B.E.T. equation (29) applied to low-temperature adsorption isotherms of gases such as nitrogen appears to yield reliable surface areas for finely divided or coarsely porous solids. A modification of this equation for adsorption in narrow capillaries also seems to be reliable but is less susceptible to independent experimental verification.

Take-up of water vapor by activated charcoal may be best described as a combination of adsorption and capillary condensation. The rate of equilibration is comparatively low. Little take-up of water occurs at relative pressures lower than about 0.5. Desorption of water vapor from active charcoal is invariably accompanied by marked hysteresis, which usually disappears at a relative pressure of 0.35–0.4.

By measuring the decrease in surface area of a sample of charcoal as a function of the amount of water in the sample, it has been found possible to obtain a pore distribution for a large number of charcoals over the pore diameter range 16 Å. to about 500 Å. Pore-size distribution curves obtained in this way for several hundred charcoals have been found to join smoothly with those obtained by a mercury porosimeter for the range 1000–150,000 Å.

By suitable combination of steaming, hydrogenation or oxidation by air, with or without impregnation by oxides of iron, chromium, nickel, and copper, it has been found possible to tailor-make a given charcoal to a great variety of pore distributions.

Surface oxygen, hydrogen, or nitrogen complexes on charcoal differ in the temperature at which they can be removed from active charcoal by high-temperature degassing in the range 25–1000°C. As a rule, most of the carbon dioxide and water vapor are removed below 600°C., carbon monoxide in the range 600–900°C., and hydrogen and nitrogen between 600° and 1200°C. Chlorine and sulfur surface complexes are also tightly held by charcoal. These various coatings profoundly influence the adsorptive properties of charcoal.

A new theoretical treatment makes it possible to estimate whether a given gas will, at room temperature, be strongly, medium strongly, or weakly adsorbed by a charcoal, provided the polarizability, fundamental frequency, and critical temperature of the gaseous adsorbate are known and provided an adsorption isotherm of at least one known gas on the same charcoal is available.

Retentivity runs have shown that water vapor will decrease the adsorbability of all adsorbates insoluble in water, will have less influence on those slightly soluble in water, and will not cause a decrease in the equilibrium adsorption or retentivity of those gases that are completely miscible with water.

In attempts to measure the surface area of cupric oxide on type A whetlerites, it was found that hydrogen sulfide, phosphine, cyanogen chloride, boron trifluoride, hydrogen chloride, acetylene, and nitric oxide seem to react in excess of a monolayer even at room temperature; hydrogen sulfide, cyanogen chloride, boron trifluoride, and hydrogen chloride were especially active and seemed to react rapidly with the entire mass of cupric oxide. Carbon monoxide, sulfur dioxide, water, cyanogen, and ammonia are all chemisorbed in not to exceed a monolayer on the cupric oxide in the whetlerite.

The extensive research that has been carried out on charcoal still fails to establish with certainty the structure of active charcoal. It seems likely, however, that the charcoal is composed of tiny graphite-like platelets a few carbon atoms thick, but 20–100 Å. in diameter. These, when properly cross-connected, would form pores whose cross-sections would be more nearly rectangular than cylindrical.

I. INTRODUCTION

As part of a fundamental program designed to throw light on the surface area, pore size, and structural characteristics of an "ideal" charcoal, a great many measurements have been made during the last five years under the sponsorship and with the support of the Office of Scientific Research and Development.[3] The present report is an attempt to discuss critically and to summarize such work, taking due cognizance of the current concepts of area and pore-size measurements of porous solids. Such tables and figures as are incorporated have been selected to illustrate the nature of the work that has been carried out and the conclusions that have been reached. For more detailed accounts of the work and for presentation of the allied topics of charcoal preparation and of the kinetics of adsorption by a bed of charcoal, the reader is referred to the original articles which are now beginning to be published (46). For convenience of presentation and discussion, the work has been subdivided into ten sections.

Before summarizing the results obtained, it will be helpful to describe briefly the principal characteristics of the various charcoals mentioned in the paper. The charcoals were of four principal kinds: (*1*) those made by the zinc chloride process applied to sawdust; (*2*) those obtained from coal; (*3*) those made by the

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[3] The individuals whose work is referred to throughout the present article and whose names appear on the government reports were working on NDRC projects located as follows:

The Johns Hopkins University: R. B. Anderson, P. H. Emmett, James Holmes, J. E. Jenkins, J. T. Kummer, C. V. Mace, and H. A. Pohl.
Northwestern University: M. Dole, I. M. Klotz, F. E. Blacet, W. C. Pierce, A. J. Juhola, T. Skei, J. W. Zabor, D. H. Volman, and G. J. Doyle.
Stanford University: P. A. Leighton.
University of Chicago: T. F. Young and S. Weller.
University of Delaware: A. P. Colburn.
University of Illinois: H. F. Johnstone, G. L. Clark, R. L. Le Tourneau, and P. G. Roach.
National Carbon Company: G. W. Heise, J. A. Slyh, M. Janes, N. M. Winslow, S. A. Taylor, and J. B. Sullivan.
University of Rochester: E. O. Wiig, J. J. Madison, J. F. Flagg, and (after July 1945) A. J. Juhola.

This list does not contain names of all of the technical personnel on the project but only those whose names actually appear on the restricted government reports quoted in this paper.

TABLE 1

Charcoals used in NDRC work and mentioned in figures, tables, or discussion

CHARCOAL NO.	RAW MATERIAL	ACTIVATION METHOD	PARTICLE DENSITY	MISCELLANEOUS DATA
CWSN S5	Hardwood sawdust	Zinc chloride		90% $ZnCl_2$ on dry weight basis; 1/16-in. extrusion
CWSN S5 (extracted with HF)	Hardwood sawdust	Zinc chloride		
CWSN 19	Hardwood sawdust	Zinc chloride	0.804	Ratio of $ZnCl_2$ to sawdust on dry weight basis = 0.9; 1/16-in. extrusion; primary calcination at 600°C. followed by rotary calcination at 850°C.
CWSN 19 TUC 45	Hardwood sawdust	Zinc chloride		CWSN 19 treated with oxygen at 400°C.
CWSN 19 TUC 46	Hardwood sawdust	Zinc chloride	0.53	CWSN 19 treated with oxygen at 400°C. to an 18.3% oxygen content
CWSN 19 TUC 742	Hardwood sawdust	Zinc chloride		CWSN 19 treated with oxygen at 400°C.
CWSN 22	Hardwood sawdust	Zinc chloride		Ratio of $ZnCl_2$ to sawdust = 0.9; 1/4-in. extrusion; calcined at 850°C.
CWSN 44	Hardwood sawdust	Zinc chloride	0.676	Ratio of $ZnCl_2$ to sawdust = 0.90; 1/16-in. extrusion
CWSN 45	Coconut shell	Carbon dioxide		Gas-activated coconut shell charcoal
CWSN 78	Hardwood sawdust	Zinc chloride		Ratio of $ZnCl_2$ to sawdust = 0.9; 1/16-in. extrusion; calcination at 600°C.
CWSN BX 110	Hardwood sawdust	Zinc chloride		1-in. extrusion; calcined at 600–900°C.; ratio of $ZnCl_2$ to sawdust = 1.1
CWSN 196 B1	Hardwood sawdust	Zinc chloride	0.534	
CWSN 196 B1X	Hardwood sawdust	Zinc chloride	0.570	Ratio of $ZnCl_2$ to sawdust = 1.10; 7-in. extrusion; oxidized; primary calcination at 600°C.; rotary recalcination at 850°C.; 1/2 hr. passage
CWSN 196 B1X TH 410	Hardwood sawdust	Zinc chloride	0.608	CWSN 196 B1X; 10 hr. heat treatment in nitrogen at 1100°C. to 4.5% weight loss
CWSN 196 B1X TH 427	Hardwood sawdust	Zinc chloride	0.574	CWSN 196 B1X impregnated with 5% Cr_2O_3; steamed to 18% weight loss at 950°C.; heated 10 hr. in nitrogen at 1100°C.
CWSN 203 AX	Hardwood sawdust	Zinc chloride		Ratio of $ZnCl_2$ to sawdust = 0.9

TABLE 1—*Continued*

CHARCOAL NO.	RAW MATERIAL	ACTIVATION METHOD	PARTICLE DENSITY	MISCELLANEOUS DATA
CWSN 291 AY1	Hardwood sawdust	Zinc chloride	0.619	Ratio of $ZnCl_2$ to sawdust = 1.10; 7-in. extrusion; dried at 200°C.; primary calcination at 700°C.; acid-caustic-water washed; rotary recalcination at 1000°C.
CWSN 291 AYY1	Hardwood sawdust	Zinc chloride	0.532	Same as 291 AY1 with additional tertiary sagger recalcination for 14 hr. at 1050°C.
CWSB X2	Nut shell	Steam		
CWSC 542	Sawdust	Steam		
CWSC 1242	Sawdust	Steam		
Coconut charcoal	Coconut shell			
MSA Grade 40	Probably coconut shell	Steam		
PCI P25	Coal	Steam		
PCI P58	Coal	Steam		
PCI P1042	Coal	Steam		
PCI P1042 (extracted with HF)	Coal	Steam		
PN 98	Coal	Steam	1.10	Powdered coal briquetted; air carbonized; steam activated for 90 min.
PN 106	Coal	Steam	0.93	Powdered coal briquetted; baked; steam activated at 1800°F. for 210 min.
PN 112	Coal	Steam	0.80	Same as PN 106 steam activated for 300 min.
RA 53	Coal	Steam	0.68	Powdered coal briquetted; air carbonized with final temperature at 850°F.; steam activated at 1800°F. for 200 min.
RC 79	Coal	Steam	0.66	Powdered coal briquetted; air carbonized; steam activated in rotary activator
NDRC SI B21	Saran	Steam		
NDRC SI B26	Saran	Not activated		
NDRC SI B42	Saran	Steam		
CFI "CC"	Coal			Activated charcoal from Colorado Fuel and Iron Co.; the coal was carbonized and activated directly without grinding and briquetting

steam activation of wood char; and (*4*) those obtained by the steam activation of coconut shell char. The list of charcoals, together with a brief description of them, is given in table 1.

II. MEASUREMENT OF SURFACE AREAS

A. Theory of the adsorption method and general application

During the last few years (55) a method has been developed for measuring the surface of the various porous and finely divided solids by means of adsorption isotherms taken near the boiling points of the gaseous adsorbates. Evidence has been obtained that the S-shaped isotherms such as shown in figure 1 correspond to the building up of a number of layers of adsorbed gas on the solid. Originally, it was suggested that the beginning of the long linear part of the isotherms (referred to as point B) represented the completion of the first layer and the beginning of the second (55). Later a theory was developed to take into account the formation of such multilayers in adsorption (29). It was shown (29) that the adsorption data can be plotted according to the equation:

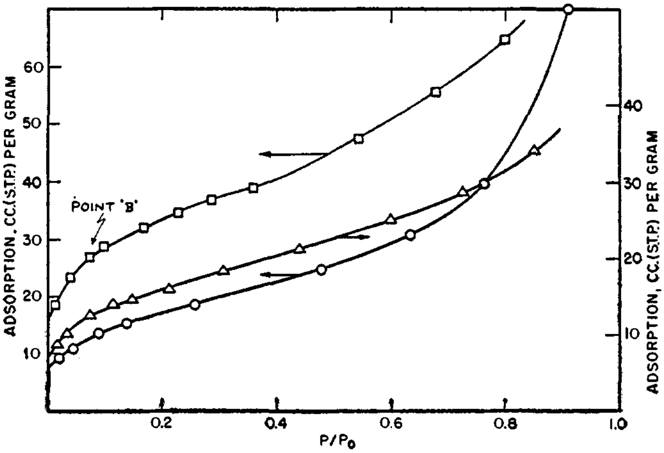

Fig. 1. Nitrogen-adsorption isotherms at −195°C.: ○, resin TR-2; △, P 33 carbon black; □, Wyex carbon black.

$$\frac{p/p_0}{V(1 - p/p_0)} = \frac{1}{V_m C} + \frac{(C - 1)p}{V_m C p_0} \tag{1}$$

to yield straight lines over the relative pressure range 0.05–0.35 (figure 2) from which V_m, the volume of gas required to form a monolayer on the adsorbent, can be evaluated. A simple multiplication of the number of adsorbate molecules in a monolayer by the average cross-sectional area of each adsorbate molecule will then yield a value for the surface area of the solid. V represents the volume of gas adsorbed (expressed at standard temperature and pressure) at the pressure p; p_0 is the liquefaction pressure of the adsorbate. C is a constant related to the heat of adsorption, E_1, by the equation:

$$C = \frac{a_1 b_2}{a_2 b_1} e^{(E_1 - E_L)/RT} \tag{2}$$

where a_1, b_2, a_2, and b_1 are constants and E_L is the heat of liquefaction of the adsorbate. It has been found experimentally that for all isotherms for which C is the order of 50 or larger, the value of V_m obtained by plotting the data by equation 1 is in good agreement with point B, the beginning of the linear portions of the isotherm (figure 1).

The validity of surface-area calculations by equation 1 has been greatly strengthened recently by an independent approach to the problem by Harkins and Jura (75). By presaturating a non-porous, solid titanium dioxide with several layers of adsorbed water vapor and then measuring the heat of immersion in water of the titanium dioxide covered with adsorbed water, they are able to calculate directly the surface area of the solid. The heat of immersion expressed in ergs, divided by the surface energy (118.5 ergs per square centimeter of surface), yields an absolute value for the area of the finely divided titanium dioxide. By this direct method Harkins and Jura obtained a surface-area value of 13.8 sq. m. per gram for the adsorbent compared to 13.9 sq. m. per gram by use of equation 1. This latter value involved the assumption that the cross-sectional area of the nitrogen molecule is 16.2 Å.^{2}, as calculated from the density of liquid nitrogen. Harkins and Jura (76) also developed a new equation for plotting the adsorption data to yield directly a value for the surface area of finely divided and porous materials. It is based on the analogy between the surface phases formed in gas–solid systems and those formed on the surfaces of liquids (76). A somewhat similar method has also been suggested by Gregg (74) and applied by Maggs (115, 116, 117). The equation of Harkins and Jura involves a constant, the numerical value of which is fixed by calibration with titanium dioxide, using the surface-area value obtained by the heat of immersion. These alternative

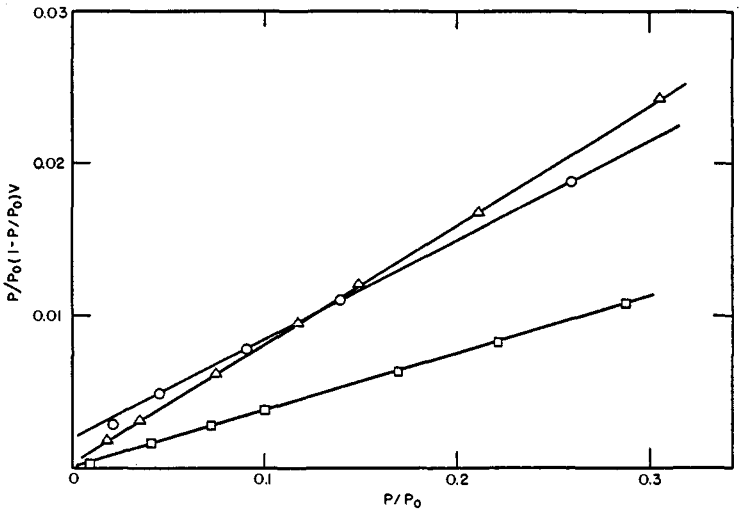

FIG. 2. Linear B.E.T. plots (29) of the isotherms from figure 1: ○, resin TR-2; △, P 33 carbon black; □, Wyex carbon black.

methods of plotting the low-temperature adsorption data need not be discussed in detail here (53). It will suffice to point out that, for a large number of porous and non-porous solids, there is good agreement between the plots of Harkins and Jura and those making use of equation 1.

Equation 1 has been applied to hundreds of different samples of adsorbents with apparent success (48, 49, 56, 76). S-shaped isotherms of the type (50) shown in figure 1 are invariably obtained if nitrogen is used as adsorbate and the measurements are made at about −195°C., provided the adsorbent does not have a large surface area located in small pores. Thus, it has been applied in measuring surface areas of carbon black (56), paint pigments (56), zinc oxide particles (56), metallic catalysts (29), metallic oxides (56), gel catalysts (29), and many other materials (48, 49). By using ethylene as an adsorbate at temperatures (−183°C.) at which the vapor pressure p_0 is $\sim$ 0.003 mm., Wooten and Brown (152) have succeeded in applying it even to areas as low as 100 sq. cm. Thermodynamic (31, 81) as well as kinetic derivations (29, 69) lead to equation 1, if one postulates that curves of the shape illustrated by figure 1 represent the building up of multilayers of adsorbed molecules on the surface. The higher the relative pressure, p/p_0, the greater the average statistical thickness of the adsorbed layer. In view of all of the experimental evidence thus far obtained, it may be concluded that by plotting low-temperature nitrogen-adsorption isotherms of the type shown in figure 1 according to equation 1, one can obtain reliable relative surface areas that are accurate to at least 5 per cent, and absolute values that are entirely reproducible on a given solid but might be in error by as much as 20 per cent, owing to uncertainties of molecular diameters and molecular packing.

B. Measurement of surface areas of charcoals and whetlerites

In the original paper by Brunauer, Emmett, and Teller (29) it was pointed out that if, for any reason, the maximum thickness to which adsorbed layers could build up on a surface is n molecular diameters, then the equation that one obtains to represent adsorption as a function of relative pressure (here designated for convenience as x rather than as p/p_0) is

$$V = \frac{V_m Cx[1 - (n + 1)x^n + nx^{n+1}]}{(1 - x)[1 + (C - 1)x - Cx^{n+1}]} \tag{3}$$

in which the symbols have the same meaning as in equation 1. Attention was also called to the fact that if $n = 1$, equation 3 reduces to the form

$$\frac{p}{V} = \frac{p_0}{CV_m} + \frac{p}{V_m} \tag{4}$$

which is identical with the Langmuir equation.

For materials such as charcoal having a large number of very fine pores, n is conveniently interpreted as one-half the diameter (expressed as number of molecular diameters) of the pores, cracks, or crevices in which the adsorption occurs. It has been shown by Deitz and Gleysteen (43) and by Joyner, Weinberger, and Montgomery (88) that equation 3 can be applied successfully to the adsorption isotherms for a number of materials having so many fine pores as not to fall in the class represented by equation 1. Figure 3 contains a number of isotherms that follow equation 3 over the relative pressure range 0.1–0.4; the values of n, C, and V_m that give a good fit to the equation are also indicated.

Pickett (129) and, more recently, Anderson (12) have questioned equation 3 on the grounds that at relative pressures of 1.0 it does not postulate the complete filling of a crevice with adsorbate but a partial filling equal to

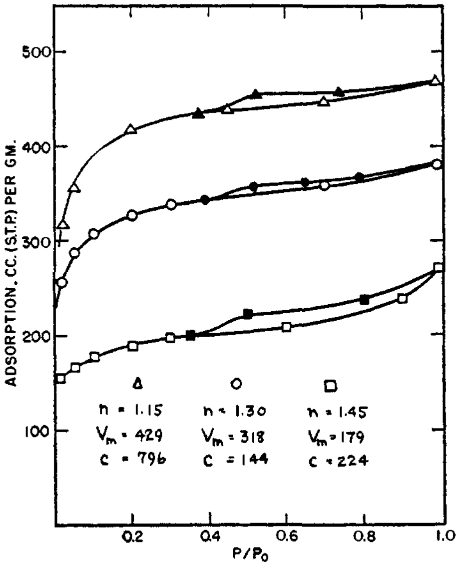

FIG. 3. Nitrogen-adsorption isotherms at −195°C. for charcoal data taken from paper by Joyner, Weinberger, and Montgomery (88).

$$(n + 1) \Big/ 2\left(1 + \frac{1}{Cn}\right)$$

They carried out the summation up to n layers in a manner different from that employed by Brunauer, Emmett, and Teller (29) and arrived at an equation of the form:

$$V = \frac{V_m Cx(1 - x^n)}{(1 - x)(1 - x + Cx)} \tag{5}$$

The derivation can be carried out in a number of ways; it is, for example (146), the result obtained if one assumes that the rate of escape of molecules from the top layer in a capillary is proportional to θ, the fraction of the surface covered by absorbed molecules and also to $1 - p/p_0$. The rate of evaporation thus is assumed to approach zero as p/p_0 approaches unity. This equation has the advantage of representing the complete filling of the capillaries at a relative pressure of 1; however, the value of V_m obtained by equation 5 is substantially the same as that obtained by equation 3. Hence, Pickett and Anderson's suggestions are much more pertinent to the question of pore volume than to that of surface area. Furthermore, equation 3 and not equation 5 is obtained by a statistical mechanical (80) or thermodynamic derivation. It seems probable, therefore, that equation 3 may be relied upon for surface-area measurements of materials having small pores, even though there may be some question as to the course followed by the adsorption isotherm near saturation.

It should be made clear at the start that the measurement of the surface area is much less exact for a material such as charcoal, chabazite, and some gels, having pores which in size approach molecular dimensions, than for non-porous substances or those having large pores. For example, equations 1 and 3 have both been derived on the assumption that the adsorption is taking place on cracks having plane parallel walls. Without doubt, the actual pores and capillaries of many materials have no such simple structure. Indeed, it may be that frequently the small pores might better be described as cylinders or cones rather than cracks or crevices. A further cause of uncertainty arises from the lack of any good independent means of checking the area of substances having pores of molecular dimensions. There is no way of resolving these uncertainties at the present time; their existence, however, should always be kept in mind.

The detailed calculation of surface areas by equation 3 was not used in most of the work that was done by the National Defense Research Committee on charcoal during the war, because the calculations involved were too time-consuming (64). For most samples, equation 4 has been employed; in a few instances (90) even equation 1 has been used. However, as pointed out by Joyner and coworkers (88), the use of equation 4 for adsorption isotherms for a sample for which $n = 1.5$ yields an area value about 15 per cent higher than obtained by using equation 3, whereas employing equation 1 for plotting the adsorption data will yield a value 18 per cent lower than that obtained by equation 3. The exact ratios between the areas obtained by equations 3 and 4 as a function of the value of n are shown in figure 4, taken from their paper. Accordingly, even though equations 1 and 4 have been used extensively as approximations for measuring the surface areas of charcoal, nevertheless, in the writer's opinion, the most reliable surface-area values by nitrogen adsorption are obtained by fitting the adsorption isotherms to equation 3 and evaluating V_m after determining the values of n and C that are needed to fit the data to the equation over the range 0.1–0.4 relative pressures. The area values obtained for charcoals by equation 4 are probably upper limits, and those obtained by equation 1 represent lower limits to the correct areas.

The numerical value of the surface area that one will obtain by the use of equation 1, 3, or 4 will, of course, depend markedly on the gas used as adsorbate. Even on non-porous or coarsely porous solids there seems to be some indication (20, 42) that surface areas obtained by large molecules are a little smaller than those obtained by smaller molecules if the molecular cross-sections are calculated from the density of liquids in the usual way (55). For materials with fine pores this effect of molecular size is, of course, much magnified. For example, it has been known for many years that chabazite, when properly dehydrated, will exhibit a screening action on molecules larger than ethane (138). Indeed, it has been shown that it is possible to make the pores so small in dehydrated chabazite as to permit the adsorption of hydrogen molecules but not nitrogen (57), nitrogen but not butane (57), and straight-chain hydrocarbons but not branched-chain hydrocarbons (18, 19). On charcoal similar screening effects are very much in evidence. On a charcoal such as Saran (65), shown in figure 5, the adsorption of isoöctane is only one-twelfth as large as it should be if nitrogen and isoöctane were being adsorbed on the same pore walls (65). On charcoals with larger pores (figure 6), such as are produced by more extensive activation, the screening is still in evidence but much less pronounced. A plot of surface area (calculated by equation 4) as a function of molecular size[4] is shown in figure 7 for CWSN 19.

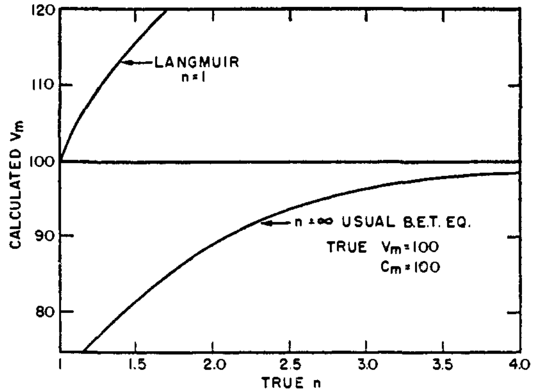

FIG. 4. Curves showing the errors involved in using equation 1 or equation 4 for measuring surface areas for charcoals for which the n values of equation 3 range from 1 to 4.

