integral values of the temperature. The entropy at 298.16°K. is 22.44 e.u., of which 0.41 e.u. is contributed by extrapolation below 16°K. Millar[3] reported a value of 21.7 ± 1.0 e.u., based on his own data from 75 to 291°K. and an extrapolation below 75°K.[5]

TABLE I

MOLAR HEAT CAPACITY OF CUPROUS OXIDE

Mol. wt. 143.14 g., 0.7844 mole

Mean T, °K.	C_p, cal. mole^{-1} deg.$^{-1}$	Mean T, °K.	C_p, cal. mole^{-1} deg.$^{-1}$
14.72	0.697	88.31	8.952
16.47	0.864	94.28	9.254
18.99	1.156	101.73	9.575
21.31	1.472	109.75	9.856
23.49	1.793	116.62	10.12
25.22	2.073	124.00	10.39
26.00	2.190	131.66	10.70
28.22	2.567	138.81	10.97
28.75	2.642	145.42	11.21
30.53	2.960	153.63	11.48
31.31	3.087	160.73	11.73
32.84	3.359	166.88	11.92
35.70	3.879	174.06	12.15
38.89	4.419	181.20	12.37
40.87	4.695	187.89	12.57
42.72	5.007	194.89	12.78
43.39	5.072	203.79	12.99
46.69	5.527	212.62	13.26
47.04	5.602	220.84	13.47
50.34	5.961	229.00	13.71
51.84	6.187	236.16	13.87
54.00	6.410	243.54	14.03
57.01	6.751	252.12	14.22
57.82	6,813	259.67	14.43
60.65	7.133	269.67	14.65
61.65	7.176	275.47	14.78
64.01	7.404	283.67	14.95
69.44	7.830	291.67	15.09
76.39	8.304	299.64	15.22
82.80	8.663		

TABLE II

THERMODYNAMIC FUNCTIONS FOR CUPROUS OXIDE

T, °K.	C_p cal. mole^{-1} deg.$^{-1}$	S^0 cal. mole^{-1} deg.$^{-1}$	$H^0 - H^0_0$ cal. mole^{-1}	$(H^0 - H^0_0)/T$ cal. mole^{-1} deg.$^{-1}$	$-(F^0 - H^0_0)/T$ cal. mole^{-1} deg.$^{-1}$
16	0.807	0.4065	4.398	0.2749	0.1316
25	2.022	1.0014	16.803	0.6721	0.3293
50	5.966	3.6809	119.28	2.3856	1.2953
75	8.205	6.5718	299.42	3.9923	2.5795
100	9.485	9.1226	521.84	5.2184	3.9042
125	10.452	11.345	771.30	6.1704	5.175
150	11.360	13.332	1044.0	6.9600	6.372
175	12.180	15.146	1338.5	7.6486	7.497
200	12.917	16.821	1652.3	8.2615	8.560
225	13.584	18.381	1983.7	8.8164	9.565
250	14.197	19.845	2331.1	9.3244	10.521
275	14.756	21.225	2693.1	9.7931	11.432
298.16	15.210	22.436	3040.3	10.197	12.239
300	15.242	22.530	3068.3	10.228	12.302

Our estimate of the uncertainty in the entropy is ±0.07 e.u., of which ±0.04 e.u. is due to the uncertainty in the extrapolated portion below 16°K.

Acknowledgments.—We wish to acknowledge the assistance of Mr. Nathan C. Hallett in checking the experimental work and in giving assistance with some of the measurements. We are also indebted to Mr. Gordon B. Skinner for making the X-ray analyses.

[5] Millar's cuprous oxide was prepared by heating pure cupric oxide under reduced pressure at 1000°.

COLUMBUS 10, OHIO RECEIVED FEBRUARY 20, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

Adsorption of Water by Carbon[1]

BY CONWAY PIERCE, R. NELSON SMITH, J. W. WILEY AND H. CORDES

Water isotherms are given for porous and non-porous carbons. A non-porous carbon adsorbs little water, as compared with other vapors, but activated charcoals hold nearly the same liquid volume of water as of other vapors. The net heat appears to be zero for the initial adsorption of water, then as more molecules are adsorbed the net heat becomes positive. This effect is ascribed to the contribution of lateral interactions with previously adsorbed molecules. At elevated temperatures the initial net heat of adsorption appears to have a large negative value, but it is shown that this effect may be due to a reaction of carbon with water which may occur slowly even at room temperature. Hydrogen and carbon dioxide are produced in the reaction and some of the oxygen is held as a surface complex, which increases the surface affinity for water. An upturn in a water isotherm below $0.95p_0$ appears to be associated with the presence of capillaries. Water isotherms are used to detect capillaries in certain carbon blacks.