As indicated, a surface-area value for charcoal will, in general, be smaller the larger the molecule employed for the adsorption measurements. The influence of molecular size on the apparent surface area of a series of charcoals is well illustrated by table 2, compiled from data published by Fineman, Guest, and McIntosh (68). The six samples of coconut shell charcoal were steam activated for different periods of time, as indicated in column 2. For the molecular cross-sectional area of butane they used two values of (*a*) 32.1 Å.^{2} and (*b*) 48.0 Å.^{2} (55). It is apparent that in the early stages of activation nitrogen isotherms yield a much larger area than butane isotherms; the areas by the two gases come closer

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[4] The molecular cross-sectional areas used in calculating the surface areas in figure 7 were obtained from (55) the equation

$$\text{Molecular area} = 4(0.866)\left[\frac{M}{4\sqrt{2}\,Ad_l}\right]^{2/3} \qquad (6)$$

where M is the molecular weight, A is Avogadro's number, and d_l is the density of the liquefied adsorbate.

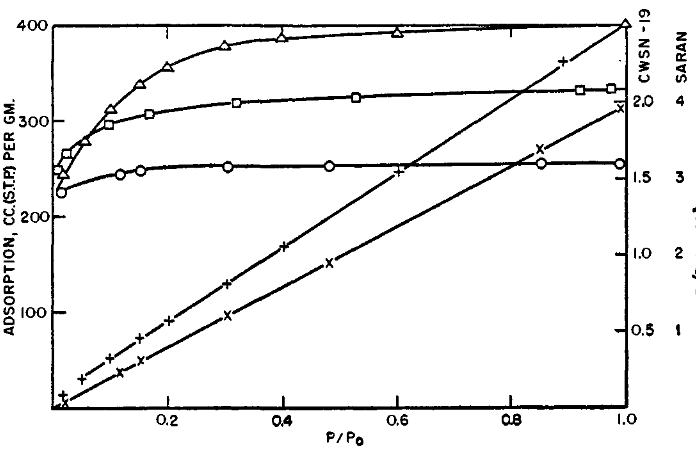

FIG. 5. Adsorption isotherms for nitrogen at −195°C.: △ CWSN 19; □, coconut charcoal; ○, Saran charcoal. Also, Langmuir plots (equation 4) of the data for Saran (×), and for CWSN 19 (+).

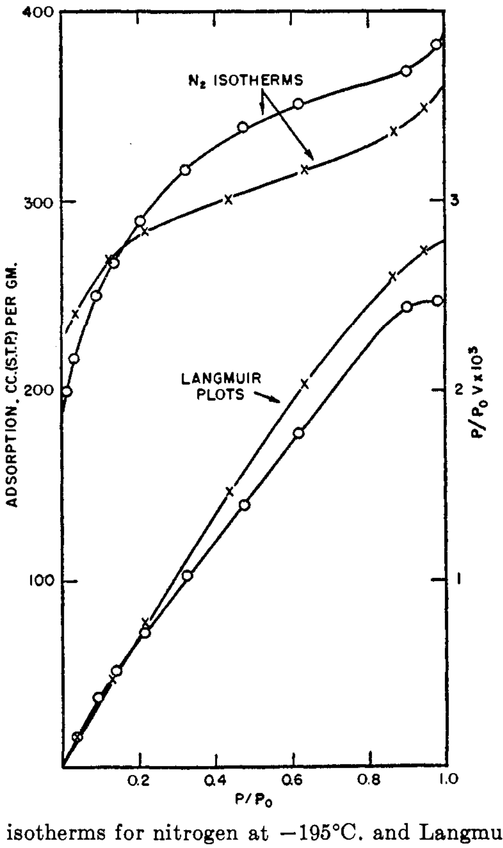

FIG. 6. Adsorption isotherms for nitrogen at −195°C. and Langmuir plots of the data for PCI P58 (×), and for a PCI special sample (○) that had been steam activated 350 min. during activation.

together as the activation proceeds, reaching area by nitrogen: area by butane ratios of 1.53 or 1.03, depending on which value is selected for the cross-sectional area of the butane molecule.

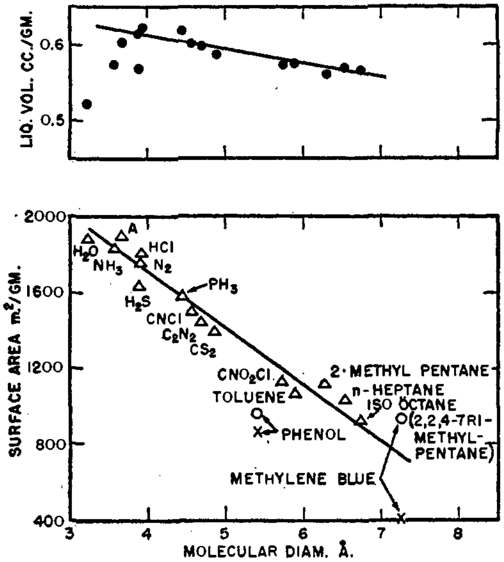

FIG. 7. Top curve is a plot of the adsorbate molecular diameter against the volume of adsorbate (calculated as liquid) taken up by CWSN 19 at $p/p_0 = 0.99$. The lower curve is a plot of surface areas (as calculated by equation 4) for the same adsorbates. The points indicated by open circles are from data by Young for the adsorption of phenol and methylene blue from solution onto crushed (100 mesh) charcoal samples; those marked X are for uncrushed samples for these same two adsorbates.

TABLE 2

Area of coconut shell charcoal (68) as measured by isotherms for nitrogen at 90.1°K. and n-butane at 0°C.

SAMPLE	ACTIVATION PERIOD	AREA IN SQUARE METERS PER GRAM			RATIO OF AREAS	
		By N_2 (17 Å.²)	By C_4H_{10}: (a) 32.1 Å.²	By C_4H_{10}: (b) 48.0 Å.²	$\frac{N_2}{C_4H_{10}(a)}$	$\frac{N_2}{C_4H_{10}(b)}$
	hours					
A	12	644	333	500	1.93	1.29
B	24	749	417	625	1.79	1.20
C	48	895	553	829	1.62	1.08
D	72	963	602	903	1.60	1.06
E	96	1070	703	1050	1.52	1.02
F	120	1136	737	1100	1.54	1.03

For obvious reasons it seems likely that the surface area measured by gas will be more important in judging the properties of charcoal than the areas measured by adsorbing molecules from a suitable liquid solvent. This is primarily due to the difficulty involved in causing a solute to diffuse through a solvent and cover the surface of capillaries when the latter are the order of a few molecular diameters in size. Nevertheless, some measurements of the surface area of charcoal by the adsorption of molecules from the solution have been made. In figure 7 a comparison is made between the area values obtained by phenol and methylene blue from solution and those obtained by adsorbing gas molecules of comparable size. The agreement on the crushed sample is fairly good; the areas on the uncrushed sample seem to be about 40 per cent lower by adsorption from liquid than by adsorption from gas. These few measurements from solution were not extensively or thoroughly studied. They are in sharp disagreement with the statement of Berl (23) that a good gas mask charcoal should adsorb only 25 mg. of methylene blue per gram of charcoal, corresponding to an area of only about 25 sq. m. per gram.[5]

TABLE 3

*Maximum millimoles of acids adsorbed, and surface areas in square meters, per gram of charcoal (104)**

CHARCOAL NO.	1	2	3	4	5	6	7	8	
Acetic acid	2.15	2.55	2.85	3.22	3.25	3.70	4.00	—†	millimoles
	338	402	449	507	512	583	630	—†	sq. m.
Propionic acid	1.63	2.04	2.47	2.91	2.93	3.46	3.75	3.96	millimoles
	257	321	389	458	462	545	590	624	sq. m.
Butyric acid	1.24	1.66	2.06	2.63	2.74	3.43	3.84	4.25	millimoles
	195	262	324	415	432	540	605	670	sq. m.
Valeric acid	0.88	1.31	1.75	2.40	2.41	3.18	3.66	4.01	millimoles
	139	203	276	378	380	501	577	632	sq. m.
Benzoic acid	0.89	1.26	1.71	2.25	2.31	2.91	3.38	3.70	millimoles
	140	198	269	354	364	458	533	583	sq. m.
Area by nitrogen adsorption‡	474	602	783	968	1045	1120	1330	—	sq. m.

* Taken from Canadian Report dated September 20, 1943.

† Insufficient charcoal.

‡ The area values by nitrogen adsorption were furnished by Dr. J. H. Morrison by private correspondence. The author averaged two sets of values furnished by Dr. Morrison and recalculated the areas on the basis of 16.2 Å.^{2} per nitrogen molecule.

It is interesting to note that the areas obtained by Lemieux and Morrison (104), using acetic, propionic, butyric, valeric, and benzoic acids, all lie in the range 583–670 sq. m. per gram on a given sample of well-activated charcoal (table 3). As would be expected, the area measured by acetic acid was much larger for small degrees of activation than that measured by valeric acid, just as the area measured by chloropicrin or other large molecules is much smaller (65, 90) than that measured by nitrogen in the early stages of activation when, presumably, the

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[5] It was assumed by Paneth that 1 mg. of methylene blue will cover an area of approximately 1 sq. m.

smaller pores are predominant. It will be noted that the areas obtained by adsorption from solution are 30–70 per cent smaller than those calculated from the nitrogen-adsorption isotherm.

III. ADSORPTION OF WATER VAPOR

A. Adsorption isotherms for various charcoals and whetlerites

Hundreds of water-adsorption isotherms have been determined (59, 60, 65, 90, 154) in the course of the present work on a variety of charcoals and whetlerites and for a number of reasons. In the first place, the question arises as to the influence of water vapor on the chemical or catalytic activity of the whetlerites. Secondly, water is known (65, 109, 110) to be capable of inhibiting the adsorption of chloropicrin and other gases by charcoals, and hence can influence the life of a canister toward such gases. Finally, water-adsorption isotherms have proved to be of great value in estimating the pore size and pore-size distribution (68) according to a number of methods, including a new one developed by Juhola (90, 91, 92).

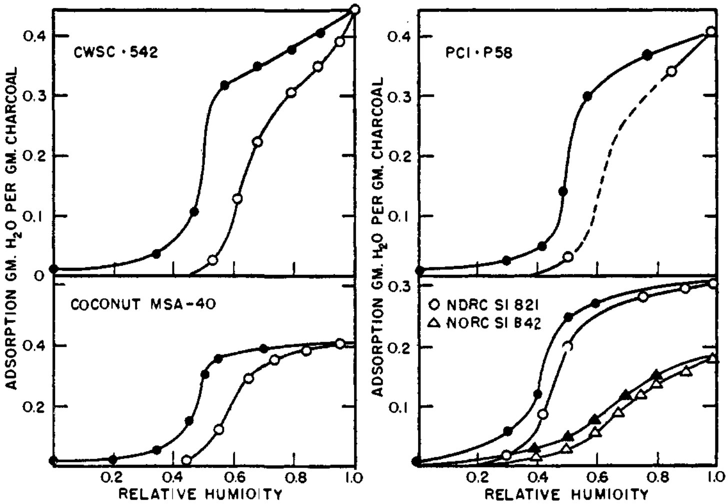

FIG. 8. Water-adsorption (open symbols) and water-desorption (solid symbols) isotherms for various charcoals at room temperature.

Various types of water isotherms (63) that have been found on charcoals by adsorbing and desorbing water vapor from a stream of air passing through the sample are illustrated in figure 8, and agree in general with those previously described in the literature (68, 96, 103). Most of the adsorptions are characterized by hysteresis that extends clear back to zero pressure when the isotherms are determined by a flow technique using air as a carrying gas. When the adsorption is measured by a static system after thorough evacuation of the sample, the shape of the hysteresis loop is somewhat altered and the desorption curve on at least some charcoals rejoins the adsorption curve at about 0.4 relative pressure

(65, 90), as illustrated in figure 9. However, Juhola has found (90) a number of examples of partially activated charcoals for which, even in a static system, hysteresis persists down to approximately zero relative pressure. In the author's opinion, any such hysteresis in physical adsorption extending to relative pressures below those corresponding to condensation on pores at least four molecular diameters in diameter is seriously to be questioned. Both slow chemical adsorption and gradual evolution of carbon monoxide or carbon dioxide from surface complex (13) or from ash in the presence of water vapor may be factors in apparent low-pressure hysteresis in water adsorption.

It has long been known that the shape of the adsorption isotherms for water vapor on a charcoal is radically influenced by the amount of oxygen present as a

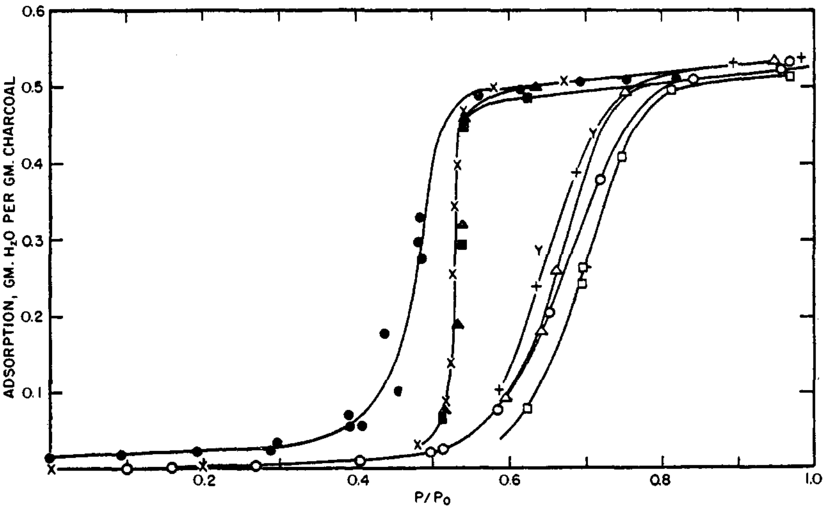

FIG. 9. Water-adsorption and water-desorption isotherms on CWSN 19 as determined by a flow system (○, ●) and by a static system. For the latter, samples were evacuated at 110°C. (+, ×, and Y for adsorption, desorption, and resorption, respectively); 500°C. (△ and ▲ for adsorption and desorption); and 900°C. (□, ■, □— for adsorption, desorption, and resorption).

surface complex. For example, it was pointed out by Lawson (103) and by King and Lawson (96) that the presence of an oxygen complex on the charcoal surface shifts the adsorption isotherm to lower pressures than those corresponding to the same adsorption in the absence of such a complex. The influence of oxygen coating a sample is illustrated by figure 10, in which the water-adsorption isotherm is shown for CWSN 19 both before and after exposing it to oxygen at 400°C. (60, 154). During this exposure the nitrogen isotherms remained practically unchanged.

The amount of water adsorbed has proved to be substantially independent (38) of the temperature between 15° and 40°C. at a given relative pressure for a number of charcoals (60, 154). This is not surprising since, for water, it is known that $E_1 - E_L$ in equation 2 is small. Consequently, the influence of temperature on the value of C and hence the amount of adsorption according to equation 3 is negligible over short temperature ranges, as illustrated (60) in figure 11 for water isotherms determined by a flow system for two different temperatures.

B. Rate of adsorption of water

The rate of adsorption of water vapor has received considerable attention because of the importance of knowing the rate at which canisters might be contaminated by picking up water vapor and the rate at which they could be dried out when necessary by sucking dry air through them. The following conclusions have been reached, although no complete mathematical analysis of the rates of adsorption and desorption has been reported (46a):

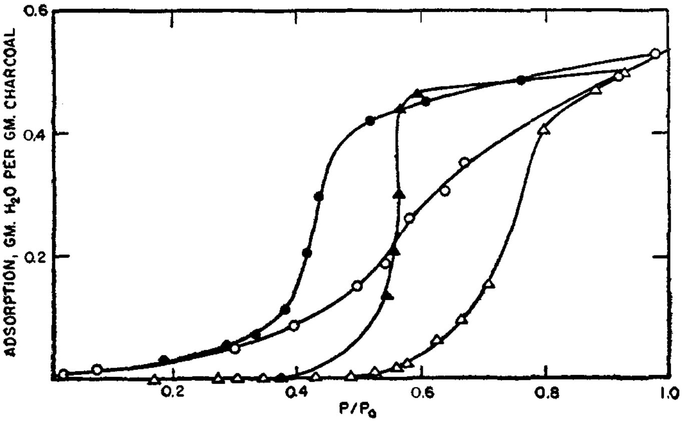

FIG. 10. Water isotherms on CWSN 19 before (△, ▲) and after (○, ●) surface oxidation. The oxidized sample (154) is CWSN 19 TUC 46.

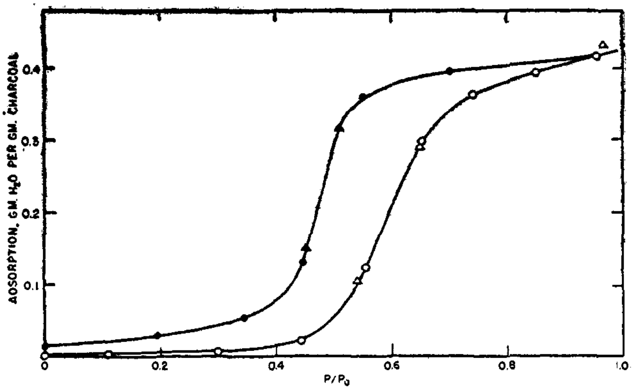

FIG. 11. Adsorption of water on Navy charcoal MSA Grade 40. Triangles are for 15°C.; circles, for 40°C. Flow system with air as carrying gas was employed.

(*1*) The rate of adsorption of water vapor by whetlerites is a little faster, and the rate of desorption somewhat slower than for the corresponding base chars (60). This is probably due to the fact that the equilibrium water-vapor curve is shifted toward lower relative pressures by whetlerization. Hence, for a gas stream of a given relative humidity the driving force for adsorption is greater than for the base char; similarly, the driving force for desorption into a dry gas stream is less for the whetlerites than for the base chars, and hence the rate of desorption is slower for the whetlerites than for the base chars.

(*2*) The rate of equilibration increases with the rate of gas passage (32, 33, 34) at a given relative humidity in the entering gas stream. This would be expected, because of the increase in the average partial pressure of water vapor throughout the charcoal column resulting from the higher gas velocity.

(*3*) Apparently (34) the slow step in the equilibration of charcoal with water vapor is not the mass transfer of the water vapor from the stream of gas to the charcoal particles, but the resistance encountered by the passage of the water vapor from outside the particle into the tiny capillaries. This has been pointed out by Colburn (34), who showed that the HTU (height of a transfer unit) for charcoal samples ranged from 3 to 25 in. under his experimental conditions compared to values of 0.2 to 1 in. for silica gel particles of similar size. This observation is consistent with the idea that some of the penetration of gases into the smallest capillaries is due to surface migration on the adsorbent (148). If the adsorption of water vapor is low, it would naturally follow that the transport of water vapor into the pores of the capillaries by surface migration and hence the rate of equilibration would be slow.

(*4*) At 30°C. and a gas flow of 600 cc. of air per minute per gram of charcoal, the time (60) for half-equilibration of several typical base chars ranged from 48 to 90 min.; the time for half-desorption into a stream of dry air at this same flow rate was about 30–40 per cent of the time of adsorption. The time required for the equilibration during the adsorption of water vapor on the whetlerites was from 30 to 60 per cent of the time required for equilibration of the base charcoals.

An analysis of the rate of adsorption of water vapor, carbon disulfide, and mixtures of these two gases has recently been published by Vreedenberg and van Nouhuys (146). According to the hypothesis of these authors, the rate of increase in the fraction, θ_1, of the surface covered by adsorbate is related to the relative pressure of water vapor, π, by the equation:

$$\frac{d\theta_1}{dt} = C\pi(1 - \theta_1) - D\theta_1(1 - \pi) \tag{7}$$

At the steady state at which $d\theta_1/dt = 0$, one then obtains an isotherm equation of the form:

$$\theta_1 = \frac{C\pi}{D + (C - D)\pi} \tag{8}$$

This contrasts with the rate equation that would be expected according to the Langmuir postulates:

$$\frac{d\theta_1}{dt} = C\pi(1 - \theta_1) - D\theta_1 \tag{9}$$

and the resulting isotherm equation:

$$\theta_1 = \frac{C\pi}{C\pi + D} \tag{10}$$

The logic behind equation 7 is not very impressive; it is argued that the desorption rate should be proportional not only to the fraction of the surface covered but to the distance between unity and the gas-phase relative pressure. Nevertheless, it must be admitted that equations 7 and 8 appear to fit the data of the authors (146) adequately, and even permit the calculation of the rate and equilibrium adsorption from mixtures. It is also true that equation 8 but not equation 10 can, by appropriate choice of constants, be made to represent the portion of the water-adsorption isotherm on charcoal that is convex to the pressure axis.

C. *Nature of water adsorption on charcoal and whetlerites*

Much has been written (38, 112, 121) relative to the nature of water adsorbed on charcoal. This is understandable, since the interpretation of the water isotherms may be a key to the calculation of the pore size and pore-size distribution of the adsorbent. If water is adsorbed in or desorbed from a state that may be called capillary condensation, then the adsorption or desorption curves may be used with the help of an appropriate equation such, possibly, as that of Kelvin to estimate the pore-size distribution. In the next section we shall see how this method has actually been applied by Juhola and others. For the present we shall limit our discussion to a presentation of the evidence that has been accumulated as to the nature of water adsorption. In particular, the evidence will be summarized on the question of whether water pickup by charcoal is adsorption, capillary condensation, or a combination of both.

McBain (120, 121) and his coworkers have contended that the sorption of water vapor by charcoal is an adsorption phenomenon and is not capillary condensation. In favor of this point of view are the following experimental facts:

(*1*) When water vapor is taken up by charcoal the latter expands (121) rather than contracts.[6] It seems agreed that pure capillary condensation would lead to a tension in the pores of the charcoal and hence to a slight contraction.

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[6] Very recent publications throw doubt on this conclusion of McBain, Porter, and Sessions (121). Haines and McIntosh (121a) have found that a carbon rod made up of active charcoal (made by the zinc chloride process) contracts during the desorption of water as the relative humidity is lowered, but at 75 per cent relative humidity reaches its normal length, and at 50 per cent relative humidity is shorter than the original rod by 75 microns (about 0.08 per cent). At still lower relative humidities as the major portion of the desorption occurs, the charcoal *expands* back to its original length as water is *removed*. Wiig and Juhola (121b) have found that a stack of activated charcoal blocks behaves on both adsorption and desorption as the rods of Haines and McIntosh behaved on desorption. These latter authors failed to detect any length change on adsorption until a relative humidity of about 70 per cent was reached. Between 70 and 96 per cent Haines and McIntosh found a linear expansion of the rod with relative humidity, the final value (~0.1 per cent) at 90 per cent for 20°C. being in good agreement with the final value of McBain, Porter, and Sessions, 0.13 per cent at 27°C. at about 100 per cent relative humidity. Both

(*2*) McBain, Porter, and Sessions (121) succeeded in drying and evacuating a sugar charcoal sufficiently to eliminate all hysteresis in an isotherm at 120°C. The results of their measurements are shown in figure 12. They are very similar in many respects to some of the "first-order" phase transitions observed by Harkins and Jura (77) and his coworkers for various gas–solid systems. The water sorption rises abruptly at a relative pressure of about 0.3 until about 80 per cent of the sorption capacity of the charcoal is satisfied. It then levels off gradually to a constant saturation value. Desorption follows the same curve. On the other hand, after the charcoal had stood in contact with the water vapor for a year with the development of detectable amounts of hydrogen, a repeat adsorption run at 120°C. showed the conventional type of adsorption (curve 2, figure 12) with hysteresis in desorption; the adsorption and desorption curves at

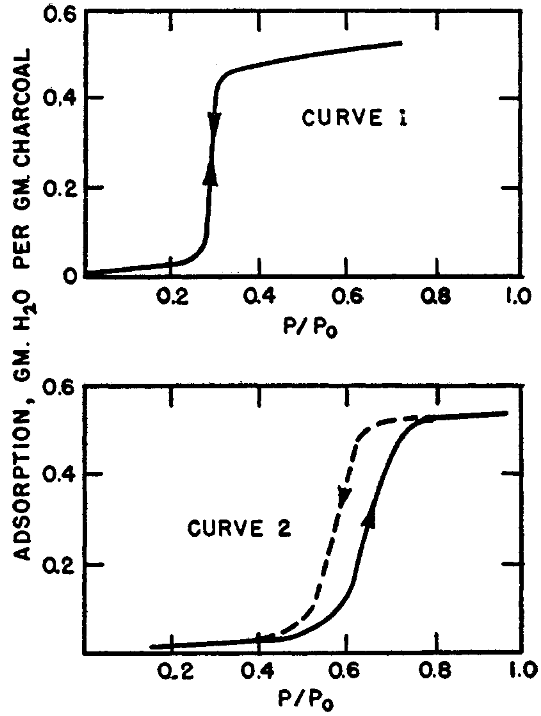

Fig. 12. Water adsorption on charcoal (121) at 120°C. Curve 1 is for a highly degassed and dried sample of sugar charcoal; curve 2 is for the same sample after continuous exposure to water vapor for 15 months.

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of the recent papers would, therefore, seem to agree that the escape of water from charcoals in the relative pressure range in which most of the desorption occurs (as in the almost vertical section of the desorption curve of the highly degassed charcoal, as shown in figure 9) is from water that seems to be held by capillary condensation.

60°C. on this sample both agreed approximately with the desorption part of curve 2 of figure 12.

(3) The shapes of the lower parts of the water isotherms such as shown in figures 8 and 9 are not very different from the shapes of the water isotherms obtained by Emmett and Anderson (54) on samples of degassed carbon black (figure 13) or by Harkins, Jura, and Loeser (78) on graphite. It will be noted that the nitrogen isotherms on the carbon black before and after evacuation at 1000°C. are practically identical. On the other hand, the water-adsorption isotherms are greatly changed. The sample after the high-temperature evacuation adsorbs no water at low relative pressures but picks up increasing amounts as the relative pressure is increased. The isotherms apparently indicate a heat of adsorption that is smaller than the heat of liquefaction. The water isotherm before evacuation rises almost linearly with relative pressure in much the way one would expect if the heat of adsorption is substantially equal to the heat of liquefaction. It seems clear that on the degassed carbon black the water adsorption cannot be due to capillary condensation, since there is no evidence of any capillaries being present. Certainly, the high-temperature evacuation did not produce capillaries, or the nitrogen-adsorption isotherms would have been quite different before and after the evacuation. The similarity between the shapes of the two carbon black water-adsorption isotherms and the shapes of the isotherms of water vapor on charcoals is striking; one must accordingly certainly be cautious about interpreting the water-adsorption isotherms on charcoal as due to capillary condensation.

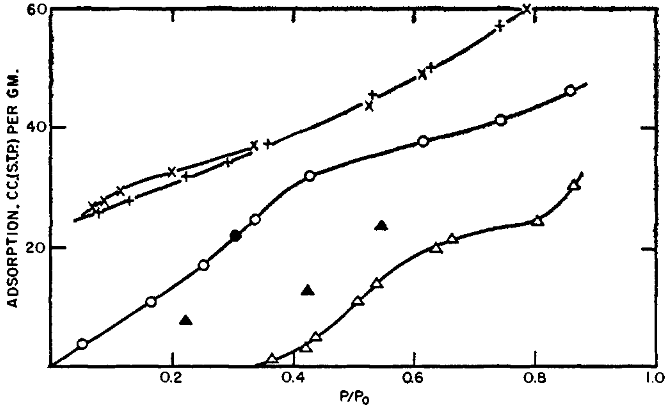


FIG. 13. Adsorption of nitrogen at −195°C. and water vapor at 25°C. on Grade 6 carbon black (54). ×, nitrogen before degassing at 1000°C.; +, nitrogen after degassing. Circles are for water isotherms before degassing at 1000°C.; triangles are for sample after degassing. Solid circles or triangles are for desorption points.

The evidence for interpreting the isotherms as an indication of water being held on the charcoal by capillary condensation is also strong:

(*1*) No satisfactory explanation of hysteresis in desorption has so far been advanced for any process other than capillary condensation. A recent paper by Gleysteen and Deitz (72) suggested that if one applies the multilayer theory of Brunauer, Emmett, and Teller to the adsorption isotherms at high relative pressures in place of the capillary condensation theory and then assumes that desorption involves a larger heat than adsorption, hysteresis can be accounted for. It remains to be explained why the heat of desorption should be larger than the heat of adsorption. However, in the water isotherms on the degassed carbon black (54) in figure 13, hysteresis appears to exist. If these observations are confirmed by further work they will tend to undermine the capillary condensation interpretation of hysteresis, since the particle size in the carbon black work is such that even capillary condensation between the particles seems to be ruled out.

(*2*) By assuming that the shape of the adsorption isotherms of water vapor on charcoal is due to capillary condensation and that cos θ in the Kelvin equation

$$\ln p/p_0 = -\frac{2\sigma V \cos\theta}{rRT} \tag{11}$$

has a value of 0.5–0.6, Juhola has been able to calculate pore-size distributions for charcoals that yield good values for the surface areas measured by nitrogen adsorption. This work will be considered in detail in the next section.

(*3*) In the writer's opinion, the most convincing evidence that even the adsorption curve is partly capillary condensation has been obtained by Juhola in his scanning runs (90). A typical set of these is shown in figure 14. Unless some explanation for hysteresis based purely on adsorption is forthcoming, these scanning runs must be considered definite evidence that a part at least of the adsorption isotherm for water on charcoal is due to capillary condensation.

Perhaps the soundest interpretation of water isotherms at the present time is that they are some combination of adsorption and capillary condensation. In water isotherms such as shown in figure 14, it seems reasonable to assume that on the adsorption part of the curve the adsorption increases with relative pressure, passes through a maximum, and then decreases as more and more of the surface is eliminated as a result of the capillaries filling with condensed water. At high relative pressure near saturation (107) this interpretation would say that most of the water pickup is due to capillary condensation (26). It should be noted, however, that if this picture is adopted and if the same angle of wetting, density, and surface tension characterizes the condensed liquid during both adsorption and desorption, then one must conclude that the capillary condensation on the adsorption part of the curve does not occur at the relative pressures indicated by the Kelvin equation. For some reason that is not as yet certain it would appear that capillaries of a particular size fill with condensation only at relative pressures that are considerably higher on the adsorption side of the curve than on the desorption branch. Perhaps the bottleneck theory of Kraemer (98) or the "open pore" theory of Cohan (37) can supply the explanation for the hysteresis. Indeed, Fineman, Guest, and McIntosh (68) conclude that Cohan's open-end pore theory yields good values for the size of capillaries in several charcoals with which they worked.

Some idea as to the nature of water in capillaries might normally be expected from measurements of freezing points and measurement of the density of the water sorbed by the charcoal. Two sets of measurements of the density of the water in the charcoal have been made. They disagree sharply with each other. Morrison and McIntosh (123) obtained values ranging from 1.01 to 1.16, 0.95 to 1.04, 0.99 to 1.15, and 0.98 to 1.17 for four charcoals exposed to relative humidities below 100 per cent. On the other hand, three runs with pure water at 100 per cent relative humidity resulted in the sorbed water having apparent densities of 0.95, 0.94, and 0.93. In contrast to this Wiig and Juhola (151) have found consistently that on activated charcoals the apparent density of water is less than unity, over the entire range of relative humidities, values of approximately 0.93 and 0.90 characterizing adsorption and desorption parts of a run. It is difficult to be sure of the cause of this discrepancy. The writer would be a little suspicious of the procedure used by the Canadian workers for getting relative humidity values smaller than 100 per cent. The use of sulfuric acid to decrease the partial pressure of water vapor in their experiments might have contaminated the charcoals with small amounts of acid spray or sulfur trioxide. Either of these would have a much higher density than water and would cause the apparent density values to be erroneously larger. In agreement with this, it should be noted that the values obtained by Morrison and McIntosh (123) using pure water (100 per cent relative humidity) for saturating the sample are in satisfactory agreement with Juhola's results.

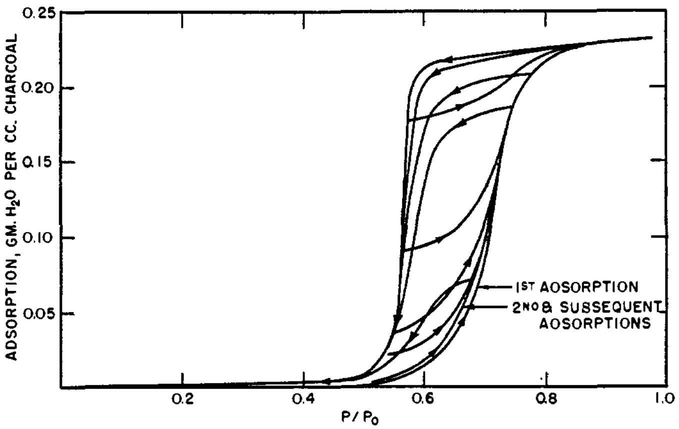


FIG. 14. Water-adsorption isotherm on CWSN 291 AY1 (90); scanning curves are also shown

Another possible source of error in the results of Morrison and McIntosh (123) has been suggested by Wiig (149). In the course of their measurements, they expanded a helium-water vapor mixture containing *p* mm. of water vapor into an adsorption bulb containing charcoal equilibrated with water vapor at *p* mm. Wiig points out that such a procedure causes the pressure of water vapor in the charcoal bulb to be greater than p, and in the helium buret less than p. Unless the 18–24 hr. equilibration time is sufficiently long to permit a reëstablishment of the partial pressure of water vapor to p mm. throughout the system, the apparent density values will be high. Because of the fact that the blocking of submicropores by capillary condensation of water or the fact that water is under tension in capillary condensation would both tend to make the density less than 1, it seems likely that the values obtained by Juhola for the apparent density of water are more nearly correct than the high density values obtained by McIntosh and Morrison.

Freezing methods have also failed (27) to help much in revealing the nature of adsorbed water. Johnstone and Clark (85) found that charcoals such as CWSN 19 when equilibrated with water sufficient to cause a 45 per cent weight increase on a dry basis (probably equilibrated at about 75 per cent relative humidity) failed to yield an ice pattern at −30°C. On the other hand, a sample soaked in water initially and then air dried to a damp powder showed ice crystals that were much smaller than those obtained by allowing moisture from the air to condense on the cold cassette. It seems likely that the water picked up during adsorption at 75 per cent relative humidity is either held by adsorption as a monolayer or else is in the form of capillary condensation in capillaries as small as 20 Å. in diameter. It is, therefore, understandable why the sample equilibrated at 75 per cent relative humidity failed to show an x-ray pattern. The pattern shown by the sample initially exposed to liquid water vapor and retaining about 75 per cent water by weight could easily be due to a thin film of water located in the larger capillaries of the charcoal or adhering to the outer periphery of the particles. A 75 per cent weight increase is considerably higher than one would expect from adsorbed water on CWSN 19 even at saturation. Accordingly, this observation does not reveal the nature of the water that is contained in the capillaries in normal water adsorption up to, say, 99 per cent relative humidity.

Culbertson and Winter (41) have shown that a considerable amount of water taken up by charcoal does not freeze until the temperature is well below 0°C. Even at −40°C. some of the water apparently remains unfrozen. However, as they point out, absence of good heat-capacity data (39) for adsorbed water prevents exact calculation as to the amount of water in a "bound" state on the charcoal surface.

Another approach toward throwing some light on the question of the nature of adsorbed water was made by comparing the nitrogen adsorption on dry charcoal with that on samples that had been partially equilibrated with water vapor. Such measurements (65) showed that on both PCI P58 and CWSN 19 charcoals there is no sudden expansion of water as the temperature is dropped until some point between −78° and −195°C. is reached. This seems to point to the conclusion that the water held by the two above-mentioned charcoals at 83.5 and 96 per cent relative humidities, respectively, is not water having a normal freezing point. However, much further work would be required before one could be sure of the influence of the size of a capillary on the freezing point of liquid contained in it. Hence even this observation is a bit indefinite as an indication of the nature of the water held in capillaries.

IV. PORE SIZE AND PORE-SIZE DISTRIBUTION

No entirely satisfactory method has been discovered for measuring pore size and pore-size distribution in charcoal and other similar small-pore materials. The difficulties encountered are many. Perhaps one of the principal complications has to do with the shape of the capillaries. Not only is it impossible to ascertain whether the capillaries are cylinders, cracks with parallel walls, crevices, cones, or other regular geometric shapes, but it is impossible to tell what combination of all of these and other irregular forms may be involved. Furthermore, it must be realized that in dealing with capillaries that are one to ten molecular diameters in size, one has little information as to the way in which density, surface tension, and other properties of the adsorbed molcules may differ from those of the adsorbate in bulk form. It would probably, therefore, be difficult to specify "pore size" even if we knew the exact shape of all capillaries present. Accordingly, progress in estimating pore diameters of charcoal is possible only by virtue of making assumptions as to the shapes of the capillaries and the properties of the adsorbed molecule. It is gratifying that, in spite of the numerous assumptions and approximations that had to be made, methods were worked out during the recent war that are certainly more satisfactory than any previously available and that give results that are useful in trying to approach the ideal type of adsorbent for gas mask work.

Methods for measuring pore size that have been employed on the charcoal work may be listed in the following five classifications: (*1*) Study of adsorption as a function of the size of the adsorbate molecules (65). (*2*) Application of the Kelvin equation to the adsorption and desorption of any gaseous adsorbate other than water vapor (65). (*3*) Application of the Kelvin equation to the adsorption (68, 112) and desorption (90) isotherms of water vapor. (*4*) Measurement of the change of surface area resulting from the pickup of water by the charcoal (90, 91, 92). (*5*) Measurement of the pressure required to force mercury (51, 59, 90, 147) into the charcoal capillaries. These five methods will now be considered in turn.

A. Molecular size as a criterion of pore size

In a general way it would seem to be possible to tell a great deal about the size of pores in charcoal by comparing the change in the amount of adsorption with the size of the adsorbate molecule. For example, experimental work on chabazite has shown rather clearly that it is possible so to prepare the adsorbent (18, 19, 57, 101, 138) as to make the pores capable of adsorbing molecules of a given adsorbate and yet screening out almost completely molecules of only a slightly larger size. Thus, as a function of the temperature and time of dehydration, as pointed out in an earlier section, chabazite can be made to adsorb hydrogen but not nitrogen, oxygen but not nitrogen, nitrogen but not butane, and normal hydrocarbons but not branched-chain hydrocarbons. However, this apparently simple method becomes very complicated if the adsorbent is one in which only a partial screening out of the larger molecules occurs. One is then faced with the task of differentiating between screening effects and the influence of the tightness of packing of odd-shaped molecules in capillaries of unknown shape. For example, it is known that if one compares the surface area of CWSN 19 obtained by the adsorption of nitrogen with that obtained by use of successively larger molecules, one obtains (figure 7) a decrease of about 50 per cent in going to isoöctane (65). It is not at all certain, however, that this means that one-half the area is located in pores intermediate in size between that of the nitrogen molecule (about 3.9 Å.) and that of the isoöctane molecule (about 6.7 Å.). Much of the decrease may be attributed to the less efficient packing of large molecules onto a given area than the corresponding packing of smaller, more symmetrical molecules. Indeed, it is not even well established as yet that, for nonporous adsorbents, the same areas can be obtained by using large molecules as measuring units as by using smaller ones (20, 53). In spite of this, adsorbates whose molecules are of different sizes have been used effectively for at least qualitative appraisal of the relative pore sizes of two different charcoals. For example, it is claimed in the literature (103, 120) that large dye molecules are almost completely excluded from the pores of many charcoals. As a matter of fact, decolorizing carbons for removing color from sugar solutions commercially are known to have much larger pores than the charcoals or activated carbons intended to adsorb large quantities of gas. Furthermore, some unmistakable screening effects can be noticed for molecules differing as little in size as nitrogen and isoöctane. For example, charcoals made from carbonization of certain plastics are known to have uniformly small pores. Thus, Saran charcoals will adsorb up to twelve times (65) as many molecules of nitrogen as of isoöctane and will equilibrate very much faster with nitrogen than with isoöctane. It seems likely that most of the pores of this material are in the range 5–10 Å. in diameter. Again, it has been found that charcoals made by the activation of coal develop pores capable of adsorbing nitrogen much earlier than they develop pores capable of adsorbing molecules as large as chloropicrin or isoöctane. Accordingly, in a qualitative sense, at least, the relative amounts of adsorbate picked up as a function of the size of the adsorbate molecule can be used to obtain some idea as to the distribution of pore sizes in charcoal.

Attention should, perhaps, be called to one other precaution in judging the size of capillaries by the size of the adsorbate molecules. If one compares the amount of adsorption in terms of the volume of adsorbate (calculated as normal liquid) picked up, he occasionally obtains some odd results. For example, on two samples of charcoals on which the pores had been partially plugged by the product from the oxidation of arsine, the volume of liquid isoöctane adsorbed near saturation was greater (66) than the volume of nitrogen (as liquid) adsorbed near saturation. Specifically, the ratios of the volumes of isoöctane to nitrogen were 1.3 and 1.6, respectively, for the two samples. This can be understood if one remembers that, if two plane parallel walls were completely covered with adsorbate molecules and were exactly 12 Å. apart, then the volume of liquid calculated for an adsorbate that had molecules 6 Å. in size would be nearly 50 per cent greater than that of an adsorbate that had molecules 4.2 Å. in size. Such extreme cases are rarely encountered, though it is observed that the liquid volume of adsorbates of successively larger size picked up by a charcoal do not fall off (figure 7) as rapidly as do the apparent surface areas as calculated from the molecular cross section. This may result from the effect of the thickness of the adsorbed molecule entering into a calculation of the volume of liquid picked up when much of the adsorption is necessarily only a single layer in thickness.

The adsorption of dyes by activated carbons and charcoals is being extensively and thoroughly studied by Deitz and his coworkers at the Bureau of Standards. Adsorption of dye and other organic molecules is being compared with the low-temperature adsorption of nitrogen. Deitz has already made it clear that such measurements are fraught with many difficulties that have not usually been taken into consideration. His work when completed should give a final answer to the extent to which adsorption of big molecules from solution may be considered as significant in pore-size determination.

B. Pore size by applying the Kelvin equation to the adsorbates other than water.

A general method for measuring the diameter (D) of pores that has often been suggested makes use of the Kelvin equation,

$$D = -\frac{4\sigma V \cos\theta}{RT\, 2.303 \log p/p_0} \tag{12}$$

where V is the molal volume, σ is the surface tension, T is the temperature at which the adsorption is measured, and p/p_0 is the relative pressure of the adsorption. θ is the angle of wetting of the walls of the capillaries by the adsorbate. The equation in this form assumes that the capillaries are circular in cross section.

Two serious complications arise from trying to use this method in practice. For substances having large enough pores to give smooth S-shaped curves of the type shown in figure 1, it becomes very difficult to differentiate between an increase in adsorption due to capillary condensation and one due to multimolecular adsorption. Indeed, some (28) interpret the upper part of the adsorption isotherms of curves such as shown in figure 1 for carbon and also those shown in figure 15 for porous glass as due entirely to multilayer adsorption rather than to capillary condensation. Wheeler (21), Ritter (133), and Shull (139) are having some success in separating the multilayer adsorption effect from the capillary condensation effect and thereby are able to obtain fairly satisfactory pore distributions from nitrogen-adsorption isotherms on gels at −195°C. For the most part, however, this confusion between multilayer adsorption and capillary condensation effects has not been satisfactorily resolved and hence makes it difficult to use equations in conjunction with non-aqueous adsorbates in calculating pore diameters of charcoal.

A second difficulty encountered in attempting to calculate pore diameters by use of the Kelvin equation has been pointed out in the literature (11, 57, 70) on a number of occasions and is especially applicable to fine-pore solids such as charcoal. It has to do with the question of whether the diameter mentioned in the Kelvin equation (equation 12) is the diameter of the capillary *after* a monolayer has been adsorbed or before it has been adsorbed. If the capillaries are large enough to permit multilayer adsorption, the thickness of the layer left on the surface after a capillary empties at some given desorption pressure also comes into consideration, since, according to the multilayer theory (29), one may have several statistical layers left on the surface at sufficiently high relative pressures. This second difficulty can perhaps best be discussed in connection with figure 16, showing the adsorption and desorption isotherms for nitrogen on several typical charcoals. It will be noted that the desorption isotherms show some hysteresis compared to the adsorption isotherms. The desorption curve, however, rejoins the adsorption curve at about 0.35–0.4 relative pressure.

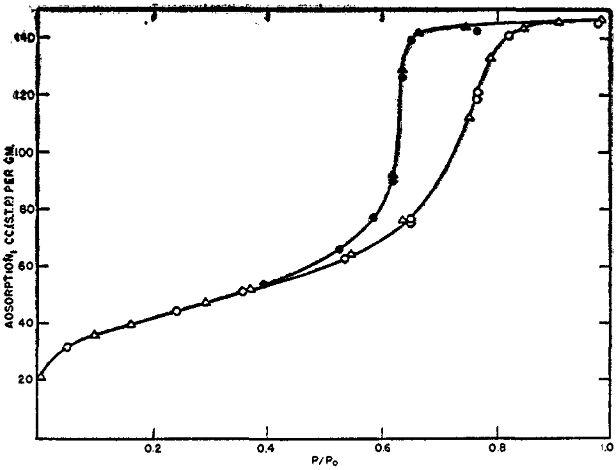


FIG. 15. Adsorption of nitrogen on porous glass at −195°C.; solid symbols are for desorption

It has been pointed out by Cohan (37) that for a large number of adsorbates the desorption isotherms rejoin the adsorption isotherms at a relative pressure which, according to the Kelvin equation, calculates out to correspond to four molecular diameters. On such a basis the adsorption of nitrogen on the charcoals shown in figure 5 would indicate only a comparatively small pore volume in the pore diameter range between 20 Å. and about 2000 Å. (this latter value being the upper limit fixed by the highest relative pressure—0.99—to which the runs were carried). For charcoals such as those shown in figure 16, on the other hand, definite qualitative evidence is given by the nitrogen isotherms as to the presence of capillaries in the range 20–2000 Å. in diameter.

The two complications discussed thus far are involved even when the desorption curve shows marked hysteresis in comparison to the volume of gas picked up at a given relative pressure during adsorption. Matters are made even more complicated by the fact that, according to some interpretations of capillary condensation, one may not obtain any hysteresis (37) even though capillary condensation is occurring. It is claimed, for example, that if capillaries are wedge-shaped no hysteresis is to be expected. Also, if they are cylindrical but have some narrow portion less than four molecular diameters in diameter they will not, according to certain hypotheses (37), give hysteresis. For all of these various reasons it may be concluded that deductions as to capillary size and distribution based on the adsorption of molecules other than water vapor are susceptible to only qualitative interpretations at best. Even if hysteresis (the usually accepted criterion for capillary condensation) occurs, the interpretation of the results on a quantitative basis is made very difficult if not impossible by the uncertainty as to the thickness of the adsorbed layer left after evaporation of the portion of the sorption that is due to capillary condensation.

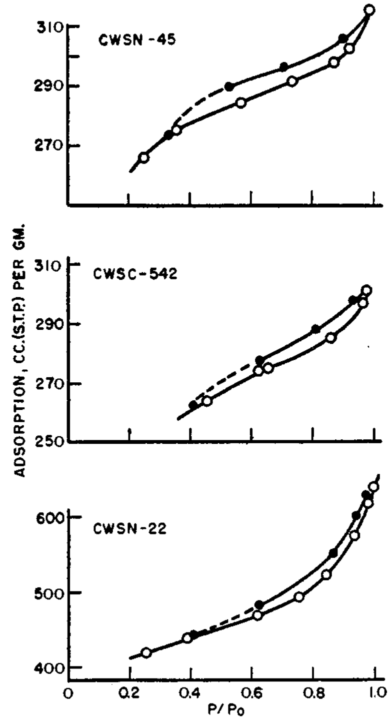


FIG. 16. Nitrogen adsorption and desorption isotherms at −195°C. on several different charcoals.

There is one adsorption region in which the Kelvin equation may be applied to nitrogen isotherms with a somewhat greater assurance than indicated above. It is the range near saturation extending up to the highest relative pressures that can be conveniently measured. By the use of the Pearson gauge (59) for measuring pressures very close to saturation, nitrogen-adsorption measurements have been made on several charcoals. Typical adsorption data (59a) are plotted in figures 17 and 18. The adsorption in the range 0.99–0.999 covers diameters between 1800 and 18,000 Å., if one assumes that the Kelvin equation is valid for the calculation. The question may well be asked as to whether the abrupt rise in some of the isotherms in this relative pressure range may not be partially due to the formation of multilayers on the surface of the large pores. It is difficult to give an exact answer in the absence of any certain knowledge as

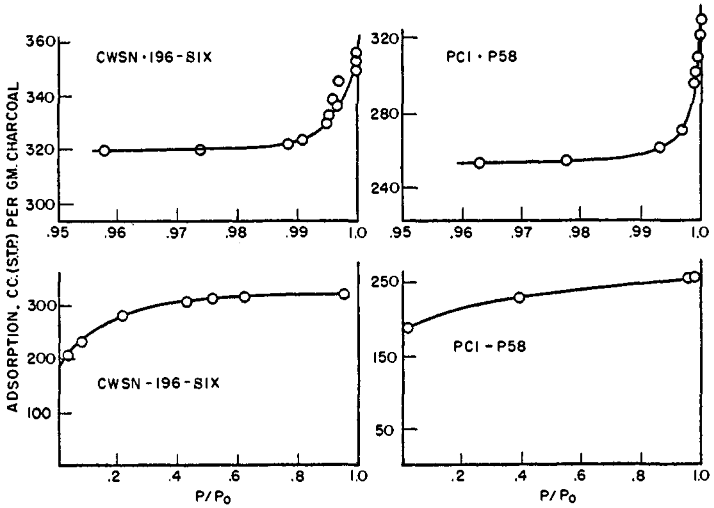


Fig. 17. Adsorption of nitrogen at −195°C. up to high relative pressure (0.999) on two different charcoals.