During the past thirty years many isotherms have been reported for adsorption of water vapor by activated charcoal, but comparatively little work has been done with non-porous carbon. The isotherms of charcoals show a variety of forms and there is little correlation of the charcoal data with those for non-porous surfaces. The work herein reported has been done with samples of both porous and non-porous carbons for which the isotherms for other adsorbates are known, with the hope of gaining a better understanding of the factors which make water adsorption unlike that of other vapors.

Water adsorption studies prior to 1946 have been reviewed by Emmett.[2] The most extensive work since this review is that done by Wiig and Juhola,[3a,b] and by Harkins, Jura and associates.[3c,d]

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[1] This is a progress report of work done under Contract N8 onr 54700 with the Office of Naval Research.

[2] P. H. Emmett, *Chem. Revs.*, **43**, 69 (1948).

[3] (a) E. O. Wiig and A. J. Juhola, THIS JOURNAL, **71**, 561 (1949); (b) A. J. Juhola and E. O. Wiig, *ibid.*, **71**, 2069, 2078 (1949); (c) W. D. Harkins, G. Jura and E. H. Loeser, *ibid.*, **68**, 554 (1946); (d) P. R. Basford, G. Jura and W. D. Harkins, *ibid.*, **70**, 1444 (1948).

Experimental

Samples were selected to give a variety of carbon surfaces, and have been studied with other vapors besides water. To conserve space, reference is made to previous publications[4-10] for descriptions of the samples and isotherms, whenever possible.

NC-1.—A very pure graphite of surface area *ca.* 4 sq. m./g. Isotherms for ethyl chloride,[4] nitrogen,[5] ammonia,[5] methanol[7] and water[9] have been given. The water isotherms indicate that little or no oxygen complex is present.

Graphon.—A partially graphitized carbon black from the Cabot Company,[11] of area *ca.* 80 sq. m./g. Insofar as can be determined by any test now known, Graphon has no capillaries. It is a particularly valuable sample because of the many studies that have been made with it. Isotherms for methanol,[7] water,[8,9] ethyl chloride,[9] benzene and cyclohexane[10] have been published from this Laboratory. Calorimetric heats of adsorption have been determined by Beebe and associates[12] and isosteric heats by Joyner and Emmett.[13]

Before determination of a water isotherm the Graphon was evacuated at 1100°, treated with hydrogen at this temperature, repumped, and cooled *in vacuo*. After sealing into the adsorption bulb, the sample was again pumped at 400° to remove any gases that might have been adsorbed in transfer (a routine procedure for all isotherms).

Spheron 6.—A medium rubber Cabot carbon black,[11] of area *ca.* 110 sq. m./g. Ignition leaves an ash residue of 0.02%. Volatile matter was removed by pumping at 1100°, followed by hydrogen treatment at 1100°. Water[14] and nitrogen[14,15] isotherms have been given by others. An ethyl chloride isotherm determined here was quite like that of Graphon and agreed with the surface area of 110 sq. m./g.

Carbolac I.—A Cabot ink black[11] of nitrogen area near 1000 sq. m./g. The ash content is *ca.* 0.2%. Volatile matter was removed by pumping at 1100° but at the time this sample was used no hydrogen treatment was given. An ethyl chloride isotherm has previously been published[8] and water[14] and nitrogen[14,15] isotherms are given by others.

Saran Charcoals.—Charcoals of apparently very uniform pores can be prepared[1] by carbonization of Saran, a polyvinyl chloride plastic made by the Dow Chemical Company. Samples of varying properties were prepared from chips of sheet Saran, treated as follows:

S 400 H.—Carbonized at 400° then treated with hydrogen at 400°. Little use was made of this sample. A water isotherm (Fig. 5) was attempted, but the behavior was such as to lead to the belief that the sample still held a surface layer of chloride which gave some chemisorption of water. No further work was done with this sample.