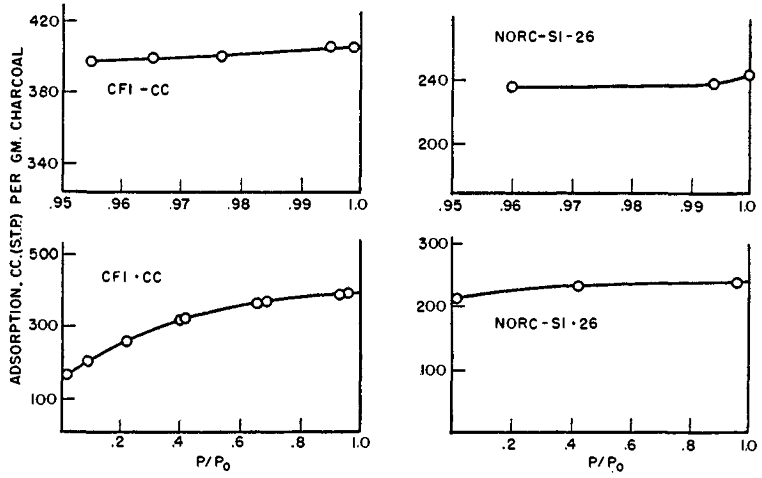


Fig. 18. Adsorption of nitrogen at −195°C. up to high relative pressure (0.999) on charcoals CFI "CC" and NDRC SI 26.

to the thickness of films that will be built up without capillary condensation. The B.E.T. equation (29) if followed would predict layers 1000 molecular diameters in thickness at a relative pressure of 0.999 and a *C* value of 100. However, this is certainly much on the high side, since the B.E.T. equation predicts adsorption that is too high at all relative pressures above 0.35. It seems more likely from the few measurements reported in the literature (37) that no more than 50 layers would be built up. This would mean that the multilayer built up would be no more than about 10 per cent of the total volume of liquid required to fill pores of this size and hence could be neglected. As shown in figure 18, both Saran and CFI "CC" charcoals show no adsorption increase between 0.99 and 0.999; on the other hand, the charcoals shown in figure 17 have a considerable increase in adsorption in this range of relative pressure.

Perhaps it would be more nearly correct to interpret adsorption isotherms at high relative pressures as leading to minimum values for the volume of pores in the size range covered by the isotherms. This precaution is suggested by the experiments of Bangham and Razouk (16), who claim that the large pores (200,000 Å.) of a charcoal with which they were working would not fill up even when p/p_0 was increased to 1. Only immersion of the samples in the liquid adsorbate caused these large pores to fill up.

It has been pointed out that by selecting proper adsorbates having large products of $V\sigma/T$ (see equation 12) it is possible to extend the pore measurements to larger diameters without working at higher relative pressures. Carbon tetrachloride (125), pyridine (126), and tributyrin (127) have been employed in this way to extend the measurements to 4000, 5000, and 13,500 Å., respectively.

C. Pore size from water adsorption and desorption isotherms

It has been suggested (68, 112) that adsorption isotherms for water vapor on charcoals can be used for calculating pore-size distributions. However, there seems good reason to doubt that all of the water picked up by charcoal during adsorption is held by capillary condensation. The similarity between the adsorption isotherms for water vapor on well-degassed, non-porous carbon black (54) and those for charcoals such as shown in figures 9, 10, 11, 12, and 14 suggests caution in making any pore-size calculations from the adsorption curves. On the other hand, the desorption isotherms for some of the charcoals give every indication of representing the emptying of capillaries with little or no residual adsorption. Therefore, calculations such as those of Juhola, described below, seem entirely warranted provided the charcoals used are those having negligible adsorption below about 0.4 relative pressure.

If one applies the Kelvin equation to a desorption isotherm such as shown in figure 14, and uses a value of unity for $\cos\theta$, one obtains pore diameters in the range 30–40 Å. for most of the sample. These clearly are too large, for they would not afford a sufficiently large area for the observed pore volume to account for the surface area measured by nitrogen adsorption or by the adsorption of other gases. There seem to be two alternatives in interpreting the desorption curves. The possibility exists that the angle of wetting is not zero degrees but an angle of such size as to yield a $\cos\theta$ between 0.5 and 0.6. As will be seen in the next section, such a choice of $\cos\theta$ yields pore-distribution curves that appear to be very reasonable. On the other hand, one might be inclined to interpret the result to mean that $\cos\theta$ is equal to 1, but that attached to each of the 30–40 Å. pores are a number of smaller pores in the range 10–20 Å. diameter which adsorb water only when the larger pores are filled. An obvious weakness in this latter interpretation is that it does not account for the absence of an appreciable number of pores in the range 20–30 Å., in which it is generally believed that capillary condensation can occur.

It must be kept in mind that it is entirely within the realm of probabilities that the value of $\cos \theta$ changes as a function of the relative pressure. As a matter of fact, the heat of adsorption would be expected to increase to a value corresponding to the heat of liquefaction of water vapor as soon as the surface is covered with a monolayer of adsorbed water vapor. From experiments on carbon black (54) that has been stripped of its surface complex by high-temperature evacuation, it appears that a monolayer of adsorbed water formed at about 0.85 relative pressure. It might not be surprising, therefore, by analogy to expect the $\cos \theta$ term to become substantially unity above 0.8–0.9 relative pressure. Furthermore, the shift (154) of the steep part of the desorption part of a water isotherm to lower relative pressures as one coats the surface with chemisorbed oxygen is an indication that $\cos \theta$ for a complex-covered surface is greater than for one without a surface coating.

D. Pore size from changes in surface area resulting from water uptake by charcoal

It is well known that for cylinders the diameter, D, the volume, V, and the area, A, are related by the equation:

$$D = \frac{4V}{A} \tag{13}$$

Similarly, if one pictures charcoal as a collection of cylindrical capillaries and imagines that a group of capillaries of a particular size are filled by capillary condensation, then the small change in available volume in the charcoal will be related to the diameter of the capillary and the change in available area by the equation:

$$D = \frac{4\Delta V}{\Delta A} \tag{14}$$

Juhola and Blacet (91) were the first to point out that by measuring the surface area of a charcoal with nitrogen at liquid nitrogen temperature as a function of the amount of water present, one could obtain a curve from which the pore-diameter distribution of the charcoal could be calculated. The water-desorption isotherms for the charcoals used are shown in figure 19. The changes in area *vs.* volume curves are shown in figure 20, and the resulting plots of pore diameters against relative pressure of condensation of water are shown in figure 21. It soon became apparent that the technique of measuring pore diameters by this procedure would be quite laborious. Juhola, therefore, suggested using the method merely as a means of evaluating the $\cos \theta$ term of equation 12 and thereafter using this latter equation for pore-size measurements in conjunction with water-desorption data. He has used this method extensively (90) for obtaining pore-size distribution over the diameter range up to about 100 Å.

Juhola states (90) that the Kelvin equation with cos θ equal to about 0.53

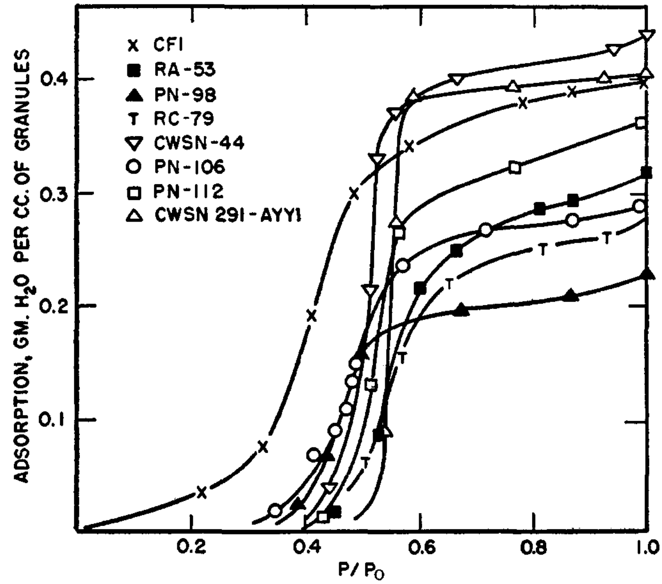


FIG. 19. Water-desorption isotherms for a series of charcoals (91)

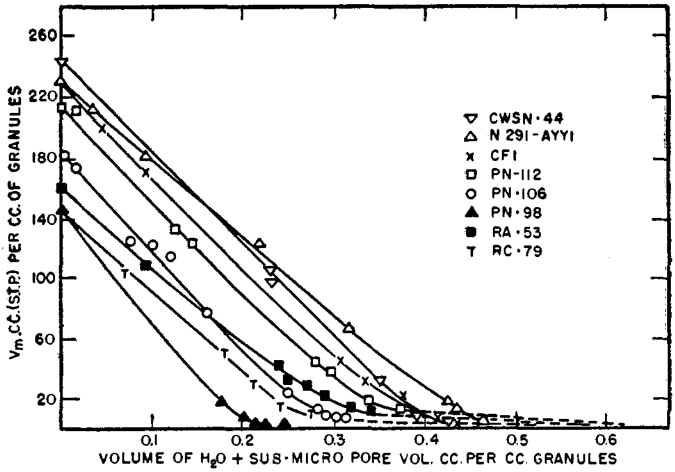


FIG. 20. V_m values for the residual surface of charcoals left after the adsorption of various amounts of water.

agrees satisfactorily with the curves obtained by use of equation 14 applied to the surface area *vs.* volume experiments at relative pressures up to about 0.9, but not above this relative pressure. Actually, there is less reason to expect the

Kelvin equation to fail at relative pressures above 0.9 than at lower relative pressures. From comparison with the water-adsorption experiments on de-

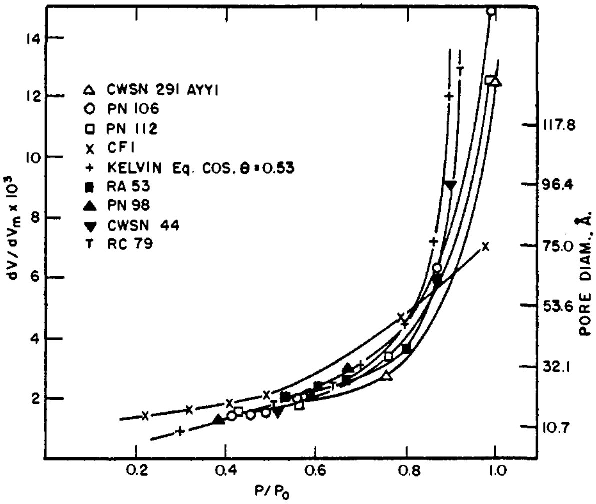


Fig. 21. Variation with p/p_0 of the pore diameters of charcoals as calculated from the curves of figure 20.

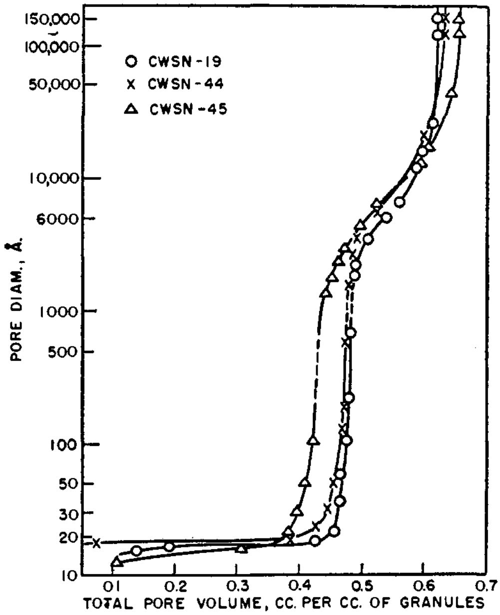


Fig. 22. Pore-diameter distribution of three charcoals (91) made by the zinc chloride process. The lower parts of the curves were obtained by measuring the change in surface area as a function of the amount of sorbed water; the upper part was measured by a mercury porosimeter (90, 91).

gassed carbon black, it seems probable that at a relative pressure of 0.9 the portion of the charcoal not covered by capillary condensation has at least a monolayer of adsorbed water vapor on it. Hence, the angle of wetting is likely to be much more nearly zero than for lower relative pressures where no such film exists. One would therefore expect that $\cos\theta$ above relative pressures of 0.9 might equal unity. Probably the lack of agreement (above about 0.9 relative pressure) of the Kelvin equation with results obtained by equation 14 is due much more to the difficulty of applying equation 14 accurately to that part of the isotherm corresponding to the pores larger than about 100 Å. Presumably, the objection to interpreting the water isotherms in this way has to do with the lack of smoothness with which the pore diameter *vs.* pore volume curves such as shown in figure 22 extrapolate from the lower pore-diameter range into the curves for the higher range determined by the mercury method discussed below. At any rate, Juhola has elected to leave the region between about 100 Å. and 2000 Å. diameters as undetermined in most of the materials he has studied.

In the application of the Kelvin equation to water-desorption isotherms for measurements of pore diameter, the $\cos\theta$ term has been considered as taking into account only the angle of wetting. Actually, it may perhaps be a constant that is taking into consideration any variation in the surface tensions (σ), the molar volume (V), or the angle of wetting in the small-pore regions where we have no direct information as to the validity of the values for these terms as determined from bulk water.

The choice of the value of 0.53 for $\cos\theta$ is, as pointed out by Juhola (90), attended with considerable uncertainty. Depending upon the density selected for water and for the adsorbed nitrogen in the experimental work, this $\cos\theta$ term might vary from 0.44 to 0.58. Nevertheless, for those charcoals in which there is negligible water adsorption at relative pressures below about 0.4, the method appears to give very reasonable values for pore diameters. Distribution curves for about 110 charcoals or charcoal-producing materials are given by Juhola in his final NDRC report (90).

E. Measurement of pore size by the high-pressure mercury method

Washburn (147) was the first to suggest that one could measure the diameter of pores by measuring the pressure necessary to force mercury into them. It can be shown that the diameter of a cylindrical capillary is related to the density, p, and surface tension, σ, of mercury, by the equation

$$D = \frac{4\sigma\cos\theta}{phg} \qquad (15)$$

where θ is the angle of wetting,[7] h is the pressure applied, and g is the gravitational

---

[7] Obviously, the value of D from equation 15 will depend on the exact value of θ, the wetting angle. Ritter and Drake (47, 134) measured this angle for numerous solids and found 140° as a representative value. This means that the pore diameters reported by them are about 0.78 as large as they would be if θ had been assumed to be 180°.

Juhola (89) made measurements by the mercury method in glass capillaries as small as 100,000 Å. and reported a value for $\cos\theta$ of 0.78 as giving good agreement between the mercury method and independent pore-diameter measurements. In spite of this, all charcoal work by Juhola (89, 90) and by other NDRC groups (63) reported in the present paper is based on the assumption of 180° for θ.

constant. This method was selected and applied (63) to a number of charcoals using pressures up to 100 atm. in some of the early war work at Johns Hopkins University; it has been much more extensively studied and applied by Juhola (90) on more than a hundred charcoals. As a matter of fact Juhola (90) tested the method (151) on a block of briquetted, carbonized coconut shell charcoal by boring a hole 0.015 in. (3.81×10^6 Å.) in diameter and measuring the pressure required to force mercury through it. Four runs, calculated by equation 15, gave results of 3.39, 3.96, 3.43, and 3.75×10^6 Å., which agree well with the actual value, 3.81×10^6 Å.

Recently, Ritter and Drake (47, 134) have published details of the method as applied to cracking catalysts and also to a number of commercially available charcoals. Their runs have extended up to 10,000 pounds per square inch pressure and therefore include measurements to pore diameters as small as 200 Å. diameter. A number of their resulting curves are shown in figures 23 and 24.

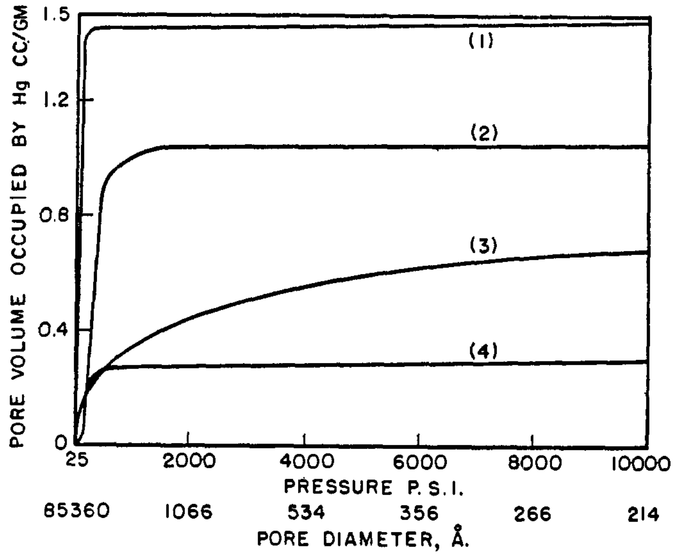


FIG. 23. Pore-size distributions as determined by Ritter and Drake (47, 134) by the high-pressure mercury method for diatomaceous earth (curves 1 and 2), Darco carbon (curve 3), and Columbia carbon (curve 4).

Several inherent characteristics of the mercury method should be noted. If bottleneck capillaries exist, it must be realized that the pore diameter measured will be that of the narrow neck rather than the larger bulk of the capillary. Accordingly, on an average, one would expect that the pore diameters obtained by the mercury method will be somewhat too small, or that the pore volume for a given pore size by the mercury method will be too large. This would mean that the curves in figures 23 and 24 should all be shifted to somewhat larger pore sizes if some method were available for estimating the difference on an average between the narrow necks and the larger main portion of the bottleneck-shaped capillaries. In agreement with this explanation, the few measurements (59, 59a) on nitrogen adsorption in the relative pressure range 0.99–0.999 corresponding to pore sizes from 1800 to 18,000 Å. show much smaller volumes for a given pore size than are shown by the mercury runs. A comparison on seven charcoals is shown in table 4.

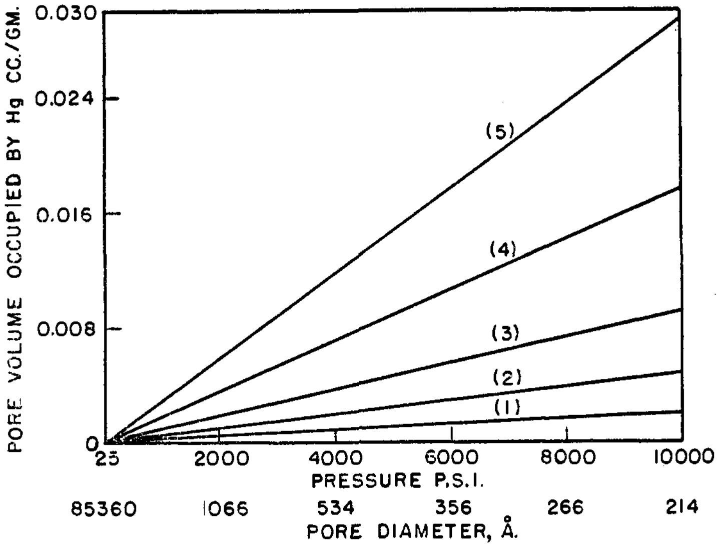


FIG. 24. Pore-size distribution as determined by Ritter and Drake (47, 134) by the high-pressure mercury method for five different silica–alumina gel catalysts.

TABLE 4

Macropore volume in the 1800–18,000 Å. diameter range

CHARCOAL	PORE VOLUME IN CC. PER GRAM	
	By nitrogen adsorption	By mercury method*
CWSN 19	0.04	0.148
CWSN 196 B1X	0.042	0.308
CWSN 196 B1X TH 427	0.039	0.327
CWSN 196 B1X TH 410	0.050	0.301
NDRC SI 26	0.006	0.0044
CFI "CC"	0.0016	0.019
PCI P58	0.062	0.106

* Using $\theta = 180°$ in equation 15.

Another method for judging the mercury method is illustrated by table 5 for these same seven charcoals. According to equation 12, nitrogen at a relative pressure of 0.99 should fill all pores up to about 1800 Å. in diameter. The pore volume then remaining free of the condensed nitrogen (called "free volume" in table 5) should then agree with the volume of mercury forced into the charcoals by 100 atm. pressure, since this pressure corresponds approximately to pores having diameters equal to or larger than 1800 Å. if $\theta = 180°$ in equation 15. The agreement shown in table 5 is as good as can be expected, since the "free volume" values may be too low if the density of liquid nitrogen in the capillaries is greater than the assumed value of 0.808; while the value by the mercury method may be too high because of pores larger than 100,000 Å. being connected to the outside of the particles by bottlenecks in the size range 1800–180,000 Å. The mercury values will also be too high if θ for mercury in contact with charcoal should be 140° instead of 180°; the mercury values, on the other hand, could be too low if any large capillaries are connected to the surface by capillaries smaller than 1800 Å.

The mercury pore-measuring experiments are accompanied (90) by a hysteresis which, for devolatilized or activated charcoals or charcoal materials, is usually equal to 90–95 per cent of the mercury in the pores. On the other hand, some of the baked charcoal stocks prior to activation show as little as 35 per cent of the total mercury in the sample retained when the pressure is released. It is a curious fact that the samples showing the smaller mercury hysteresis are also those that show little or no water hysteresis. Juhola (90) has suggested that this may be interpreted as evidence for the formation of "bottleneck" pores during activation, the narrow constrictions in the small pores being responsible for the water hysteresis, and the narrow constrictions in the larger pores for mercury hysteresis.

TABLE 5

"Free volume" of charcoals compared to macropore volume to 100 atm. by mercury method*

CHARCOALS	"FREE VOLUME"	VOLUME BY MERCURY METHOD TO 100 ATM.†
	cc./gram	*cc./gram*
CWSN 19	0.162	0.199
CWSN 196 B1X	0.402	0.475
CWSN 196 B1X TH 427	0.482	0.491
CWSN 196 B1X TH 410	0.467	0.461
NDRC SI 26	0.007	0.026
CFI "CC"	0.009	0.050
PCI P58	0.265	0.304

* "Free volume" is the difference between the total pore volume and the nitrogen adsorption at 0.99 relative pressure (calculated as liquid).

† Using $\theta = 180°$ in equation 15.

V. PORE-SIZE ALTERATION

The possibility of a relation between pore distribution and the effectiveness of gas mask charcoal (156) naturally led to a detailed study of ways and means of altering pore size and distribution in adsorbents. The relation between the findings and the production of effective gas mask charcoals cannot be discussed here. Nevertheless, the influence of certain treatments on pore distribution seems of sufficient interest to warrant inclusion in this paper (83).

The alteration in pore size has been judged mostly by the change in the appearance of the nitrogen-adsorption isotherms up to relative pressures of 0.99 (62). In discussing the influence of various factors on the shapes of the isotherms, it will be convenient to differentiate between the total adsorption in the relative pressure region (called *AB*) up to 0.4, the slope of the isotherm in the region between 0.4 and 0.7 (called *BC*; this is roughly the pore size that would be filled with water vapor by capillary condensation at 80 per cent relative humidity if cos θ for water on charcoal is about 0.6), and the slope of the isotherm in the region 0.7 and 0.99 (called *CD*; this region is the portion of the macropore region having diameters between about 52 and 1850 Å. according to equation 12).

It is also important to differentiate between changes in isotherms per gram of charcoal and changes per cubic centimeter of granules (this means per cubic centimeter of actual charcoal volume as measured by mercury pycnometers at 1 atm. pressure).

In a general way it can be said that it is possible (58, 83) to tailor-make the pore distributions in charcoals by a combination of steaming and hydrogenating with and without impregnants. The region *AB* can be increased or decreased on either a per gram or a per cubic centimeter basis; the slope of the isotherms in both the *BC* and *CD* regions can be left unchanged or increased. An increase in slope of either of these last two regions is interpreted as an increase in pore volume in these respective ranges. On the other hand, an increase in *AB* might mean an increase in the number of small pores or it might mean an increase in the total surface area caused possibly by increases in the number of pores in the *BC* region.

In figures 25, 26, and 27 are shown a few typical examples (58, 83) of the effect of steaming, air oxidizing, hydrogenating and, to a limited extent, treating with impregnants. For more details and for examples not included here the reader is referred to a paper by Holmes and Emmett (83) containing all of the results that were obtained on pore alteration. Below is discussed the influence of a few of the operations on the shape of the isotherms insofar as any general conclusions can be drawn.

A. Steaming without impregnation

Moderate steaming at 750°C. on standard charcoal samples increased the adsorption in region *AB*. This presumably means that added steaming beyond the point usually used for steam-activated charcoals continues to open up small pores. This was always true on a weight basis on the four charcoals studied: CWSN 19, CWSN S5, coconut charcoal, and PCI P58. The adsorption per cubic centimeter was increased in the *AB* region for the first of these four but decreases slightly for the other three. Examples for some of these charcoals are given by curves in figures 25, 26, and 27. There is nothing unusual in these steaming results, since new small pores can certainly be opened up by the treatment with a resulting increase in adsorption per gram. If the steaming is carried too far, of course, the adsorption per cubic centimeter of granules must start to decrease because of overlapping of the small pores. Also, if considerable portions of the charcoal are removed by steaming along the walls of capillaries larger than 1860 Å. in diameter the adsorption per cubic centimeter can be greatly lowered without affecting the adsorption per gram.