S 600 H.—Saran carbonized at 600° then hydrogen treated at 600°. A water isotherm with the carbonized material showed indications of chemisorption which was attributed to adsorbed chloride of some type. Treatment with hydrogen at 600° caused formation of considerable HCl. This was pumped off and the sample cooled *in vacuo*. After this treatment the water isotherm was of the type expected for a fine pore charcoal, with no indication of chemisorption. Water isotherms at 0° and 28.6° are shown in Fig. 2. Ethyl chloride[6] isotherms have previously been published for two temperatures.

S 84.—Saran carbonized at 600° was steam activated at 900° to 84% weight loss, in an attempt to prepare a charcoal of very high pore volume. After activation, the sample was cooled in nitrogen to prevent formation of an oxygen complex. Ethyl chloride,[6] carbon tetrachloride[6] and water isotherms[6,9] have previously been published.

Darco G 60.—A commercial decolorizing charcoal from the Darco Corporation, New York. Prior to determination of water isotherms, the sample was hydrogen treated at 1100°.

Procedure.—All water isotherms were determined gravimetrically, by weighing the sample bulb after each addition or removal of vapor. The bulb was made with a standard taper joint for attachment to the system, and closed by a vacuum-type stopcock. The taper joint was lubricated with a heavy stopcock grease. Before weighing the grease was removed from the joint by benzene. To compensate for moisture adsorption on the outer glass surface, a counterpoise was used in all weighings and the bulb allowed to stand in the balance case until the weight was constant. Weighings were reproducible to 0.1 mg. (equivalent to about 0.12 cc. of water vapor at S.T.P.). The weight of sample varied from 30 g. for NC-1 to 1 g. for the porous charcoals. The free volume in the bulb was determined by helium at room temperature and a correction applied for the computed weight of unadsorbed vapor in the free volume. Since the pressures were quite low, no allowance was made for deviations of water vapor from a perfect gas.

At 0° the bath was a dewar flask filled with an ice–water mixture. Water thermostats controlled by Merc-to-Merc regulators were used for the 28.6° and the 80° baths. A check was made for temperature control by taking a p_0 reading with each isotherm point. The water bulb for this was mounted close to the sample bulb.

Vapor pressures were measured by a mercury manometer for the 80° isotherm but for the 0° and 28.6° isotherms the pressures were measured by manometers filled with Dow Corning Silicone No. 703, which has a density near one. These manometers showed some drift on prolonged standing in contact with water vapor. Reproducible readings were, however, obtained by pumping out the vapor just before each reading, then readmitting vapor to the approximate equilibrium pressure, opening to the sample, and reading the final pressure. Accuracy was constantly checked by p_0 readings taken immediately after the sample reading.

For the 80° isotherms it was necessary to design a system that could be completely immersed in the bath, since if any part of the system is at a temperature below that of the bath vapor will condense at the cold spot. The design used is shown in Fig. 1. Before each point the system is attached to a vacuum line by a taper joint at A, with the sample bulb attached at B. After evacuation the desired amount of water is condensed in the graduated side tube. Then the main stopcock, S, is closed, the taper joint is capped, and the entire unit including the sample bulb is immersed in the bath to the point P until an equilibrium pressure reading is attained. Usually the period is 5–6 hours. Before removing from the bath, the stopcock on the sample bulb is closed, to prevent distillation of vapor from the sample as the system cools. After cooling the sample bulb is removed, dried and weighed. Following the weighing, the vapor is pumped, at room temperature, from the sample bulb and a second weighing is made. The difference in weighings, after correction for vapor in the free space, gives the amount of vapor adsorbed. Pumping down after each point was done for 80° isotherms because of the danger of change in weight by loss of stopcock grease when the stopcocks are under water at 80°. All stopcocks were of the vacuum seal type, lubricated with a heavy body grease (Cenco vacuum grease).

Along with each isotherm point a p_0 reading was taken with a separate unit consisting of a bulb of outgassed water connected to a mercury manometer. The water bulb was mounted beside the sample bulb. The reproducibility of p_0 readings indicated a temperature control of ±0.1°.

Discussion

By comparison of the isotherms for a variety of samples ranging from those with no pores to those with very large pore volume per gram, certain deductions regarding the nature of water adsorption by carbon can be made. The authors believe that these deductions are in keeping with the experimental facts and that they provide a self-consistent

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(4) C. Pierce and R. N. Smith, *J. Phys. Colloid Chem.*, **52**, 1111 (1948).

(5) R. N. Smith and C. Pierce, *ibid.*, **52**, 1115 (1948).

(6) C. Pierce, J. W. Wiley and R. N. Smith, *ibid.*, **53**, 669 (1949).

(7) C. Pierce and R. N. Smith, *ibid.*, **54**, 354 (1950).

(8) C. Pierce and R. N. Smith, *ibid.*, **54**, 795 (1950).

(9) C. Pierce and R. N. Smith, *ibid.*, **54**, 784 (1950).

(10) R. N. Smith, C. Pierce and H. Cordes, THIS JOURNAL, **72**, 5595 (1950).

(11) The samples were provided through courtesy of Dr. W. R. Smith of the Cabot Company, Boston, Mass. Properties are described in a Cabot publication "Cabot Carbon Blacks under the Electron Microscope," October, 1949.

(12) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, THIS JOURNAL, **69**, 95 (1947).

(13) L. G. Joyner and P. H. Emmett, *ibid.*, **70**, 2353 (1948).

(14) P. H. Emmett and R. B. Anderson, *ibid.*, **67**, 1492 (1945).

(15) J. Holmes and P. H. Emmett, *J. Phys. Colloid Chem.*, **51**, 1262 (1947).

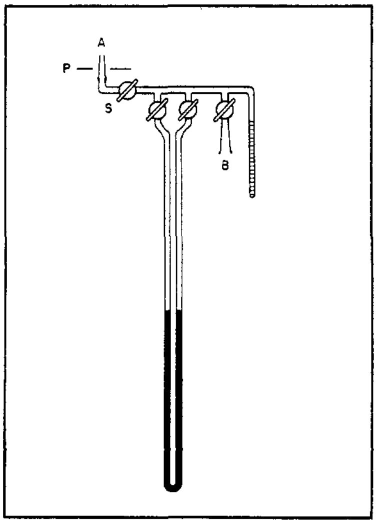

Fig. 1.—Apparatus for isotherms at 80°.

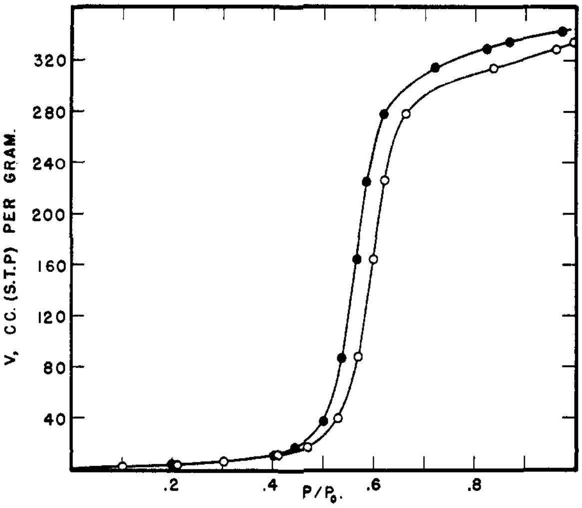

Fig. 2.—Water isotherms for charcoal S 600 H: ○, adsorption at 28.6°; ●, adsorption at 0°.

interpretation. It must however be recognized that other interpretations can be offered for at least some of the same phenomena. At this time the interpretations given are those we believe to be most logical with respect to all the present data, but as more data are obtained the picture may well have to be modified.

Heat of Adsorption.—In 1927, Coolidge[16] found by comparison of charcoal isotherms at different temperatures that near room temperature the initial adsorption of water occurs with zero net heat. As more adsorption occurs the net heat becomes positive $(E - E_L) > 0$. Our results for S 600 H, Fig. 2, are in agreement with Coolidge. Below 0.4 p_0 the isotherms for 0° and 28.6° are within experimental limits identical. Above 0.4 p_0 the isotherm at 0° shows more adsorption for a given relative pressure than the one at 28.6°.

As shown in a previous paper,[8] Graphon also adsorbs water initially with zero net heat. In this case the isotherms for 0° and 28.6° coincide up to 0.9 p_0 but as with charcoal the isotherms separate after the steep rise begins, and $E - E_L$ becomes positive.