B. Hydrogenation without impregnation

It does not seem to be generally recognized in the literature that hydrogenation can alter pore sizes and distribution just as effectively as can steaming. Usually, however, a somewhat higher temperature is needed for hydrogenation than

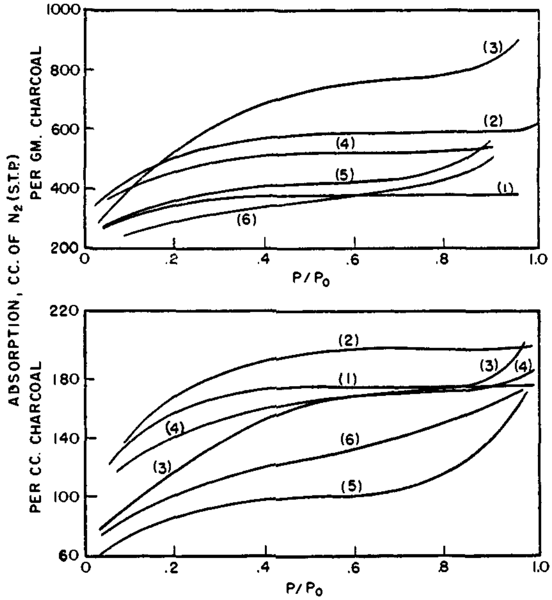


FIG. 25. Nitrogen isotherms showing pore alterations on charcoal CWSN 19 as follows:

Curve 1. Normal CWSN 19
Curve 2. Sample steamed at 750°C. to a 43 per cent loss
Curve 3. Hydrogenated at 1000°C. to 74 per cent loss
Curve 4. Impregnated with 5 per cent Fe_2O_3 and steamed at 750°C. to 37 per cent loss
Curve 5. Impregnated with 5 per cent Fe_2O_3 and hydrogenated at 600°C. to 50 per cent loss
Curve 6. Impregnated with 5 per cent Fe_2O_3 and air oxidized at 350°C. to 48 per cent loss

for steaming. In figures 25, 26, and 27 are shown curves illustrating the effect of hydrogenation on two of the charcoals studied. For all of them, the adsorption in the *AB* region per gram either increases or remains constant; the slope of the adsorption in the intermediate *BC* region remains unchanged; and the slope of the adsorption in the *CD* region increases sharply with an especially rapid increase close to a relative pressure of 0.99. In fact, the rapid rise in the adsorption between 0.9 and 0.99 relative pressure is rather characteristic of hydrogenation in the absence of impregnants.

Only for charcoal CWSN 19 is there an increase in the total adsorption per cubic centimeter of granules during mild hydrogenation. Presumably, the major attack is on pores in the *CD* region.

C. Partial combustion in nitrogen containing limited amounts of oxygen and no impregnants

Mild oxidation on CWSN 19 increased the adsorption in the *AB* region by a small amount both on a per gram and a per cubic centimeter basis. On the other hand, it had little influence on the slope of the isotherm above 0.4 relative presure. Presumably such oxidation primarily effects the formation of new pores (83).

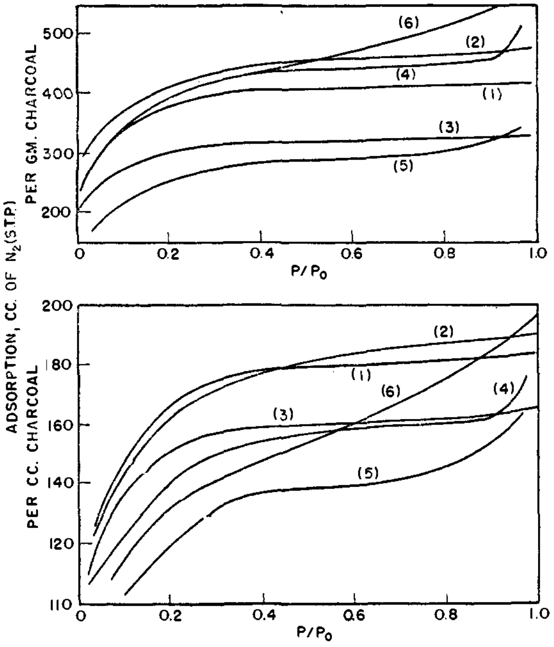


FIG. 26. Nitrogen isotherms showing pore alterations on charcoal CWSN S5 as follows:
Curve 1. Normal CWSN S5
Curve 2. Sample heated in pure nitrogen to 1200°C. and then steamed at 750°C. to 69 per cent loss
Curve 3. Heated for 2 hr. in pure nitrogen at 1200°C.
Curve 4. Hydrogenated at 1000°C. to 37 per cent loss
Curve 5. Impregnated with 5 per cent Fe_2O_3 and treated with tank nitrogen at 1000°C. to 25 per cent loss
Curve 6. Impregnated with 5 per cent Fe_2O_3 and hydrogenated at 600°C. to 30 per cent loss

D. Influence of impregnants on steaming, hydrogenation, and partial oxidation

In the course of the work the action of chromic oxide, ferric oxide, molybdic oxide, sodium carbonate, and cupric oxide on the various processes for altering pore size was studied. These compounds were formed in amounts ranging from

0.2 to 5.0 per cent by various procedures, as described by Holmes and Emmett (83). It is difficult to generalize in regard to the effects noted, because the impregnant at times produced results that differed as a function of the particular compounds used in getting the given oxide on the sample. However, in a general way the results were as follows:

(*1*) Fe_2O_3 gave definite evidence of catalyzing the attack on the charcoal.

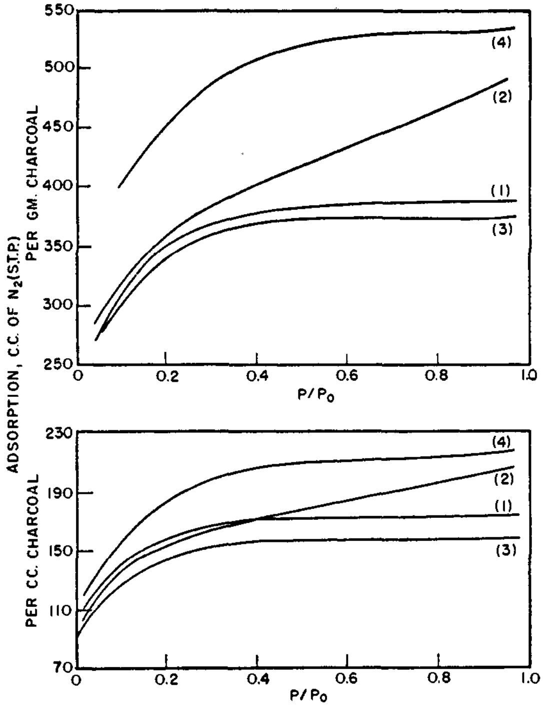


FIG. 27. Nitrogen isotherms showing pore alterations on CWSN 19 produced by hydrogenation as follows:

Curve 1. Normal CWSN 19

Curve 2. Impregnation with 5 per cent NiO from nickel nitrate, followed by hydrogenation at 1000°C. to 27 per cent loss

Curve 3. Impregnation with NiO from nickel chloride followed by hydrogenation at 1000°C. to a 25 per cent loss

Curve 4. Hydrogenation at 1000°C. to a 26 per cent loss

For example, at 600°C. in the presence of 5 per cent ferric oxide impregnant a 50 per cent weight loss of CWSN 19 was brought about by hydrogenation, whereas in the absence of the impregnant practically no loss occurred. Another evidence is the fact that even on a weight basis, the adsorption up to 0.4 relative pressure decreased in a majority of treatments with ferric oxide as impregnant. This is definite evidence of an attack on the smaller pores greater in extent than any formation of small pores that is taking place. The ferric oxide invariably causes a considerable rise in the isotherms between 0.7 and 0.99, regardless of the gas being employed for activation.

One result with ferric oxide is especially noteworthy (83). In a run using 5 per cent ferric oxide and carried out with tank nitrogen at 1000°C. to a 13 per cent weight loss, the total pore volume on both the per gram and per cubic centimeter basis dropped about 20 per cent. This means the closing up of enough small pores either by plugging with impregnants or by the effect of treating to 1000°C. to more than compensate for the increase in the number of pores indicated by the 0.7–0.99 relative pressure region. This is the only instance in which on CWSN 19 positive evidence was obtained of a pore-closing or pore-plugging effect.

(*2*) Impregnation with Cr_2O_3 combined with steaming seems to have little added effect over steaming by itself, on CWSN 19. On hydrogenation, however, the effect is similar to that of the iron in that a considerable decrease in the *AB* region occurs on a volume basis with a marked increase in the *CD* region (83).

The results on CWSN S5 are confused by the fact that heating this charcoal to 1200°C. even in pure nitrogen (figure 26) causes a shrinkage, the result of which is that the adsorption per unit weight decreases *more* than the adsorption per unit volume. This would be expected if the shrinkage causes an increase in the apparent particle density. At 750°C. steaming after impregnation with chromic oxide produces a very different effect from steaming alone. The low-pressure adsorption increases per cubic centimeter of charcoal, whereas the slopes of the *BC* and *CD* regions are both increased by about 15 per cent (83). The hydrogenation at 1000°C. with chromic oxide present seems to produce the same sintering effect caused by heating this charcoal to 1200°C., but in addition causes a 20 per cent increase in the slope of the *CD* portion of the isotherm (83).

Steaming coconut charcoal impregnated with 0.2 per cent chromic oxide caused nearly a 100 per cent increase in the adsorption up to 0.4 relative pressure on a weight basis, a 30 per cent increase on a volume basis, and a 15 per cent slope increase in the *CD* region. Presumably, the chromic oxide catalyzed the burning away of pore walls to make larger capillaries and also the formation of new small capillaries. Strangely enough, 5 per cent chromic oxide and steaming produced very little more effect than straight steaming to a similar weight loss, though the slopes of the *BC* and *CD* regions were 10–20 per cent greater than those resulting from steaming alone. Hydrogenation of coconut charcoal impregnated with 0.2 or 5 per cent chromic oxide caused none of the slope change (83) characterizing similar runs on CWSN 19 or CWSN S5, the slope of the isotherms being identical with that of the original charcoal and the absolute adsorption values a little lower; in fact the marked turn-up of the isotherm between 0.9 and 0.99 produced by straight hydrogenation is absent when chromic oxide is present.

PCI P58 impregnated with chromic oxide behaved little differently on steaming from samples not impregnated as regards the slope of the isotherms; however, the larger (5 per cent) chromic oxide content caused a drop in the absolute adsorption of 15 or 20 per cent on both the weight and the volume basis. Hydrogenation after impregnation with chromic oxide produced the same slope increase in the *CD* region that was obtained without any impregnation; the total pore volume, however, of this charcoal was decreased by the impregnation both on the weight and the volume basis, much as though a pore plugging had taken place that decreased the adsorption on both a weight and a volume basis.

In a word, it is apparent that chromic oxide as an impregnant can effect marked changes in charcoals when combined with steaming and hydrogenation, though the effects are apparently quite specific and dependent on the kind of charcoal used.

(*3*) NiO on CWSN 19 produces on steaming no change in slope of the isotherms, just as was true of straight steaming; however, it appears (83) to drop the total pore volume on both a weight and a volume basis by about 35 per cent compared to the volume after steaming in the absence of nickelous oxide. For hydrogenation, the nickel results are especially noteworthy in that they show a decided specificity upon the particular nickel salt used in impregnation. For example, if the nitrate is used together with precipitation by ammonium hydroxide, hydrogenation to a weight loss of 27 per cent results in a nitrogen isotherm that is a straight line from 0.4 to 0.99 relative pressure with an increase in volume of 20 per cent over this range. In contrast to this, the same per cent of nickelous oxide produced from nickel chloride plus ammonium hydroxide caused no change in slope and only a few per cent decrease in total adsorption compared to the initial CWSN 19 (figure 27), thus apparently having little effect on the hydrogenation.

On CWSN S5 the single experiment tried indicated that impregnation with 5 per cent nickelous oxide combined with hydrogenation at 1000°C. resulted in no change in slope of the isotherm compared to the original and a decrease of about 15 per cent total adsorption on both a weight and a volume basis (83).

(*4*) Impregnation with 5 per cent Mo_2O_3 produced no specific effects in either steaming or hydrogenating CWSN 19 other than those observed without the impregnation. Likewise, 5 per cent sodium oxide from sodium carbonate produced no noticeable modification in the hydrogenation of CWSN 19 at 1000°C.

(*5*) The two experiments on steaming type A whetlerites (copper impregnation) behaved quite differently. On CWSN 19, steaming whetlerite to 26 per cent loss at 750°C. left the isotherm unchanged in slope from the original charcoal but about 35 per cent smaller in volume than would have resulted from a steaming to a 40 per cent weight loss in the absence of the impregnant. On the other hand, steaming type A whetlerite made from CWSN S5 caused the slope of the *BC* and *CD* sections of the isotherm to increase greatly, the adsorption at 0.99 relative pressure being about 20 per cent greater than at 0.4 relative pressure.

VI. OXYGEN SURFACE COMPLEXES ON CHARCOALS

A. Introduction

It has long been known (45, 103, 112, 113, 114, 121), that charcoals and activated carbons are covered with carbon–oxygen complexes, the composition of which varies as a function of the method of treatment of the sample. Research on surface complexes of charcoal during the war has been carried out primarily because of the help it might furnish in (*a*) showing the proper surface treatment to give maximum adsorption of certain gases such as ammonia that are apparently very sensitive to the nature of the charcoal surface, (*b*) interpreting the aging of base charcoal that from time to time was thought to be taking place on storage under humid conditions, and (*c*) indicating the type of surface complex that might be most effective in any desired minimizing of the adsorption of water vapor, especially at high relative humidities.

The actual results obtained that are applicable to the three main objects of the work are, for the most part, restricted to item (*a*) above. The surface complex studies failed to throw much light on item (*b*) (59). As for (*c*), the behavior of charcoal and whetlerites toward water vapor appears to be much more dependent on the pore-size distribution in the region between 0.8 and 0.99 relative pressure than it does on the nature of the surface complex. The latter is more likely to influence the amount of water adsorption occurring at low relative pressures but is less influential on the adsorption at high relative pressures.

The work that has been done on the surface complexes divides itself rather naturally into two parts: (*1*) the study of oxygen adsorption by the charcoal in relation to the adsorptive properties toward ammonia, acids, and bases; and (*2*) the measurement of the gas evolution as a function of the temperature to which the various charcoals have been heated. The first of these two groups of experiments was carried out chiefly by Young (153, 154) and his coworkers; the second by Anderson (13, 59). These two researches contribute a great many useful data and correlations that will now be briefly summarized.

B. Oxygen adsorption by charcoals and its influence on their properties

As pointed out by Young (153), the existence of several different carbon-oxygen surface complexes on charcoal and carbon black has been claimed in the literature (102, 105, 132, 136, 137, 141, 143). Two (105, 136, 137) of these appear to be formed by the picking up of oxygen at room temperature; another is said to be formed by exposure of charcoal to oxygen at about 400°C.; and a fourth (95) is supposed to form above 850°C. in the presence of oxidizing gases. Oxygen complexes have been reported for graphite and diamond (17) as well as for charcoal and carbon black. The experiments reviewed and summarized in the present section were directed not so much toward the verification of these various complexes as toward the study of the influence of the complexes formed at 400°C. in free oxygen upon the properties of the various charcoals as adsorbents for acids, bases, ammonia, hydrogen chloride, and water vapor. Some few experiments were also made upon the rate of oxygen pickup by various charcoals at room temperature. The various results and observations made during this work may be summarized as follows:

1. Oxygen pickup by charcoals

Lowry (112) pointed out that oxygen is slowly picked up by charcoals at room temperature in the form of a chemical adsorption. The equilibrium pressure of this tightly bound oxygen is substantially zero at room temperature (118). In addition there is a rapid physical adsorption which is easily reversible and which amounts to about 10 per cent of a monolayer at 1 atm. pressure. The slow chemical adsorption varies in amount and rate with different charcoals. In figure 28 are shown the results obtained by Young (153) on a typical group of charcoals. The total oxygen picked up irreversibly by even CWSN 44 is apparently only a very small fraction of a monolayer.

By exposing charcoals to oxygen at 400°C. Young has succeeded in building up an oxygen content of as much as 18 per cent on the charcoals. This oxygen coating was accompanied by a 56 per cent weight loss. It should be noted that even 18 per cent oxygen corresponds to only about a monolayer of oxygen on the surface of the carbon.

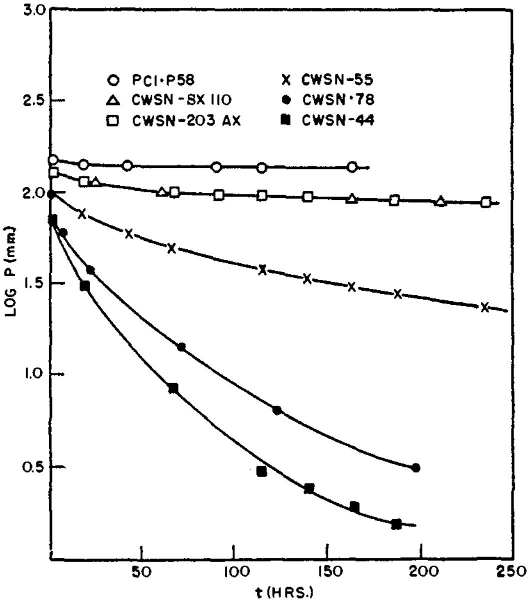
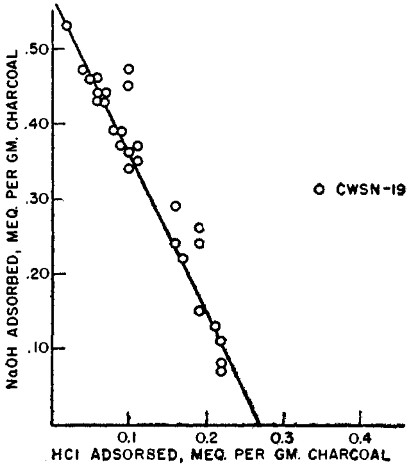


FIG. 28. Rate of oxygen chemisorption at 25°C. by charcoal samples

2. Influence of oxygen treatment on the base and acid adsorptive properties

CWSN 19, upon which most of the oxygen complex work has been done, originally adsorbed (153) 0.27 milliequivalent of hydrochloric acid per gram and no sodium hydroxide. The time allowed for equilibration in adsorption in these experiments was 30 min., and the original concentration of the adsorbate solution was 0.03 *N*. Treating the charcoal with oxygen increased the base adsorption and decreased the acid adsorption. The results shown in figure 29 are taken from the paper of Young (153). In the same figure is shown the sodium hydroxide adsorption as a function of the weight loss in the oxidation process.

In figure 30 is shown the variation of the rate of pickup of sodium hydroxide with time, temperature, and the amount of crushing to which the sample has been subjected. Evidently, crushing the sample increases greatly the rate of adsorption, as does also increasing the temperature. Neither temperature increase nor crushing has any effect on the final equilibrium value of the adsorption. In figure 30, also, is shown the adsorption curve obtained by allowing 24 hr. equilibration and by using adsorption solutions that were 0.5 *N*. As pointed out by Young, the slope of this curve indicates that for every equivalent of acid-forming power lost by the charcoal, four to five equivalents of base-forming power are gained.



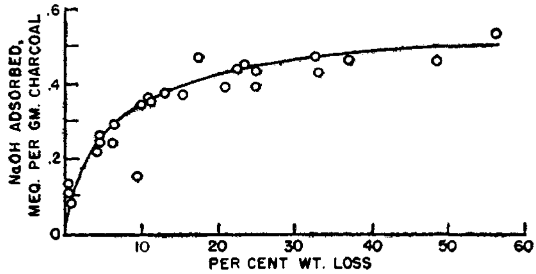
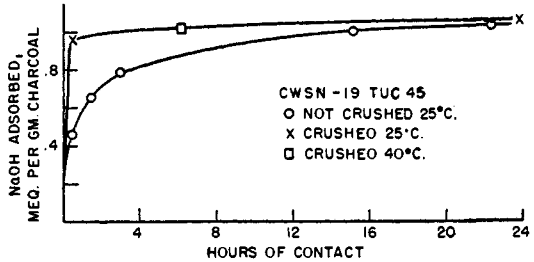


FIG. 29A (top). Plot of the adsorption of sodium hydroxide against that of hydrochloric acid on charcoal samples treated with oxygen at 400°C. (153).

FIG. 29B (bottom). Plot of the adsorption of sodium hydroxide against the weight loss of the sample of charcoal during oxidation (153).

Experiments by King (95) and also by Young (153) lead to the conclusion that both the H^+ and the Cl^- are adsorbed from solutions by the charcoals. Also, both Na^+ and OH^- are adsorbed. It is still unknown whether the alkali "adsorption" is a process in which the Na^+ by base exchange displaces an H^+ from the surface which then reacts with the OH^- or whether the Na^+ and OH^- are actually adsorbed.

Washing experiments showed that most of the hydrochloric acid adsorbed by the untreated CWSN 19 and most of the sodium hydroxide adsorbed by the oxygen-treated samples were irreversibly adsorbed. In other words, they were not removed by thorough washing. However, these quantities of "irreversibly held" adsorbates could be titrated with base and acid, respectively. The samples could then be washed and caused to readsorb the original amount of adsorbate. For example, the original CWSN 19 held 0.24 milliequivalent of hydrochloric acid irreversibly. This, on titration, picked up 0.24 milliequivalent of sodium hydroxide with the evolution of this amount of sodium chloride into the solution. The sample after washing could then pick up 0.24 milliequivalent of hydrochloric acid and the process could be repeated.



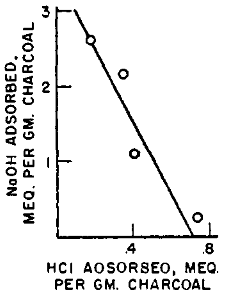


FIG. 30A (top). Adsorption of sodium hydroxide as a function of the time of contact between the solution and the charcoal.

FIG. 30B (bottom). Comparison of the sodium hydroxide and hydrochloric acid adsorption by oxygen-treated charcoal on 24-hr. exposure of the charcoal to 0.5 *N* solutions.

3. Influence of surface complex on the adsorption of water vapor

It has already been pointed out in the section on water adsorption that adding oxygen complex to a charcoal increases the low-pressure adsorption of water vapor and displaces the desorption hysteresis loop to lower relative pressures. Conversely, treating charcoals with hydrogen or with steam at high temperature tends to shift the adsorption curves to higher relative pressure and decreases markedly the adsorption below 0.5 relative pressure. It should also be noted that similar effects have been observed for carbon black samples, as shown in figure 13.

4. Influence of surface complex on the adsorption of ammonia and of hydrogen chloride

Treating a charcoal with oxygen at 400°C. increases the ammonia adsorption over the entire relative pressure range (65, 153). In figure 31 are shown two typical curves that illustrate the effect of oxygen coating. The extra ammonia pickup would appear to be due to a kind of chemical adsorption of ammonia, since the increase in adsorption is between 75 and 100 cc. throughout the entire pressure range. However, the heat of binding of such chemisorption is not great, as is evidenced by the fact that the extra ammonia will pump off slowly at 25°C. and completely in a short time at 100°C. (65). It should also be recorded that nitrogen isotherms prove that this enhanced ammonia adsorption is definitely not the result of an increase in surface of the charcoal resulting from the oxygen treatment. It is due to the specific nature of the surface containing the oxygen complex.

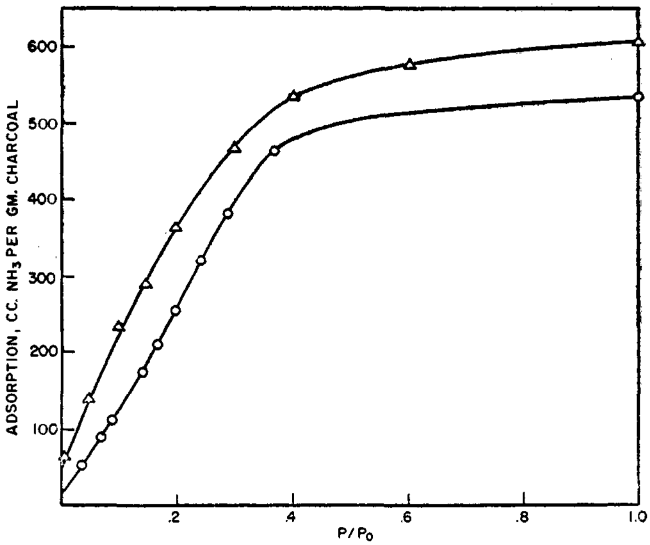


FIG. 31. Adsorption isotherm for ammonia at −46°C. on a sample of CWSN 19 TUC 742 (circles) and on a sample of this charcoal after it had been subjected to surface oxidation by free oxygen at 400°C. (triangles).

The adsorption of hydrogen chloride gas by CWSN 19 is not altered (52) in any marked way by oxygen coating. The changes in the adsorption are small and apparently no greater than the corresponding changes in the nitrogen adsorption.

5. Heat of binding of oxygen to carbon in the surface complex

By a series of careful measurements on the heat of combustion of charcoal as a function of the amount of oxygen complex on the surface, Young (153) has been able to show that the oxygen is held to the surface of a carbon by a heat of about 60,000–65,000 cal. per mole of oxygen. The heat of adsorption at 400°C. thus estimated appears to be independent of the fraction of the surface covered by complex. These heat of adsorption values are in good agreement with the following values: 70,000 cal. found by Keyes and Marshall (94) for charcoal at 0°C., 60,000 cal. reported by Blanch and Garner (25) for adsorption at room temperature, 70,000 cal. found by McKie at 20°C. (122), and 70,000–129,000 cal. reported by Marshall and MacInnes (119). There can be no doubt that the oxygen is held to the carbon surface by very strong chemical bonds (1, 93).