In discussing this phenomenon we have suggested[8] that the occurrence of spontaneous transfer of water molecules from bulk liquid to adsorbed film when $\Delta H = 0$ is due to an increase in entropy which is related to the random distribution of the first adsorbed molecules on the surface. The positive value for $E - E_L$ with increasing surface coverage is attributed to the effect of lateral interactions with previously adsorbed molecules. This explanation seems to us more logical than to assume that $E - E_L$ is zero for some surface sites but positive for others that adsorb later. Further, other systems have shown a rise in the net heat of adsorption that has been attributed to the effect of lateral interactions. Beebe and associates[12] find such an effect in the calorimetric heat of adsorption for nitrogen on Graphon, and Joyner and Emmett[13] in the isosteric heat for the same process. Rhodin[17] finds a rise of 1–2 kcal. per mole in the heat of adsorption of nitrogen on a single crystal face of copper, as the V_m point is approached. We feel that an increase in heat must always accompany the completion of the first layer in adsorption but that if a surface is very non-uniform the effect of this may be masked by a general fall in the heat of adsorption as the more active sites become filled first. Only for somewhat uniform surfaces may one expect to find a maximum in the heat of adsorption near completion of the first layer. To date, Graphon is the only carbon sample for which the heats of adsorption generally show such a maximum; this we believe to indicate that its surface is more uniform than that of other samples, such as the carbon blacks. The initial heat of adsorption for nitrogen or hydrocarbons on Graphon is less than that on Spheron 6, which may indicate that graphitization has destroyed the most active sites.

When Coolidge[16] determined water isotherms for charcoal at temperatures of 100° and above, he found that the initial adsorption at a given relative pressure increases with the temperature, but that after the steep rise begins the isotherms assume their normal positions with the greatest adsorption at the lowest temperature. His isotherms indicate that $E - E_L$ is initially negative, then zero, and finally positive.

Since this behavior of water vapor on charcoal is so different from that of other adsorption systems, it was thought desirable to study the water adsorption of non-porous Graphon at elevated temperature. Isotherms at 80° and 28.6° are shown in Fig. 3. We find, in agreement with Coolidge, that the initial adsorption is greater at 80° but unlike the charcoal case, the 80° isotherm lies above that for 28.6° at all relative pressures. If the Clapeyron equation is applicable, $E - E_L$ is negative throughout the adsorption, which seems unreasonable since it requires an increase in entropy for all the adsorption process.

Further work showed that the 80° isotherm is not directly comparable with the original 28.6° isotherm. At the higher temperature, water reacts quite rapidly with carbon to form a surface

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[16] A. S. Coolidge, THIS JOURNAL, **49**, 708 (1927).

[17] T. N. Rhodin, Jr., *ibid.*, **72**, 5691 (1950).

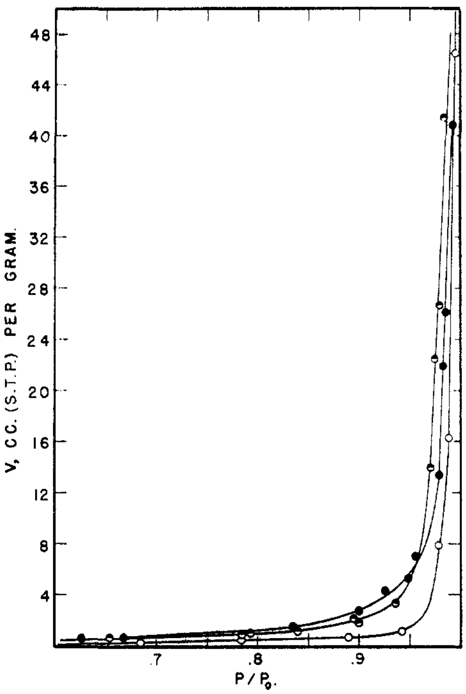

Fig. 3.—Water isotherms of Graphon, showing effect of reaction of surface with water vapor on the isotherm: O, original 28.6°; ●, 80°; ◓, 28.6° after surface complex is formed.

complex which appears to adsorb water more readily than a clean carbon surface. The existence of such a reaction was postulated by McBain, Porter and Sessions[18] in 1933. Proof for the reaction is found in two ways:

(1) When a 28.6° isotherm is determined after one at 80°, it does not agree with the original isotherm for a clean carbon surface. Figure 3 shows an original 28.6° isotherm, an 80° isotherm, and a 28.6° isotherm made concurrently with the 80° isotherm. The latter shows much more adsorption than the original 28.6° isotherm and up to 0.95 p_0 is almost coincident with the 80° isotherm.

(2) Samples of Graphon were put in sealed tubes with outgassed water and held at predetermined temperatures for varying periods. The tubes were then opened *in vacuo* and the gases pumped off and analyzed by a micro method. For all temperatures throughout the range 25° to 150° reaction was found to occur, the rate being dependent on the temperature. In all cases the gases consisted of CO_2 and H_2. Presumably the reaction is

$$C + H_2O = CO_2 + H_2 + \text{C–O complex}$$

This indicates that part of the oxygen is retained as a C–O complex, which is known to adsorb water better than a clean carbon surface.

After making several preliminary measurements at 80°, the 80° and 28.6° isotherms of Fig. 3 were determined concurrently. The sequence was as follows. After an equilibrium pressure reading at 80° the sample bulb is removed and weighed. Next it is put in the 28.6° thermostat and the line filled with water vapor to the same relative pressure (allowance is made for the excess vapor in the dead space of the bulb in setting up the approximate line pressure). The stopcock leading from the bulb to line is then opened and time allowed to establish adsorption equilibrium. The final pressure is read, then the bulb is removed and reweighed. A correction is applied for the weight of unadsorbed vapor in the dead space at each temperature. Finally the sample is pumped down at room temperature and reweighed. The difference between weight with vapor and weight after pumping down gives the amount adsorbed plus amount in the dead space.

This procedure is open to some question because of possible adsorption–desorption changes when the temperature changes from 80° to room temperature, and then to 28.6°. It is however the best we could devise for the comparison at 80° and 28.6° since the nature of the surface is continually changing, particularly at 80°, because of reaction. This procedure does give a comparison for the two temperatures, under the same surface condition.

The small separation between the 80° and 28.6° isotherms in the region 0.8–0.95 p_0 may be real or may be due to some effect attendant upon the continuous alteration of the surface, which is constantly taking place when the sample is exposed to vapor. We cannot say then whether $E - E_L = 0$ or has a small negative value in the range 0.8–0.95 p_0. It is however established that the large negative value of $E - E_L$ which is indicated by comparison of the 80° isotherm with the original 28.6° isotherm is spurious; the isotherms are not for the same surface.

It should be noted that the amount of complex formed by the carbon–water reaction is small, even though it does have a large effect upon the isotherm. The sample bulb weights after pumping down did not show any large change from the original dry weight, even after several weeks contact with vapor.

The low temperature carbon–water reaction

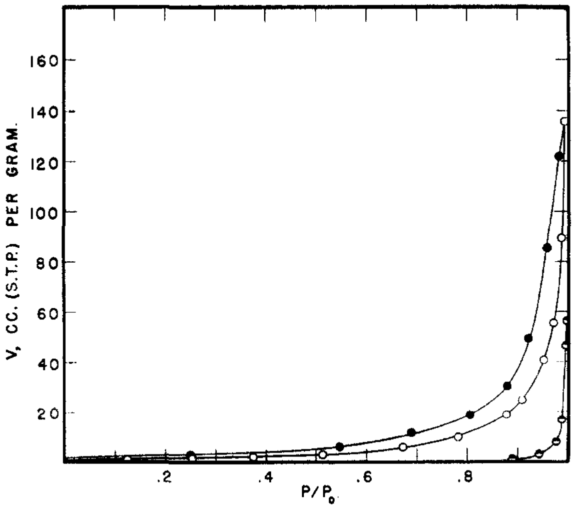

Fig. 4.—Effect of oxygen complex on water adsorption by Graphon, at 28.6°: ◓, before oxygen treatment; O, adsorption after treatment; ●, desorption after treatment.

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[18] J. W. McBain, J. L. Porter and R. F. Sessions, This Journal, 55, 2294 (1933).

provides an explanation for the frequently observed phenomenon that in some water isotherms the sample cannot be pumped down at room temperature to its original weight after desorption is completed. When the contact with water vapor is prolonged there is some reaction and oxygen is firmly held by the surface.