C. Gas evolution from charcoals as a function of the temperature to which they are heated

Lowry (112) has described the apparatus used and the results obtained in degassing a series of charcoals which at the end of World War I may be considered as typical of those used by the United States, Great Britain, and Germany. In general, he showed that all charcoals evolved considerable quantities of carbon monoxide, carbon dioxide, and water vapor up to about 900°C. Between 900 and 1200°C. increasingly large quantities of hydrogen were given off. Part of this hydrogen appeared to come from the surface of the charcoal, though it is also possible that part of it resulted from decomposition of hydrogen–carbon complexes that were not located at the actual surface of the charcoal.

Using a very similar apparatus, Anderson (13, 59) has carried out an extended series of experiments on various charcoals of interest in the recent research work in World War II. The evolved gas was collected during periods of about 7 hr. for each temperature interval studied. The experiments were grouped to cover the range 25–300°C., 300–600°C., 600–900°C., and 900–1200°C. The variables studied included the nature of the charcoal, the ash content (150) of the charcoal, and the type of treatment to which the charcoal had been subjected. The principal results (59) obtained may be briefly summarized as follows:

(*1*) In table 6 are shown the volumes of carbon monoxide, hydrogen, carbon dioxide, methane, and water evolved from a number of typical charcoals as a function of the temperature to which they were heated. In table 7 the results are summarized to cover the region up to 900°C. and up to 1200°C.; in this latter table also are shown the results of gas evolution to 1200°C., calculated in terms of equivalent per cent hydrogen and oxygen in the original charcoal. For comparison is also shown the per cent oxygen present in the ash wherever ash analysis was available or could be guessed from the method of preparation of the charcoal.

Several general conclusions can be drawn from the results in these two tables. In the first place it should be noted that the evolution of carbon monoxide and carbon dioxide is smaller from the PCI, CWSC, CFI, and CWSB X (nut shell) than from the CWSN samples prepared by the zinc chloride process. However, a detailed study (13) of the gas evolution from one of the samples, CWSN S5, at 60° intervals showed that most of the carbon monoxide and water were evolved in the temperature range 600–800°C. Concomitantly with the gas burst, a deposit of zinc metal was formed on the cooler part of the reaction vessel. In all probability, therefore, the excessive evolution of carbon monoxide and water from the CWSN samples in the temperature range up to 900°C. may be attributed to a large extent to the reduction of zinc oxide ash by carbon and by hydrogen. Consistent with this interpretation is the fact that CWSN 19, which had only 0.2 per cent ash, yielded volumes of carbon monoxide and water in the temperature range up to 900°C. approximately the same as obtained from charcoals not made by the zinc chloride process.

At temperatures above 900°C., a burst of carbon monoxide was obtained from all of the charcoals that had appreciable percentages of ash other than zinc oxide. There seems to be little doubt but that this higher temperature evolution of carbon monoxide is caused by the reduction of the ash components by carbon.

TABLE 6

Degassing experiments on charcoals

SAMPLE	GAS EVOLVED, CC. (S.T.P.) PER GRAM															
	25–300°C.			300–600°C.				600–900°C.				900–1200°C.				
	CO	CO_2	H_2O	H_2	CO	CO_2	H_2O	H_2	CO	CO_2	H_2O	H_2	CO	CH_4†	CO_2	H_2O
CWSN 19	0.2	0.3	0.4	0.3	3.8	1.5	1.3	10.4	11.7	0.5	0.4	46.4	1.0	2.1	1.0	0.0
CWSN S5	0.5	2.0	2.3	1.0	4.6	2.3	5.3	92.0	21.7	1.4	6.0	36.9	0.6	0.6	0.0	0.0
CWSN S5 (extracted with HF)	0.9	3.0	5.8	2.5	87.2	39.9	1.9	66.9	27.7	1.2	2.0	21.8	0.4	0.6	0.7	0.1
CWSN 44	0.7	3.3	3.5	1.4	6.6	3.2	4.6	97.5	22.8	1.1	4.0	51.8	2.6	3.3	0.1	0.0
CWSN 196 B1	0.5	2.7	3.3	1.4	5.5	3.0	4.6	93.0	29.5	0.5	1.8	36.5	0.5	0.8	0.2	0.0
CWSN 196 B1X	0.2	1.5	1.6	1.0	3.3	6.8	1.6	53.1	11.8	0.2	0.1	33.8	0.4	0.8	0.2	0.1
PCI P58	0.1	0.2	0.9	0.1	1.2	0.7	0.7	16.2	11.4	0.5	0.2	38.3	7.8	4.7	0.0	0.0
CWSC 1242	0.3	0.6	0.9	0.0	0.7	1.2	1.1	5.8	4.0	0.3	0.2	19.3	0.9	0.1	0.2	0.1
CFI "CC"	0.1	0.2	1.2	0.0	0.7	0.3	1.1	7.8	5.5	0.2	0.2	38.5	63.4	0.8	0.2	0.0
CWSB X2	0.2	3.1	2.3					13.4*	7.8*	2.2*	1.9*	36.3	5.4	0.6	0.3	0.1
	25–120°C.			120–600°C.												
PCI P25	0.0	0.0	0.5	0.5	2.0	1.0	3.0	10.5	9.9	0.4	0.5	35.3	88.5	2.7	0.3	0.0
PCI P1042	0.0	0.2	0.6	0.3	2.6	1.2	1.3	7.5	9.6	0.3	0.3	43.2	93.1	2.3	0.4	0.0
PCI P1042 (extracted with HF)	0.0	0.0	0.7	0.6	51.2	9.4	4.3	20.8	20.9	3.0	0.3	22.3	0.8	0.8	0.4	0.0

* 300–900°C.

† Some methane was evolved below 900°C. Since the low-temperature formation was, however, small, it is not included in table 6. However, subtraction of the methane values for the 900–1200°C. range from those shown in table 7 for the 25–1200°C. region gives the total methane produced below 900°C. A similar procedure can be used in obtaining the amount of methane evolved below 900°C. in the samples shown in table 8.

Ash for the most part on analyzed samples was found to consist of silica and alumina (150). Data in the literature (30) indicate that for the reduction of silica by carbon to form silicon carbides and carbon monoxide, the partial pressure of evolved gas at 900°C. at equilibrium is about 0.1 mm. and at 1200°C. is about 10.7 mm. Accordingly, since the maximum pressure in the present experiments was about 0.02 mm. it is entirely possible that the evolution of carbon monoxide at higher temperature could have come from the reduction of silica components in the ash. In line with this conclusion is the fact that the gas evolved at temperatures in excess of 900°C. from a sample of PCI that had been rendered substantially ash free by extraction with hydrofluoric acid contained practically no carbon monoxide.

One other peculiarity of these results should be noted. Two different samples that had been extracted by hydrofluoric acid evolved excessive amounts of carbon monoxide and carbon dioxide in the region between 300° and 900°C. Thus, CWSN S5 after extraction evolved 115.8 cc. of carbon monoxide and 44.1 cc. of carbon dioxide, compared to 26.8 cc. of carbon monoxide and 5.7 cc. of carbon dioxide from the sample that had not been extracted. Corresponding results for PCI P1042 showed 72.1 cc. of carbon monoxide and 12.4 cc. of carbon dioxide after extraction, compared to 12.2 cc. of carbon monoxide and 1.5 cc. of carbon dioxide before extraction. The cause of this excessive evolution of gas from the extracted samples is not clear. Possibly, the reagents used have a catalytic effect on the oxidation of the surface by air during extraction or drying.

TABLE 7

Degassing experiments on charcoals

SAMPLE	TOTAL GAS EVOLVED, CC. (S.T.P.) PER GRAM									PER CENT BY WEIGHT OF		
	25-900°C.				25-1200°C.					H_2 evolved	O_2 evolved (as CO, CO_2, or H_2O)	O_2 in ash
	H_2	CO	CO_2	H_2O	H_2	CO	CH_4†	CO_2	H_2O			
CWSN 19	10.7	15.7	2.3	2.1	57.1	16.7	2.7	3.3	2.1	0.58	1.81	0.04*
CWSN S5	93.0	26.8	5.7	13.5	129.9	27.4	1.4	5.7	13.6	1.31	3.74	2.0 (118)
CWSN S5 (extracted with HF)	69.4	115.8	44.1	9.7	91.2	116.2	1.8	44.8	9.8	0.93	16.10	
CWSN 44	98.9	30.1	7.6	12.1	147.5	32.7	8.3	7.7	12.1	1.58	4.30	0.8*
CWSN 196 B1	94.4	35.5	6.2	9.7	130.9	36.0	1.8	6.4	9.8	1.29	4.18	0.6*
CWSN 196 B1X	54.1	15.3	8.5	3.3	87.9	15.7	1.5	8.7	3.4	0.84	2.59	1.0*
PCI P58	16.3	12.7	1.4	1.8	54.6	110.5	5.0	1.4	1.8	0.59	8.22	
CWSC 1242	5.8	5.0	2.1	2.1	25.1	5.9	0.2	2.3	2.3	0.25	0.91	
CFI "CC"	7.8	6.3	0.7	2.5	49.7	13.4	0.8	5.6	4.3	0.50	2.06	
CWSB X2	13.4	8.0	5.3	4.2	46.3	69.7	0.8	0.9	2.5	0.45	5.28	
PCI P25	11.0	11.9	1.4	4.0	46.3	100.5	2.8	1.7	4.0	0.40	7.70	
PCI P1042	7.8	12.2	1.7	2.2	51.0	102.3	2.5	2.1	2.2	0.58	7.76	
PCI P1042 (extracted with HF)	21.4	72.1	12.4	5.3	43.7	72.9	1.2	12.8	5.3	0.46	7.42	

* Ash was assumed to be zinc oxide in computation of these values.

† See footnote to table 6.

Strong evolution of hydrogen from certain charcoals was noted a number of years ago (112). The runs in tables 6 and 7 show that some of the charcoals evolve as much as 147 cc. of hydrogen per gram on being heated to 1200°C. In general, it appears that the zinc chloride charcoals evolved much more hydrogen than the others. Furthermore, with the exception of CWSN 19, all of the zinc chloride charcoals tested appeared to evolve most of their hydrogen in the 600–900°C. region rather than the 900–1200°C. region. CWSN 19, for some unknown reason, evolved the normal amount of hydrogen in the higher temperature region but very little hydrogen up to 900°C. The amount of hydrogen present in the charcoals is probably related to their pretreatment, since it is known that the higher the temperature of calcining of the various charcoals in the course of preparation and activation, the smaller the per cent of hydrogen that they contain. There is some evidence that steaming at 900°C. will put hydrogen onto a charcoal. Thus, a sample of CWSN 196 B1X that had been heat treated in nitrogen at 1000°C. until it would evolve only 15.6 cc. of hydrogen to 1200°C., was found to evolve 47 cc. of hydrogen after being steamed at 900°C. to a 56 per cent weight loss. In contrast to this, short steaming to a few per cent weight loss at 300°, 400°, and 750°C. caused no appreciable increase in the evolution of hydrogen above the 15.6 cc. of the original sample (13). There is a chance, of course, that the excessive steaming made possible the escape of some hydrogen that originally was buried so deep in the charcoal as not to be able to escape at temperatures up to 1200°C. Hence, the interpretation of this result must remain uncertain until more work is done.

(*2*) Heat treating samples of charcoal to 1000°C. in a stream of nitrogen was found (13, 59) to remove practically all of the carbon monoxide, carbon dioxide, and water from the surface and about two-thirds of the hydrogen. This would be expected on the basis of the degassing experiments shown in tables 6 and 7 and hence needs no special comment.

(*3*) It is interesting to note (59) that exposing to air at room temperature for a week a sample of CWSN 196 B1X that had been treated with nitrogen at 1000°C. and cooled in a stream of nitrogen restored the original complex to such an extent that the evolution of carbon dioxide on heating to 1200°C. was as large as with the original untreated sample, and that of carbon monoxide was two-thirds as large. Exposure of a heat-treated sample of this charcoal to oxygen at 300°C. for 30 min. put on more complex than was characteristic of the original charcoal, as shown in table 8; the carbon monoxide and carbon dioxide content was still, however, much smaller than that of some of the CWSN samples treated with oxygen at 400°C. by Young (153).

(*4*) A few experiments were carried out to compare the surface complex of charcoals aged at high relative humidity (24) for a considerable time with the complex of unaged samples. The oxygen content of the charcoals increased during aging in all cases by about 2 per cent in absolute value (33–100 per cent relative increase in oxygen). The increase in oxygen (13, 59) found by our degassing experiments on charcoals CWSN S5, CWSN 44, and PCI P58 was 2.12, 1.85, and 1.43 compared with values of 2.6, 2.3, and 1.2 found by ultimate analyses by Young (153). It should be noted that heating aged samples of CWSN S5 for 3 hr. at 115°C. produced no detectable change in composition or amounts of evolved gas.

(*5*) English workers (3, 4, 5, 7, 8, 9, 35, 107) have reported results which indicate that in the process of adsorbing vapors on charcoals, part of the surface complex is driven off into the gas phase. The displaced gases were reported to be equal in some cases to the equilibrium partial pressure of the adsorbate and to cause marked changes in the adsorptive characteristics of the charcoal. The actual volumes of displaced gas were not mentioned. To check this important factor, several experiments shown in table 9 were carried out (13, 59) on a charcoal made by the zinc chloride process and on a PCI sample made from coal.

TABLE 8

Effect of heat treatment on CWSN charcoals

SAMPLE	GAS EVOLVED, CC. (S.T.P.) PER GRAM															
	25–300°C.			300–600°C.				600–900°C.				900–1200°C.				
	CO	CO_2	H_2O	H_2	CO	CO_2	H_2O	H_2	CO	CO_2	H_2O	H_2	CO	CO_2	CH_4	H_2O
7. CWSN 196 B1X heated in nitrogen to 1000°C., cooled in nitrogen, and transferred in nitrogen	0.0	0.0	0.1	2.1	0.3	0.2	0.8	2.7	0.7	0.1	0.1	33.2	1.3	0.6	0.1	0.0
8. Same as No. 7 exposed to air for 1 week	0.3	3.5	3.9	1.2	1.5	5.6	2.6	4.5	6.0	0.3	0.1	33.2	1.2	0.7	0.3	0.1
11. CWSN 196 B1X exposed to oxygen at 300°C.	0.1	0.4	0.7	0.2	4.1	9.5	1.8	42.9	22.9	1.0	0.4	35.0	0.4	0.4	0.1	0.0

SAMPLE	TOTAL GAS EVOLVED, CC. (S.T.P.) PER GRAM									PER CENT BY WEIGHT EVOLVED		
	25–900°C.				25–1200°C.					H_2	O_2 (as CO, CO_2, and H_2O)	Weight per cent O_2 in ash
	H_2	CO	CO_2	H_2O	H_2	CO	CH_4†	CO_2	H_2O			
7. CWSN 196 B1X heated in nitrogen at 1000°C., cooled in nitrogen, and transferred in nitrogen	4.8	1.0	0.3	1.0	38.0	2.3	0.6	0.4	1.0	0.36	0.29	1.0*
8. Same as No. 7 exposed to air for 1 week	5.7	7.8	9.6	6.6	38.9	9.0	0.8	9.9	6.7	0.41	2.54	1.0*
11. CWSN 196 B1X exposed to oxygen at 300°C.	43.1	27.1	10.9	2.9	78.3	27.5	0.6	11.0	2.9	0.73	3.74	1.0*

* Ash assumed to be zinc oxide in computations of these values.

† See footnote to table 6.

The samples were evacuated at 120°C. before the run in each instance, at which temperature practically none of the carbon monoxide or carbon dioxide in the complex should be removed. The results clearly indicate that the amount of complex evolved by the adsorption of either carbon tetrachloride or chlorobenzene is very small, being equivalent in all cases to less than 0.01 per cent of the complex known to be present. Only water vapor displaced an appreciable amount of gas from the charcoals; the gas evolved by water was entirely carbon dioxide and was limited, for the most part, to the sample made by the zinc chloride process. It seems likely that most of this evolved carbon dioxide may have resulted from the attack on the zinc carbonate ash content by water condensed in capillaries. The total evolution of carbon dioxide in one case amounted to about 8 per cent of that which would have been evolved by heating the sample to 1200°C. The results as a whole fail to check the English work and certainly give no indication that physical adsorption of vapors is capable of seriously altering the composition of the surface complex on these typical charcoals.

(*6*) In view of the fact that most charcoals are activated by steam, it seemed worthwhile to ascertain the effect of steam activation on the surface complex. In table 10 the results are shown for such a series of experiments on charcoal CWSN 196 B1X after it had been extracted with hydrofluoric acid and heated 3 hr. in nitrogen at 1000°C. In general, the results obtained agree with those of Müller and Cobb (124), who studied the chemisorption of water vapor on an acid-extracted wood charcoal at temperatures ranging from 300°C. to 1100°C. Steaming at pressures up to and including 750°C. produced only a slight increase in the amount of adsorbed water and a total fixation of only 4.1 cc. of water vapor in a form evolved as carbon monoxide and carbon dioxide on heating. Over this temperature range, the hydrogen fixed was no greater than that calculated from the amount of oxygen fixed. The sample steamed at 900°C. to a 56 per cent weight loss clearly fixed more hydrogen than oxygen. This is in agreement with the experiments of Müller and Cobb (124), who noted more hydrogen than oxygen being fixed by steaming in the range 700–900°C. It does not agree with Ockrent's conclusion (128) that activated charcoal is covered with a layer of chemisorbed water. The total oxygen fixed at 900°C. was no greater than that on steaming at 750°C. In view of these results, it is easy to understand why the carbon monoxide and carbon dioxide complex is so low on samples of charcoal made by steaming at high temperature and not exposed excessively to air before cooling.

TABLE 9

Displacement of complex by adsorption of vapors at 25°C.

CHARCOAL	VAPOR	VOLUME OF LIQUID PER GRAM OF CHARCOAL	TIME OF ADSORPTION	GASES EVOLVED, CC. (S.T.P.) PER GRAM	
				CO	CO_2
		cc.	*hours*		
CWSN 196 B1	CCl_4	0.5	18	0.0028	0.0036
	C_6H_5Cl	0.4	5	0.00036	0.00039
	H_2O	0.4	4½	0.0014	0.495
	H_2O	0.2	2½	0.0024	0.205
	H_2O	0.1	16	0.0016	0.235
PCI P58	C_6H_5Cl	0.15	3	0.0016	0.00003
	H_2O	0.08	1	0.0025	0.0094

VII. SPECIAL SURFACE COATINGS ON CHARCOAL

There are statements in the literature (142) to indicate that the relative amount of different gases adsorbed may well depend upon the exact nature of

TABLE 10

Complex formed during steam activation

TEMPERATURE RANGE	GASES EVOLVED DURING DEGASSING, CC. (S.T.P.) PER GRAM OF CHARCOAL				
	H_2	CO	CH_4	CO_2	H_2O (vapor)
A. CWSN 196 B1X sample extracted with hydrofluoric acid and heated in nitrogen at 1000°C. for 3 hr.					
°*C.*					
25– 300	0.0	0.0	0.0	0.0	0.6
300– 600	0.3	0.0	0.0	0.1	0.2
600– 900	1.2	0.1	0.1	0.1	0.1
900–1200	14.2	0.2	0.3	0.4	0.0
Total.............	15.7	0.3	0.4	0.6	0.9
B. Treated as in A, then exposed to water vapor at 300°C. for 3½ hr. (weight loss = 0.4 per cent)					
25– 300	0.0	0.0	0.0	0.1	0.8
300– 600	0.2	0.1	0.0	0.9	0.8
600– 900	1.1	0.6	0.1	0.2	0.1
900–1200	11.4	0.4	0.2	0.2	0.0
Total.............	12.7	1.1	0.3	1.4	1.7
C. Treated as in A, then exposed to water vapor at 600°C. for 3½ hr. (weight loss = 1.0 per cent)					
25– 300	0.0	0.1	0.0	0.0	1.3
300– 600	0.1	0.0	0.0	0.3	0.6
600– 900	1.5	1.8	0.0	0.1	0.2
900–1200	12.3	2.3	0.2	0.3	0.1
Total.............	13.9	4.2	0.2	0.7	2.2
D. Treated as in A, then exposed to water vapor at 750°C. for 1 hr. (weight loss = 1.6 per cent)					
25– 600	0.2	0.0	0.0	0.3	1.7
600– 900	2.7	2.3	0.1	0.3	0.4
900–1200	16.9	1.9	0.2	0.1	0.0
Total.............	19.8	4.2	0.3	0.7	2.1
E. Treated as in A, then exposed to water vapor at 900°C. for 3½ hr. (weight loss = 56 per cent)					
25– 300	0.0	0.0	0.0	0.4	0.6
300– 600	0.6	0.1	0.0	1.1	1.1
600– 900	5.8	1.3	0.2	0.2	0.2
900–1200	40.5	2.2	0.5	0.1	0.1
Total.............	46.9	3.6	0.7	1.8	2.0

the surface coating of the charcoal. Because of the obvious importance of knowing the nature of any such changes that might be produced, a few experiments were carried out in an effort to coat charcoals with complexes other than carbon–oxygen complexes. Specifically, the influence of covering the surface with nitrogen, with chlorine, and with sulfur was investigated. The principal results obtained on samples with these coatings will now be considered.

A. Coating of charcoals with nitrogen

Literature references (22, 106) indicate that high-temperature treatment of charcoals with ammonia is capable of forming carbon–nitrogen complexes that are more stable than carbon–oxygen complexes. Accordingly, two sets of experiments were carried out (13, 59) in which an acid-extracted degassed sample of CWSN 196 B1X charcoal was heated in ammonia at 750°C. and at 900°C. The samples were then heated by Anderson to various temperatures up to 1200°C. and the evolved gases analyzed. The results, as shown in table 11, clearly confirm the previously published work. A nitrogen complex is formed that is evolved only on heating in the 900–1200°C. region. Most of the nitrogen comes off as free nitrogen, though some is evolved as hydrogen cyanide, cyanogen, and ammonia. It will also be noted that the hydrogen content of the charcoal is increased by the ammonia treatment from a value of 15.6 on the original sample to values of 30.5 and 39.3 cc. for the ammonia treatments at 750°C. and 900°C., respectively. Unfortunately, time did not permit further work with these ammonia-treated samples.

TABLE 11

Complex formed during ammonia activation of ash-extracted CWSN 196 B1X

TEMPERATURE RANGE	GASES EVOLVED DURING DEGASSING, CC. (S.T.P.) PER GRAM OF CHARCOAL					
	H_2	CO	N_2	C_2N_2 + HCN	NH_3	H_2O
A. Sample exposed to ammonia at 750°C. for 3 hr. (weight loss = 0.4 per cent)						
°C.						
25– 600	0.6	0.0	0.1	0.2	0.1	0.5
600– 900	3.3	0.1	0.2	0.1	0.1	0.5
900–1200	26.6	0.4	5.2	2.3	0.3	0.1
Total...........	30.5	0.5	5.5	2.6	0.5	1.1
B. Sample exposed to ammonia at 900°C. for 3 hr. (weight loss = 17.1 per cent)						
25– 300	0.0	0.0	0.0	0.0	0.0	0.6
300– 600	2.3	0.0	0.1	0.2	0.2	0.6
600– 900	5.2	0.1	0.1	0.2	0.2	0.3
900–1200	31.8	0.7	6.3	2.5	0.8	0.2
Total...........	39.3	0.8	6.5	2.9	1.2	1.7

B. Treatment of charcoals with chlorine

Chlorine complexes that are so stable (2) that the chlorine cannot be removed by evacuation (131) at temperatures as high as 600°C. or by the action of boiling 10 per cent sodium hydroxide over the period of an hour have been reported (135) in the literature. In the present work (59) charcoal has been made to retain as much as 17 per cent of its weight of chlorine even after evacuation for an extended period at 400°C. The results are shown in table 12 and in figure 32.

TABLE 12

Adsorption of chlorine by CWSN 196 B1X

TEMPERATURE OF EXPERIMENT USED IN ADSORPTION FLOW SYSTEM EMPLOYED	WEIGHT OF CHLORINE ADSORBED PER GRAM OF CHARCOAL AT VARIOUS TEMPERATURES				
	Physically adsorbed at 1 atm. and room temperature	Chemisorption retained after evacuation at			
		Room temperature	100°C.	200°C.	400°C.
Room temperature; flow experiment No. 1	0.626	0.252			
Room temperature; flow experiment No. 2	0.719	0.202	0.081		
100°C.; flow experiment No. 3	0.634	0.250	0.215	0.142	0.098
200°C.; flow experiment No. 4	0.665	0.352	0.273	0.239	0.178
400°C.; flow experiment No. 5	0.722	0.342	0.317		

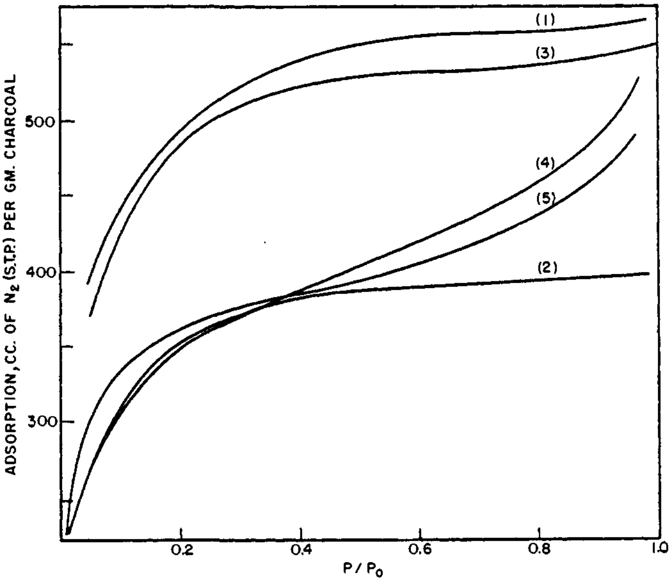


FIG. 32. Adsorption of nitrogen at −195°C. as a function of treatment of the charcoal with chlorine. (1) Untreated CWSN 196 B1X; (2) after chlorine adsorption at 200°C. and evacuation at room temperature; (3) after evacuation at 100°C.; and (4) and (5) after evacuation at 200°C.