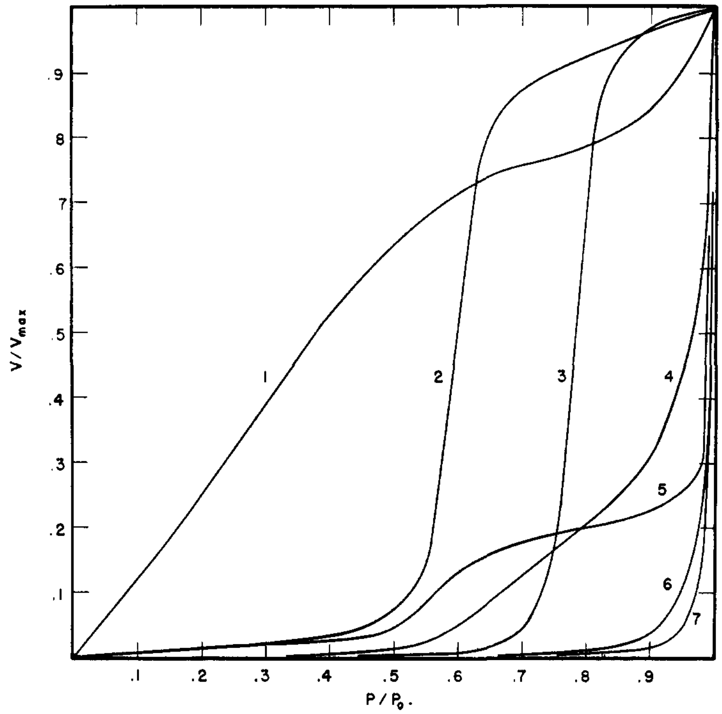

Fig. 5.—Water isotherms plotted as fraction of saturation: 1, S 400 H; 2, S 600 H; 3, S 84; 4, Carbolac I; 5, Spheron Grade 6; 6, NC-1; 7, Graphon.

Surface Complexes.—It has been previously shown by several workers[1] that when carbon is exposed to oxygen at elevated temperatures some of the oxygen is firmly held as a surface complex. Weller and Young[19] for example, find 3–18% oxygen on a charcoal after treating with oxygen at 400°. The C–O complex has been shown to have an effect on water adsorption. It is difficult to remove by pumping, except at high temperature.

The effect of oxygen complex on water absorption is shown in Fig. 4, which gives water isotherms for Graphon with and without oxygen. The sample was heated to 600° then poured in air from one beaker to another as it cooled. It was then sealed into an adsorption tube and outgassed by gentle flaming until a good vacuum was obtained. The water isotherm of the oxygen-treated sample shows much greater adsorption than that of the untreated Graphon, and there is pronounced desorption hysteresis, even though the sample is non-porous. Emmett and Anderson[14] have shown similar results for carbon blacks, before and after degassing at 1000°, which presumably removes the chemisorbed oxygen along with other volatile matter.

As normally manufactured, charcoals are cooled in air following steam activation. Presumably these charcoals will have a variable amount of oxygen complex, depending upon the availability of air as cooling occurs. It is possible, therefore, that many of the published water isotherms may be, to an undetermined extent, affected by the presence of an oxygen complex unless the sample is outgassed at high temperature or treated with hydrogen prior to use. On a charcoal the effect of oxygen complex on the water isotherm is noted chiefly by an enhancement of the low pressure adsorption; the adsorption after the steep rise begins is not greatly affected by the complex. Adsorption of carbophilic adsorbates is not appreciably altered by an oxygen complex at any relative pressure.

Effect of Capillaries on Water Adsorption.—Comparison of water isotherms for porous and non-porous carbon surfaces shows striking differences. Graphon has little adsorption of water below 0.95 p_0 and a relative pressure of 0.99 p_0 is required for adsorption of one statistical layer (computed on basis of 10 sq. Å. per water molecule). At saturation ($p/p_0 > 0.997$), Graphon holds only two statistical layers of water vapor, whereas it can hold in excess of 30 statistical layers of ethyl chloride. On the other hand, a charcoal will hold only slightly less liquid volume of water than of other vapors.