The physical adsorption shown in column 2 is the amount that would pump off at room temperature after the sample was cooled from the temperature of the run to room temperature and was allowed to equilibrate with chlorine. Apparently the amount of stable chlorine held by the charcoal increases with the temperature of treatment. The amount retained at room temperature after evacuation is in general greater the higher the temperature of the original treatment, as is also the fraction of the total chemisorption that is retained on evacuation to 400°C.

Insufficient nitrogen-adsorption runs were carried out on the chlorinated sample to answer the question as to the location of the chemisorbed chlorine. In general, it may be said that the chemisorbed chlorine did not decrease the volume of nitrogen held by the charcoal at 0.99 as much as one would expect, though conclusions are uncertain until more runs are made. Figure 32 indicates clearly that on treating a sample at 200°C. with chlorine and then evacuating it at 200°C. a drastic change in pore size occurs. If these few experiments are to be believed, the change occurs during the long evacuation at 200°C. rather than during the original treatment, since evacuation at 100°C. left an isotherm similar to but 11 per cent smaller than the one for the untreated sample. The attack on the charcoal is not especially surprising, in view of the fact that one proposed method of producing active charcoal (144) involves burning hydrocarbons in chlorine under such conditions as to deposit a considerable portion of the hydrocarbon as free carbon.

C. Treatment of charcoals with sulfur

Young and his coworkers (154) prepared a number of samples of charcoal coated with sulfur by heating charcoal and sulfur together at 400°C. in a rotating furnace. Comparatively little work was done on the properties of the coated charcoals, though the following facts were established:

(*1*) As much as 41 per cent sulfur by weight could be incorporated into the charcoal. The amount of sulfur picked up was proportional to the amount included in the original mix.

(*2*) The 41 per cent sulfur content of one of the charcoals was reduced to 29 per cent by extraction with either of two different solvents. Apparently some of the sulfur is present in an extractable form and part of it in a more tightly bound form.

(*3*) The hydrogen content of the charcoal decreases to about a third of its orginal value as the sulfur content increases to 40 per cent.

(*4*) Water-adsorption isotherms show that if the sulfurized sample were protected from oxidation it picked up very little water below 0.5 relative pressure. The samples are definitely still hydrophobic. The sulfur, however, apparently decreases the pore volume of the charcoal considerably, as evidenced by the fact that the sample containing 41 per cent sulfur had only about 0.12 cc. of water sorptive capacity at saturation.

(*5*) There seems to be no relation between the acid and base adsorptive properties and the sulfur content.

VIII. RELATION BETWEEN ADSORPTION AND MOLECULAR STRUCTURE

In view of the fact that the efficiency of removal of war gases by gas mask charcoal is known to depend upon a rate factor and upon a capacity factor, N_0, it seemed worthwhile to carry out a study with a view to predicting the sorption capacity of a given charcoal for a gas at various relative pressures, as a function of the properties of that gas. It would be especially helpful to be able to predict approximately the shape of the adsorption isotherm of a gas on charcoal if only a few of the fundamental properties of the adsorbate gas are known. The analysis of the problem and the experimental results here presented are the work of Kummer (99); they give us a much better insight into the factors upon which the adsorbability of a gas depends than we have ever had before and enable us to predict with a fair approximation whether a gas will be adsorbed strongly, medium strongly, or weakly by a sample of charcoal.

All of the experimental measurements relative to this study were made on a single charcoal CWSN 19. It was one of the early samples of charcoal made by the zinc chloride process. It had an apparent density of 0.482, a particle density of 0.804, a carbon density (as determined by helium at 25°C.) of 2.09, an ash content of about 0.3 per cent (made up mostly of zinc oxide and zinc chloride), and a heat of wetting in benzene of 22.69 cal. per gram. As indicated in one of the earlier sections, the charcoal is characterized by a comparatively low amount of surface complex (59); on being heated to 1200°C. it evolved 57 cc. of hydrogen, 16.7 cc. of carbon monoxide, 2.7 cc. of methane, 3.3 cc. of carbon dioxide, and 2.1 cc. of water vapor, as is shown in table 7.

A. Experimental data for the adsorption of gases on CWSN 19

In figures 33 and 34 are shown the adsorption isotherms for a large number of gases. The data are plotted in the manner suggested by Goldman and Polanyi (73) as the fraction of the total sorption capacity taking place as a function of $RT \ln p_0/p$. A few regular isotherms plotted with relative pressure as the abscissa are given in figure 35. The adsorption data are summarized in table 13. It will be noted that the total liquid volume of gas adsorbed at saturation pressure is substantially constant and independent of the nature of the adsorbate (39). We shall now turn to the theoretical part of this work and summarize Kummer's derivation of relationships (99) that will enable one to predict the general nature of the adsorption of any adsorbate from its physical properties and the behavior of some other one adsorbate on the same charcoal.

B. Theory

In deriving a relation between the structure and adsorbability of a molecule, a number of equations were used. The Polanyi (73) relationship

$$T_1 \log p_1/p_{0_1} = T_2 \log p_2/p_{0_2} \tag{16}$$

was employed to account for the dependence on temperature of adsorption of a given adsorbate where T_1 and T_2 are the two different temperatures of the adsorptions, p_1 and p_2 are the isotherm pressures corresponding to some definite amount of adsorption, and p_{0_1} and p_{0_2} are the vapor pressures of the liquid adsorbate at the two temperatures.

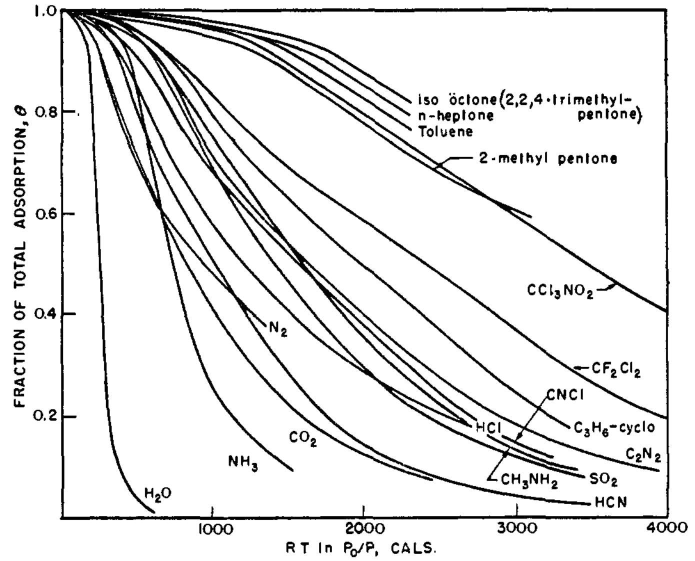


FIG. 33. Physical adsorption of gases on CWSN 19, plotted as the fraction θ of the adsorption at a given relative pressure compared to that at $p/p_0 = 0.99$ *vs.* $RT \ln p_0/p$.

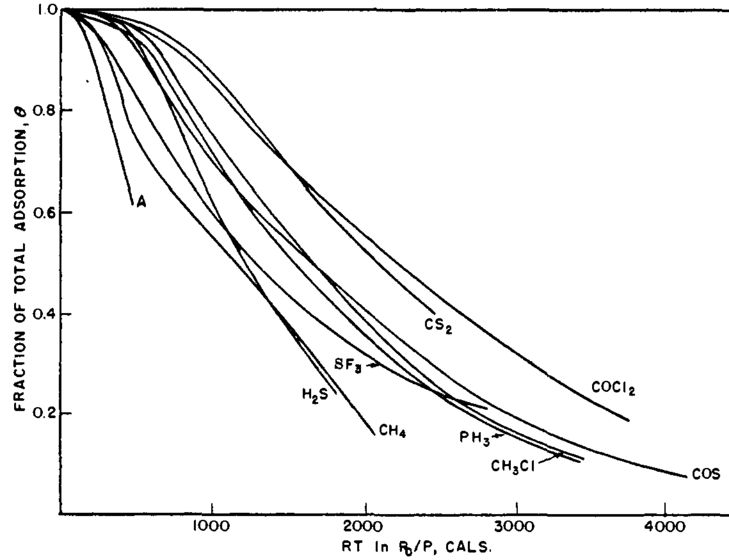


FIG. 34. Physical adsorption of gases on CWSN 19, plotted as in figure 33

The amount of adsorption as a function of the pressure of the adsorbate was, for convenience, expressed in terms of the empirical equation

$$-RT \ln p/p_0 = K(1 - \theta)^{1/3} - B \ln \theta \qquad (17)$$

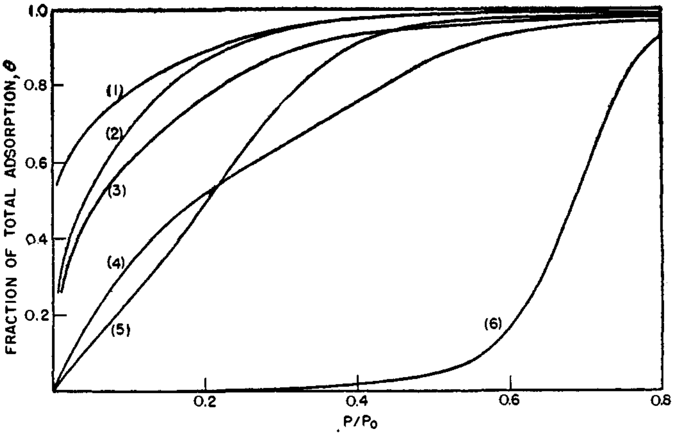


Fig. 35. Isotherms of a variety of gases on CWSN 19 plotted as the fraction, θ, of the maximum adsorption against relative pressure. Curve 1, nitrogen at —195°C.; curve 2, hydrogen sulfide at —78°C.; curve 3, cyanogen chloride at 0°C.; curve 4, hydrogen cyanide at 25°C.; curve 5, ammonia at —46°C.; curve 6, water at 25°C.

TABLE 13

Adsorption data for various gases on CWSN 19

GAS	TEMPERATURE OF ADSORPTION	ADSORPTION AT A RELATIVE PRESSURE OF 0.99; CC. OF GAS (S.T.P.) PER GRAM OF CHARCOAL	ADSORPTION AT A RELATIVE PRESSURE OF 0.99; CC. OF LIQUID ADSORBATE PER GRAM OF CHARCOAL
	°C.		
N_2	−194	397	0.616
A	−194	490	0.600
CH_4	−160	360	0.610
BF_3	−78	291	0.600
PH_3	−78	298	0.615
HCl	−78	442	0.613
CO_2	−78	355	0.554*
H_2S	−78	371	0.566
CF_2Cl_2	−20	166	0.609
NH_3	−46	526	0.572
COS	−46	262	0.608
CH_3Cl	−20	264	0.600
C_2N_2	−21	245	0.595
Cyclopropane	−39	216	0.590
CH_3NH_2	0	296	0.596
SO_2	0	298	0.595
$COCl_2$	0	193	0.596
CNCl	0	267	0.598
HCN	25	350	0.607
CS_2	25	216	0.585
H_2O	40	644	0.520
n-Heptane	25	87	0.567
Toluene	25	120	0.574
CCl_3NO_2	25	128	0.570
2-Methylpentane	25	95	0.560
Isoöctane (2,2,4-trimethylpentane)	25	76	0.563

* Liquid density.

where θ represents the fraction of the saturation value of the adsorption that is occurring at pressure p, and K and B are constants. The relation was found to hold fairly well for all adsorbates on CWSN 19. It gives an isotherm in which the slope dV/dP decreases continuously as the pressure increases and equals zero when $p = p_0$. For those charcoals which give an S-shaped isotherm equation 17 would not hold above $p/p_0 = \sim 0.5$. However, since a gas mask is rarely called upon to afford protection from gases which have attained a partial pressure in the air equal to one-half the vapor pressure of the liquid adsorbate, equation 17 will be used even though it is inapplicable above a relative pressure of 0.5.

If constants K and B could be evaluated from molecular data for the adsorbate, the given problem would be completely solved. It is extremely difficult to do this with exactness. Accordingly, a somewhat simpler but useful approach to the problem was made by outlining a method for calculating the difference between the integral heat of adsorption, $-\Delta H_I$, and the heat of liquefaction, $-\Delta H_L$, for the adsorbate on the basis of the fundamental properties of the adsorbate molecule. Since it was well established that at a given temperature adsorption isotherms follow curves of A, B, or C type shown in figure 36, depending upon whether the heat of adsorption is greater than, equal to, or less than the heat of liquefaction, it would obviously then be possible with the help of the calculated value of $(\Delta H_I - \Delta H_L)$ to indicate the general nature of adsorption.

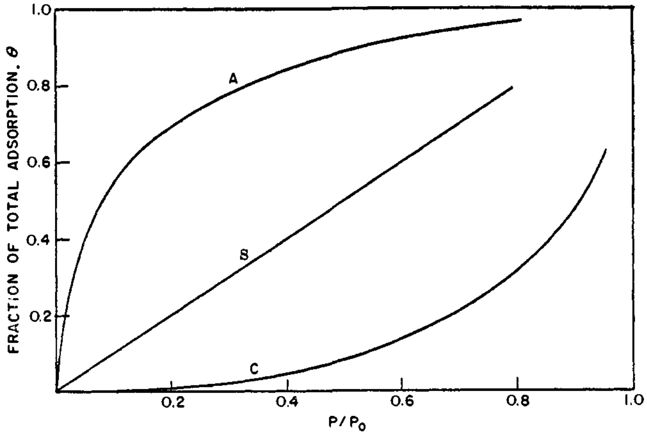


FIG. 36. Shape of hypothetical isotherms as a function of the heat of adsorption at a given temperature. Curves A, B, and C correspond respectively to heat of adsorption greater than, equal to, or less than the heat of liquefaction.

In obtaining a solution to the problem, the thermodynamic equation

$$-RT \ln p_0/p = +\left(\frac{\partial(\Delta H_a)}{\partial n}\right)_T - \Delta H_L - T\left(\frac{\partial \Delta S}{\partial n}\right)_T \tag{18}$$

for the transfer of a mole of absorbate from bulk liquid to an adsorbed form at pressure p on a solid was set up to relate the relative pressure p/p_0 of the adsorption to $\partial(\Delta H_a)/\partial n$, the differential molal enthalpy of adsorption for the gas going to the adsorbed phase, to ΔH_L, the molal change in heat content during condensation of gaseous adsorbate to bulk liquid, and to $\partial(\Delta S)/\partial n$, the differential molal entropy change when the bulk liquid is transferred to the surface layer.

If equation 16 holds, it can be shown that the entropy term disappears and that

$$-RT \ln p_0/p = \frac{\partial(\Delta H_a)}{\partial n} - \Delta H_L \tag{19}$$

Coolidge's data (38) show that many of the organic gases follow equation 16 very closely, whereas water does not.

In order to estimate the entropy term, some assumptions were necessary. For one thing, it was necessary to assume some shape factor for the capillaries in order to be able to know the fraction of liquid adsorbate in contact with the surface of the charcoal. Kummer pointed out that the exact form of the assumption is not too important, because with a variety of choices the final calculated difference between the integral heat of adsorption and the heat of liquefaction does not change much. For simplicity, it was assumed that the charcoal pores had plane parallel walls four molecular diameters apart. The entropy term is usually written in the form $RT \ln \phi/1 - \phi$, where ϕ represents the fraction of the surface covered by adsorption. However, it appeared simpler for physical adsorption to assume that the rate of condensation on the surface is proportional to the total surface rather than to $1 - \phi$; hence, the entropy term was written

$$\frac{\partial(\Delta S)}{\partial n} = -R \ln \phi \tag{20}$$

This expression is assumed to hold for all values of ϕ less than 1. For ϕ greater than 1 the entropy term becomes zero, since rate of evaporation and condensation both are constant and independent of ϕ. If, as is likely, most of the first layer will form before the second begins, then $\phi = 2\theta$.

Combining equations 17, 18, and 20 gives

$$-\partial\left(\frac{\Delta H_a}{\partial n}\right)_T + \Delta H_L = K(1 - \theta)^{1/3} - B \ln \theta + RT \ln 2\theta \tag{21}$$

The integral heat of adsorption was found by integrating the entire expression including the last term from $\theta = 0$ to $\theta = 0.5$; and, without the last term, from 0.5 to 1. The integral heat of adsorption, $-\Delta H_I$, obtained in this way was:

$$-\Delta H_I = -\Delta H_L + 3/4K + B - 1/2RT = -\Delta H_L - \Delta H_x \tag{22}$$

The integral heat of adsorption up to complete filling of the pores was used, because complete filling represents a definite physical state which is the same for all gases and which lends itself to theoretical calculations.

In order to calculate the integral heat at saturation, the following simple process was visualized: (*1*) One mole of gas was condensed into a bulk liquid, the enthalpy change being by definition ΔH_L. (*2*) Next, this bulk liquid was spread out into a sheet four molecules thick. The enthalpy change for this step would be one-half the enthalpy change on bringing a mole of adsorbate from the interior or bulk liquid to the surface of the liquid, or $\Delta H_s/2$. (*3*) Both sides of this sheet were allowed to come in contact with a charcoal surface, giving an enthalpy change of $\Delta H_c/2$, where $-\Delta H_c$ is the heat that would be evolved if all of the molecules in the mole of adsorbate were brought as a sheet of liquid into contact with the carbon surface. Then

$$\Delta H_I = \Delta H_L + \Delta H_c/2 + \Delta H_s/2 \tag{23}$$

Next, a means was sought and found for evaluating ΔH_c and ΔH_s that depends upon the physical properties of the adsorbate molecule. The enthalpy change when a molecule is brought from the interior of a liquid to the surface is largely independent of the temperature and can be calculated by

$$\Delta H_s = +2.22k_e(T_c - 6) \tag{24}$$

where k_e is Eötvös' constant and T_c is the critical temperature. One, therefore, has a ready means of calculating $\Delta H_s/2$, the heat required to form a mole of liquid into a sheet four molecules thick, provided T_c and k_e are known. If k_e is not known, it may be taken as about 2 for most substances.

The heat quantity ΔH_c was evaluated by means of the theory of London (99, 111) and was shown by him to be given by the expression

$$-\Delta H_c = \frac{3N\alpha_c\,\alpha_g 2V_{0c}\,V_{0g}}{4h^3(V_{0c} + V_{0g})} \tag{25}$$

where α_c is the polarizability of the carbon surface, α_g is the polarizability of the gas molecules, V_{0c} is the fundamental frequency of the carbon surface, V_{0g} is the fundamental frequency of the gas molecules, N is the number of atoms per cubic centimeter of adsorbent, and h is the distance between the carbon surface and the molecules of adsorbate when the sheet is at its equilibrium position. As a first approximation[8] $3N\alpha_c V_{0c}/2h^3(V_{0c} + V_{0g})$ may be taken as a constant C_1 and the equation simplified to:

$$-\Delta H_c = C_1\alpha_g V_{0g} \tag{26}$$

C_1 was evaluated from some one adsorbate and then was assumed to be constant for other adsorbates. Substituting expressions 23, 24, and 26 in equation 22 led to the equation

$$\tfrac{1}{2}[C_1\alpha_g V_{0g} - 2.2k_e(T_c - 6)] = \tfrac{3}{4}K + B - \tfrac{1}{2}RT = -\Delta H_x \tag{27}$$

This equation when rearranged became

$$C_1\frac{\alpha_g}{2}V_{0g} = -\Delta H_x + 1.11(T_c - 6)k_e = -\Delta H_x + \tfrac{1}{2}\Delta H_s \tag{28}$$

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[8] The approximate nature of this assumption is evident when one realizes that if h is taken as the sum of the van der Waals radius for carbon and for the adsorbate molecule, it will vary from 3.44 to 4.28 for the adsorbates shown in table 15, and $V_{0c} + V_{0g}$ will vary from 447 to 694. Nevertheless, since α_g varies from 1.48 to 10.8 and V_{0g} from 188 to 435, this approximation will not result in large discrepancies. A refined procedure that introduces values for h for the different adsorbates is now being submitted for publication by Kummer.

TABLE 14

Fundamental data on the adsorbate gases

GAS	MOLECULAR WEIGHT	DENSITY	TEMPERATURE	$-\Delta H_L$	MOLAL VOLUME	AVERAGE RADIUS CALCULATED FROM LIQUID DENSITY	DIPOLE MOMENT $\mu \times 10^{18}$	POLARIZIBILITY, α_g	FUNDAMENTAL FREQUENCY, V_0	ISOTHERM CONSTANTS		TOTAL SURFACE ENERGY, ΔH_s	$-\Delta H_x$	$\alpha_g V_{0g}$	$-\Delta H_x +$ $1/2\Delta H_s$
										K	*B*				
		g./cc.	*°C.*	*cal./mole*	*cc.*	*Å.*	*debyes*	*cc.* $\times 10^{24}$	*kg.-cal.*			*cal./mole*	*cal./mole*		*cal./mole*
N_2	28.02	0.805	−194	1335	34.9	2.16	0.0	1.74	402			561		700	
A	39.94	1.454	−194	1590	27.4	2.00	0.0	1.63	396			643		645	
CH_4	16.04	0.422	−160	2040	38.0	2.23	0.0	2.54	324	240	1210	817	1268	822	1677
BF_3	67.82	1.47	−78	4620	43.0	2.32	0.0	2.40	435	295	1555	1460	1581	1043	2311
PH_3	34.04	0.736	−78	3489	46.3	2.37	0.55	3.50	(300)	650	1485	1410	1778	1050	2483
HCl	36.46	1.174	−78	3860	31.1	2.08	1.03	2.63	311	394	1300		1401	818	
CO_2	44.01	1.26 (liq.)	−78	4130	34.9	2.16	0.0	2.57	357	292	816	1320	8840	916	1500
H_2S	34.08	0.993	−78	4463	34.3	2.15	1.10	3.64	257	1060	608		1208	935	
COS	60.07	1.154	−46	4423	52.0	2.47	0.65	5.05	313	765	1417	1740	1741	1580	2620
C_3H_6	42.05	0.688	−39		61.1	2.61	0.0	4.45	307	1170	1451		2061	1675	
NH_3	17.03	0.697	−46	5720	24.4	1.92	1.49	2.14	271			1290		580	
CH_3Cl	50.5	0.99	−20	5170	51.0	2.45	1.86	4.41	312	1117	1081	1910	1667	1380	2622
C_2N_2	52.02	0.953	−21	5576	54.6	2.51	0.0	4.65	285	870	1290	1840	1689	1322	2609
SO_2	64.06	1.432	0	5960	44.7	2.35	1.67	3.76	272	1020	915	2050	1407	1022	2432
$COCl_2$	98.92	1.428	0	5990	69.3	2.72		6.51	274	1735	1409	2100	2256	1785	3306
CNCl	61.48	1.226	0	6300	50.1	2.44		4.58	(300)	938	1150		1581	1372	
HCN	27.02	0.695	25	6027	38.9	2.24	2.6	2.46	321	552	765	1100	881	790	1431
CS_2	76.13	1.256	25	6490	60.6	2.60	0.0	8.03	188	1610	1192	2520	2102	1510	3362
n-Heptane	100.2	0.684	25	7650	146.1	3.49	0.0	13.7				2490			
H_2O	18.02	0.995	40	10400	18.1	1.74	1.85	1.48	311	360	10	1520	0	460	760
Toluene	92.13	0.862	25	7980	107.0	3.14	0.4	12.3				2870			
CH_3NH_2	31.06	0.687	0		45.2	2.36	0.99	3.88	294	1110	990	1145	1549	1140	2121
2-Methylpentane	86.1	0.654	25	7000	132.0	3.37		11.8							
Isoöctane	114.1	0.692	25	8200	165.0	3.63		15.5							
CCl_3NO_2	164.4	1.641	25		100.0	3.08		10.82	(280)	2620	2000	3640	3667	3030	5487
CF_2Cl_2	120.9	1.47	−20	4760	82.1	2.88		6.55	(300)	1160	1910	1850	2530	1970	3455

Table 14 shows values of K, B, and ΔH_x as calculated by Kummer from the isotherms, together with ΔH_s and physical data for the various adsorbate molecules. Figure 37 is a plot of $\alpha_g V_{0g}$ against $-\Delta H_x + 1/2\Delta H_s$. The value of C_1 turns out to be 3.75 and is equal to twice the slope of the plot.

As pointed out above, complete solution of the problem requires a method for evaluating the absolute values of K and B. This has not yet been accomplished. However, at the present stage of development as pointed out by Kummer (99), it is possible to evaluate $\Delta H_I - \Delta H_L$ for any adsorbate from the experimental adsorption values for some standard adsorbate at a given temperature on a charcoal, together with fundamental data for the standard adsorbate and for the adsorbate for which $\Delta H_I - \Delta H_L$ is sought. For the standard adsorbate one can calculate K and B for the given charcoal from an isotherm. From equation 27 and values for T_c, for the Eötvös constant, for the polarizability of the standard molecule, and for its fundamental frequency one can then obtain a value for the constant C_1.[9] For other adsorbates then on the same charcoal, one has merely to insert values for α_g and V_{0g} in equation 26, and obtain a value for ΔH_c. Knowing ΔH_s from the Eötvös equation, one can then calculate ΔH_x and hence by equation 23 obtain a value for $\Delta H_I - \Delta H_L$. In other words, by knowing a single adsorption isotherm of any one adsorbate on a given charcoal and by knowing the polarizability, critical temperature, Eötvös constant, and fundamental frequency of the molecules of the adsorbate whose adsorption one wishes to evaluate, and

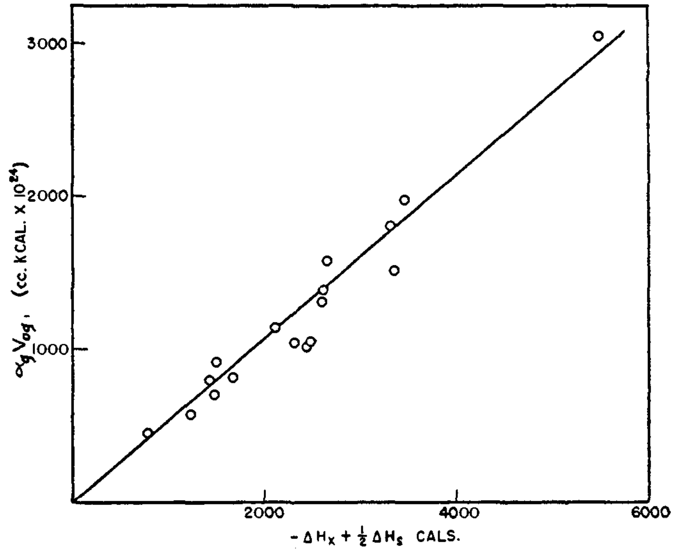

Fig. 37. Evaluation of the constant C_1 of equation 28 by plotting $\alpha_g V_{0g}$ against $-\Delta H_x + 1/2\Delta H_s$.

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[9] The value of α_g can be readily calculated by the method of Denbigh (44) from the structure of the molecule. The value of V_{0g} for organic molecules lies (111) within ± 20 per cent of the value 286 kg.-cal. per mole.

of the standard adsorbate, one is able to tell whether the difference between the integral heat of adsorption and the heat of liquefaction is a large positive quantity, a small positive quantity, or zero.

To show the usefulness of this method of procedure, there are listed in table 15 values for $-(\Delta H_I - \Delta H_L)$ for the various adsorbates as determined experimentally and as calculated using the isotherm for chloromethane for evaluating the constant C_1. It is readily apparent that one would not be misled as to the nature of the adsorption isotherm of any of the gases listed by the calculated value for the difference between the integral heat of adsorption and the heat of liquefaction of the adsorbate.

TABLE 15

Calculation of $-(\Delta H_I - \Delta H_L)$ for various adsorbates on CWSN 19, assuming adsorbate is in capillaries with parallel walls four molecular diameters apart

Heat values are in calories per mole

GAS	TEMPERATURE OF ADSORPTION	$-(\Delta H_I - \Delta H_L)$ FROM ACTUAL ISOTHERMS BY EQUATION 22	$-(\Delta H_I - \Delta H_L)$ CALCULATED FROM CONSTANT C_1 FOR CH_3Cl AND VALUES FOR $\alpha_g V_{0g}$ AND ΔH_s	$\frac{\text{COLUMN 4*}}{T\ (°K.)}$
	°C.			*cal./mole degree*
CH_4	−160	1269	1131	10.0
BF_3	−78	1589	1230	6.3
PH_3	−78	1778	1255	6.4
CO_2	−78	840	1050	5.4
COS	−46	1750	2080	9.2
CH_3Cl	−20	1667	1667	6.4
C_2N_2	−21	1689	1560	6.2
SO_2	0	1407	895	3.3
$COCl_2$	0	2256	2290	8.4
HCN	25	881	925	3.1
CS_2	25	2102	1570	5.3
CH_3NH_2	0	1549	1568	5.9
CCl_3NO_2	25	3667	3860	13.0
CF_2Cl_2	−20	2530	2755	10.9
H_2O	40	0	−23	<1.0

* The temperature used in calculating this column is the absolute temperature at which the isotherm for each gas was determined.

The question naturally arises as to the extent to which the results in table 15 are dependent upon the nature of the assumption made as to the shape of the pores in the capillary. If one assumes that the adsorption is taking place in pores that are cylindrical and four molecules in diameter, one obtains an equation similar to 21, except that the constant 2 is changed to about 1.5. Values for $-(\Delta H_I - \Delta H_L)$ as calculated for this postulate by the proper modification of equations 23, 26, 27, and 28 are shown in table 16; it is evident that to a close approximation one can estimate the magnitude of the difference between the heat of adsorption and the heat of liquefaction without too much error being entailed by the nature of the assumption that has to be made relative to the shape of the pores of the charcoal. The procedure here presented should, therefore, be very useful in quickly evaluating the probable adsorption characteristics of any adsorbate if the polarizability, the fundamental frequency, and surface energy of the adsorbate molecule are known. It has been stated above that in a qualitative sense, as illustrated in figure 36, gases will be strongly, weakly, or very weakly adsorbed depending on whether the heat of adsorption is greater than, equal to, or less than the heat of liquefaction. However, strictly speaking, it is the constant C in equation 3 that is important in fixing the extent of adsorption of an adsorbate at a definite, relative pressure on a given adsorbent. C, as defined in equation 2, is proportional to $e^{(E_1-E_L)/RT}$. Hence, both the energy of adsorption and the temperature must be taken into consideration. Furthermore, $E_1 - E_L$ is not exactly the same as $-(\Delta H_I - \Delta H_L)$, because the $-\Delta H_I$ is the integral heat of adsorption all the way to a relative pressure of 1, whereas E_1 is the average heat of adsorption for the first layer. Nevertheless, for an adsorbent such as charcoal, which has such narrow pores as to permit only a few layers to be adsorbed, there should not be much error involved in using $-(\Delta H_I - \Delta H_L)$ in place of $E_1 - E_L$ in equation 3. It follows, then, that $-(\Delta H_I - \Delta H_L)/T$ should be used in estimating the extent to which a given adsorbate will be taken up by charcoal. To facilitate such a comparison the calculated $-(\Delta H_I - \Delta H_L)/T$ values for the various gases are shown in column 5

TABLE 16

Calculation of $-(\Delta H_I - \Delta H_L)$ for various adsorbates on CWSN 19, assuming adsorbate is in cylinders four molecules in diameter

Heat values are in calories per mole

GAS	TEMPERATURE OF ADSORPTION	$-(\Delta H_I - \Delta H_L)$ FROM ACTUAL ISOTHERM DATA	$-(\Delta H_I - \Delta H_L)$ CALCULATED FROM CONSTANT C_1 FOR CH_3Cl AND VALUES FOR $\alpha_g V_{0g}$ AND ΔH_s	$\frac{\text{COLUMN 4*}}{T\ (°K.)}$
	°C.			*cal./mole degree*
CH_4	−160	1232	1155	10.2
BF_3	−78	1524	1185	6.1
PH_3	−78	1713	1230	6.3
CO_2	−78	775	1020	5.3
COS	−46	1684	2110	9.3
CH_3Cl	−20	1584	1584	6.2
C_2N_2	−21	1606	1514	6.0
SO_2	0	1316	760	2.8
$COCl_2$	0	2165	2290	8.4
HCN	25	781	965	3.2
CS_2	25	2002	1440	4.8
CH_3NH_2	0	1459	1582	5.8
CCl_3NO_2	25	3567	3854	12.9
CF_2Cl_2	−20	2457	2438	9.6
H_2O	40	−113	−64	<1

* The temperature used in calculating this column is the absolute temperature at which the isotherm for each gas was determined.

of tables 15 and 16. The higher the value of the ratio, the stronger the adsorption at the temperature, T, of column 2. Thus, at about room temperature, water vapor would be least strongly, and chloropicrin most strongly adsorbed.

If one wishes to estimate the amount of adsorption at room temperature rather than at the temperature T of column 2 of tables 15 and 16, one should make use of equation 3. V_m of the adsorbate for which one wishes to estimate an adsorption value can be obtained by noting the V_m value for the standard adsorbate and multiplying this latter value by the ratio of the molecular cross-sectional area of the standard molecule to that of the adsorbate being studied. By inserting the value of V_m, C (taken as $e^{-(\Delta H_I - \Delta H_L)/RT}$, and n (as estimated from the standard adsorbate) into equation 3, one can calcuate the adsorption for the desired adsorbate at relative pressure x. Since actual adsorption usually deviates at low relative pressure in the direction of being greater than that estimated from equation 3, the method here outlined for estimating the adsorbability of a substance present in low concentrations is conservative and would give adsorption values which, if in error at all, would be likely to be too low.

Volman and Klotz (157) have contributed one of the few helpful suggestions for explaining why some adsorbates such as water vapor are not strongly adsorbed by charcoal. They point out that molecules of water, methanol, ethanol, ammonia, and a few other substances are strongly hydrogen bonded in the liquid phase. Were it not for such hydrogen bonding water would presumably boil at $-80°$ to $-100°$C. and might have a vapor pressure of the order of 20,000 mm. of mercury at room temperature. Consequently, they conclude that at a relative pressure of, say, 0.3, water behaves in adsorption not involving hydrogen bonding as though it were an adsorbate at 0.0003 relative pressure and therefore is only slightly adsorbed. Only at higher relative pressures where water molecules have a chance to form hydrogen bonds with each other in the adsorbed phase does the adsorption increase rapidly with pressure.

Apparently Kummer's calculations take these facts into consideration by using the actual properties of the liquid phase including the Eötvös constant, critical temperature, and boiling point in calculating the probable behavior of an adsorbate. His calculations, however, do not explicitly call attention to the hydrogen-bonding explanation.

In concluding this section, it may be well to emphasize the type of information that is furnished by the theoretical considerations of Kummer and of Volman and Klotz. As discussed above, Kummer's calculations enable one to predict whether an adsorbate is going to be slightly, medium strongly, or strongly adsorbed on a particular sample of charcoal for which one has an adsorption isotherm of some standard adsorbate. For example, it enables one to predict that the water isotherm (curve 6, figure 35) will resemble curve C, figure 36, in showing very slight adsorption; that hydrogen cyanide (curve 4, figure 35) will be medium strongly adsorbed and will resemble curve B, figure 36; and that chloropicrin will be strongly adsorbed and will resemble curve A, figure 36. Thus, even though his calculations involve integral heats of adsorption, they do assign the isotherms to general adsorption types and thereby give information as to the adsorption at low relative pressures as well as at higher relative pressures. Volman and Klotz's suggestion enables one to predict that for any molecules tending to form hydrogen bonds in the liquid phase, adsorption on an adsorbent with which hydrogen bonds will not be formed will be smaller than one would expect. Accordingly, with the help of the ideas advanced by Kummer and those proposed by Volman and Klotz, it is now possible to predict, much more accurately than formerly, the possible behavior of a given adsorbate on a sample of charcoal, even though the adsorbate is present in amounts corresponding to a low relative pressure.

IX. RETENTIVITY OF CHARCOALS

Allmand (6, 10) and his coworkers showed many years ago that it is possible to use a retentivity method for determining approximate adsorption isotherms for a vapor on a solid adsorbent. Thus, by saturating a sample of charcoal with given partial pressures of vapors and then noting the change in concentration of the effluent gas when vapor-free air is passed into the sample, an approximate adsorption isotherm can be constructed which would give the amount of adsorbate left on the sample as a function of the exit partial pressure of the adsorbate. Ordinarily, the approximate isotherms so obtained will be somewhat lower than a true isotherm, because the charge left on the charcoal at any stage in the desorption is not uniformly distributed but is concentrated more at the exit than the entrance to the bed of adsorbent. Nevertheless, such approximate isotherms serve as a useful means of predicting the initial exit concentration of vapor that one could expect from a bed of charcoal as a function of the amount of adsorbate that has been taken up and has been permitted to become redistributed throughout the charcoal. This technique also permits one to determine the influence of moisture on the retentivity.

During the war Volman, Doyle, and Blacet (145) have obtained some interesting retentivity results for a number of organic vapors as a function of the moisture content of the charcoal and gas stream. Approximate isotherms were constructed by the retentivity method for carbon tetrachloride, chloroform, carbon disulfide, ethylene dichloride, methyl ethyl ether, neopentane, acetone, and methanol (145). It was concluded that water vapor decreased the amount of adsorbate that could be held at equilibrium and decreased the retentivity very markedly for all vapors that were insoluble in water. For those that were slightly soluble the effect was less pronounced, and for those that are miscible in all proportions with water, no appreciable decrease in the total sorption capacity or retentivity of the charcoal was found to occur. As a matter of fact, for methanol it was shown that the isotherm in the presence of water could be derived from the dry isotherm and the water isotherm. These results seem to be consistent with similar work that has already been published, including the influence of water vapor on the adsorption of chloropicrin (108).

X. CHEMISORPTION ON THE CUPRIC OXIDE IN TYPE A WHETLERITES

In order to obtain some idea as to the extent of surface of the inorganic material added to base charcoals in the course of making type A whetlerites, a search was made for a gas that would not be strongly adsorbed on charcoal and that would form only a layer of chemically bound adsorbate on the cupric oxide attached to the charcoal. At the same time, measurements were made on two different samples of cupric oxide of known surface areas.

The detailed results of the work need not be given here (67). It will suffice to point out that hydrogen sulfide, phosphine, cyanogen chloride, boron trifluoride, hydrogen chloride, acetylene, and nitric oxide all appear to react at room temperature with the cupric oxide in type A whetlerites to a depth in excess of a monolayer and hence will not serve for measuring the surface area of the whetlerizing ingredients. Hydrogen sulfide, cyanogen chloride, boron trifluoride, and hydrogen chloride seem especially reactive and probably combine almost stoichiometrically with the copper oxides present. Nitric oxide reacts extensively even with the base charcoal.

Carbon monoxide, sulfur dioxide, water, cyanogen, and ammonia are all chemisorbed in amounts that do not exceed a monolayer. The results obtained with these gases indicate that on the three type A whetlerites investigated, about 3 cc. of gas is required to form a monolayer on the copper oxides of the whetlerite. This corresponds to a particle size of about 100 Å. for the cupric oxide crystals.

XI. THE STRUCTURE OF CHARCOAL

There are very few things about which we can be sure as regards the structure of charcoal. Perhaps one of the few things we can say with confidence is that an active adsorptive charcoal must contain a network of capillaries, some large and some small. This seems essential in order to provide avenues by which the molecules that are to be adsorbed can gain entrance to the interior of the charcoal particles and to the large surface area that must necessarily be located in small pores. When, however, we come to a discussion of the pore shape and ask whether we should consider charcoal as a honeycomb structure of approximately cylindrical pores, or as a collection of platelets more or less parallel to each other and forming box-like capillaries of rectangular cross section, or some combination of these, or some arrangement involving pores of still different shapes, we find ourselves in the realm of speculation and are unable to speak with certainty. Perhaps the best procedure to follow in summarizing the evidence is to consider the results obtained from each of the principal tools and types of measurement from which we can hope to obtain information as to the pore shape and the general structure of charcoal. These various approaches will include x-ray diffraction studies, microscopic studies, electron microscope studies, measurements and calculations of area and pore volume, chemical behavior of charcoal, expansion of charcoal during adsorption, and measurements of the true density of the carbon in charcoal. These will now be discussed in turn.

A. X-ray structure work on charcoal

In an extended series of papers Johnstone and Clark (84, 86) have reported the results of their study of the structural characteristics of some 1200 samples of carbons, cokes, activated charcoals, resins, and gas mask adsorbents of all kinds. A number of their observations relating to the charcoals are as follows: (*1*) Charcoals sinter and turn into graphite much less readily than does petroleum coke. (*2*) The value of c (twice the spacing between planes in the c direction) is about 7.72 Å. for a coconut charcoal and 7.47 Å. for a charcoal made by the zinc chloride process, provided the samples have not been heated over 1100°C. This compares with 6.70 Å. for graphite. (*3*) These charcoals appear to contain a number of platelets which in the c direction are about 10 Å. in thickness; for a few other charcoals this thickness is as high as 12 Å. This is in good agreement with the work of Berl (23) and of Hofmann and Sinkel (82). The discs or platelets of carbon revealed by the x-ray studies are broader than they are thick. For coconut charcoal they range in width from about 20 Å. for samples that have been heated to no more than 500°C., to 39 Å. for samples that have been heated to 1000°C. Values for this L_a dimension for zinc chloride charcoals start at 20 Å. as for the coconut charcoal, but extend up to 45 Å. for samples heated to 900°C. and to 63 Å. for samples heated to 1100°C.

The x-ray results taken as a whole constitute strong evidence that much of the carbon in charcoal is arranged in platelets. The preferential growth of these in one direction seems to be especially convincing evidence of their reality. Johnstone and Clark conclude (84) that "the data obtained from the x-ray study evidently give credence to the idea that activation is essentially a process of cleaning out capillaries, in changing their size and perhaps their shape, without greatly affecting the matrix structure of carbon."

B. Microscopic studies

During the recent war no extensive microscopic studies of charcoals were reported. However, it is well known from published reports (71, 100) that it is possible to show up by photomicrographs the presence of large capillaries in the surface of charcoal particles. Necessarily, the limit to such studies is about 0.5 micron, so that capillaries smaller than about 5000 Å. will not be observable. These microscopic studies, accordingly, will merely confirm the presence of the large connecting channels by which the gases that are to be adsorbed gain access to the interior of the particles. They show nothing about the shape or distribution of the fine pores.

C. Electron microscope studies

Electron microscope pictures push the microscopic observations out to capillaries smaller by perhaps a factor of 50 than those observable in the ordinary light microscope. The results have been well expressed in a summary of the report by Johnstone, Clark, and Le Tourneau (87): "Thirty-six electromicrographs of various charcoals are presented. While they do not reveal the ultimate pore structure of the charcoal, they do show a pore structure in the size range between several hundred and 1000 Å. in diameter, in the nut shell charcoals as ordinarily prepared, in CWSC charcoal, in low density CWSN charcoals, and in highly activated (steamed) Saran charcoals. The importance of these large pores is not fully established, but they may affect the rates of adsorption of gases by the charcoal."

D. Measurements of area and pore size

Young (155) early calculated the diameter and length of the cylindrical capillary that would be required to be equivalent to the area and pore volumes of typical charcoals. For CWSN 19 using a value of 1227 sq. m. per gram for the area, he concluded that a total length of 2.05×10^{13} cm. of pores 20.8 Å. in diameter would be needed. To illustrate the enormous length of capillary thus involved, he pointed out that the length of capillary in a 1-g. sample would be equivalent to 40,000 times the circumference of the earth. If one assumes that these cylindrical capillaries are arranged as a honeycomb in a particle of charcoal, it turns out that the minimum wall thickness between the cylinders would be only about 4 Å. It is a little difficult to reconcile such a picture with the x-ray observations of platelets 10 Å. thick and 20–60 Å. wide as making up most of the charcoal. Even though cylindrical capillaries have, for convenience, been used in calculating pore diameters from water-desorption isotherms, the x-ray results, if they can be relied upon, certainly would dictate the use of caution in formulating any such picture of the charcoal structure.

Young also calculated that if all of the capillary space consists of rectangular parallelepiped capillaries with parallel walls, the distance between the walls would on an average have to be 10.4 Å. for CWSN 19, in order to account for the observed area and pore volume. Such a picture would be entirely consistent with the x-ray data. As a matter of fact, it was found that on one particular sample of CWSN charcoal, the apparent area dropped from 2040 sq. m. per gram to 1670 sq. m. per gram as the sample was heat treated up to 1100°C. During this heat treating the L_a dimension of the discs or platelets increased from 20 to 63 Å. in size. It is entirely reasonable on a platelet structure to explain such particle growth with comparatively little change in surface area. It would be much more difficult to explain if the charcoal consisted of a honeycomb structure of cylindrical capillaries.

E. Chemical behavior of charcoal

It is well known that standard charcoals can all be converted by proper chemical treatment into compounds that appear to have a central nucleus of carbon atoms arranged much as though they were in a plane of graphite. Thus mellitic acid has been reported (97) to be formed in good yield by controlled oxidation with nitric acid. This certainly indicated that much of the carbon is arranged in two-dimensional graphite-like sheets or platelets and again is consistent with the x-ray picture of the structure of charcoals.

F. Expansion of charcoals during adsorption

At least five different observers (14, 15, 16, 121, 121a, 121b, 140) have noted that when charcoal picks up water vapor in the higher relative pressure ranges it expands.[10] It should be noted, as pointed out by Kummer (99), that it is much easier to imagine the expansion of charcoals if they are made up of platelets

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[10] See footnote 6.

capable of being pried apart[11] to some extent by entering water molecules in much the same way that various molecules can pry apart the planes of montmorillonite (79) and certain other clays (40). If the pore structure consists of a honeycomb of cylinders, the possibility of expansion seems much more limited.

G. True density of carbon in charcoal

The true density of carbon in graphite is about 2.25 g./cc. as determined both from x-ray work and from actual density measurement. If the c dimension in charcoal is as large as 7.5 Å., as indicated by the x-ray work, and the a dimension is substantially the same as for graphite, it would seem to follow that the apparent density of the carbon in charcoal cannot be as high as 2.25, since the c distance for graphite is only 6.7 Å. As a matter of fact, on the basis of the x-ray measurements the density should be somewhere between 2.0 and 2.1. Carbon densities determined by helium have been reported over the entire range from 1.77 to 2.36 for various charcoals; a large number of the apparent densities are in the range 1.95–2.15. Accordingly, it may be said that the density values of the carbon in charcoals are also consistent with the x-ray data. It should be noted in this connection that an interplanar distance of 3.75 Å. that one would deduce from the c dimension is probably too small to permit the entrance of helium atoms between planes during density measurements. Hence, the density determinations on helium would really yield values for the density of the platelets.

H. General conclusion as to structure

As stated in the introduction to this section, it is not possible to speak with certainty as regards the structure of charcoal. When all of the evidence listed above is taken as a whole, however, it seems to favor capillaries of rectangular cross section for the most part, rather than cylindrical capillaries. Immediately, one is confronted with the question as to what happens to the very nice calculations of pore diameter made by Juhola if the pores are really box-like structures rather than cylinders. The answer is that the distance between parallel walls that one calculates from the Kelvin equation is just one-half as great as the diameter calculated from cylindrical capillaries. Accordingly, capillaries which with a $\cos\theta$ of 1.0 appeared to be about 36 Å. in diameter if present as cylinders would calculate to be 18 Å. between parallel platelets. However, the calculation of the distance between parallel planes from the relation of the increment of surface area A covered up by each increment of volume V is given by the equation:

$$d = \frac{2\Delta V}{\Delta A} \tag{29}$$

Hence if $\cos\theta$ were taken as 0.53, the measurement of the slope of the surface area *vs.* volume of water curve would lead to a value of about 9 Å. for the distance d. This, in the writer's opinion, is too small a size to permit the occurrence of what

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[11] The water molecules probably do not penetrate in between the graphite-like layers of each platelet but do enter the space between the platelets.

we might call capillary condensation. On the other hand, if one assumes that the charcoal is made up of platelets and accepts the distance d as 18–20 Å., the surface area per gram of charcoal is about 800 sq. m. per gram compared to values ranging from 1300 to 1700 for CWSN 19 that would be obtained by different methods of estimating the area. Possibly the answer to the dilemma is to be found by assuming that the capillaries are for the most part rectangular in cross section and for CWSN 19 about 18–20 Å. between platelets, and that even smaller crevices leading off the 20 Å. openings become covered with adsorbed water only when the larger 20 Å. openings are full. In desorption, this would mean that the water was desorbed by capillary condensation from the hemicylindrical surface at the edge of the rectangular capillary opening. This explanation is, furthermore, not inconsistent with the value of d obtained from equation 29, because such a calculation is necessarily an average for the main capillaries and any smaller side capillaries that fill and empty at the same time as the main 20 Å. capillaries fill and empty. It does, however, entail assuming that $\cos \theta = 1$, an assumption that does not seem very reasonable at relative pressures at which water vapor is only slightly adsorbed.

Possibly the capillaries are neither cylinders nor rectangular parallelepipeds, but some irregular collection of openings of odd shapes that will not permit of any simple presentation. The final answer still seems obscured. As stated above, however, if the choice were between cylindrical capillaries and rectangular capillaries the bulk of the evidence would, in the writer's opinion, favor the latter.

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