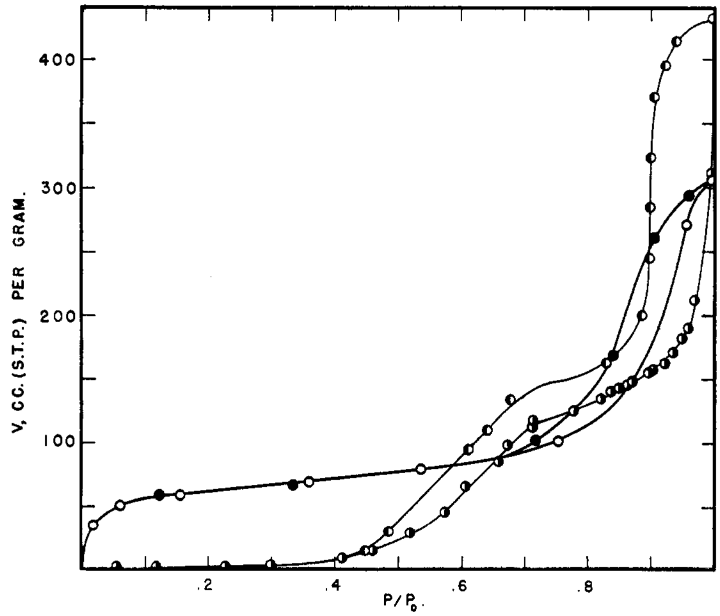

Fig. 6.—Isotherms for water at 28.6° and ethyl chloride at 0° on Darco G60: ◑, water adsorption; ◐, water desorption; ○, ethyl chloride adsorption; ●, ethyl chloride desorption.

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[19] S. Weller and T. F. Young, THIS JOURNAL, **70**, 4155 (1948).

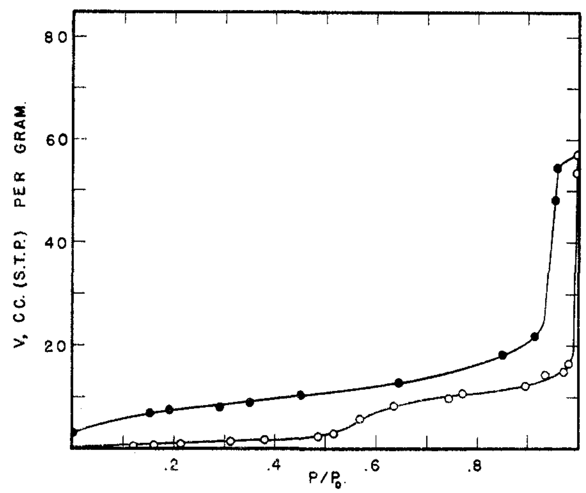

Fig. 7.—Water isotherms of Spheron Grade 6 at 28.6°: O, adsorption; ●, desorption.

Another effect as one passes from non-porous to porous surfaces is shown in Fig. 5, which gives isotherms for several carbon samples. To facilitate comparison these are plotted as fraction of saturation, V/V_s. The isotherm for the fine pore charcoal S 600 H shows a sharp rise starting at about 0.55 p_0. For S 84 with larger pores, the isotherm rises at 0.75 p_0. Graphon and NC-1 isotherms show practically no adsorption below 0.95 p_0.

On the basis of this comparison, we believe that the existence of a sharp rise below 0.9 p_0 in the water isotherm of a carbon sample provides indication for the presence of capillaries. Further, it is indicated that the smaller the capillary width, the lower the relative pressure at which the sharp rise begins.

If this interpretation is correct, the shape of a water isotherm for a clean carbon sample may be used to detect the presence of capillaries and the amount of adsorption at the nearly vertical portion of the isotherm permits one to compute the volume held in these capillaries.

The water isotherm for Darco G 60, Fig. 6, illustrates such a computation. An upturn begins at about 0.55 p_0 and at about 0.7 p_0 the isotherm flattens again. The adsorption in this region amounts to some 90 cc. of vapor (S.T.P.). If our interpretation is correct this indicates that there are present small capillaries which fill at 0.55–0.7 p_0. The liquid volume held in these capillaries is equivalent to 90 cc. of water vapor, or 4 millimoles. Assuming a density of one for the liquid water, this gives a liquid volume of 4 × 0.018 = 0.072 cc. in these capillaries.

It is of interest to compare the water isotherm for Darco G 60 with that for ethyl chloride, Fig. 6. At "point B" about 60 cc. (S.T.P.) of ethyl chloride is adsorbed. If we assume, as appears logical, that the capillaries which the water fills at 0.55–0.7 p_0 are very narrow, these capillaries may already be filled by ethyl chloride when the isotherm levels out at point B. (These capillaries might be but two or three molecular diameters in width.) To fill a capillary volume of 0.072 cc. requires about 1 millimole or 22.4 cc. (S.T.P.) of ethyl chloride vapor (assuming a density of 0.93 at 0° for liquid ethyl chloride). Therefore the free surface in capillaries not filled at point B is covered by 60 − 22 = 38 cc. (S.T.P.) of ethyl chloride vapor. As pressure is increased, the multilayer film of ethyl chloride now builds up on this free surface only, since the surface in the small capillaries has presumably disappeared with the filling of the small capillaries. The ethyl chloride isotherm shows that there are also still larger capillaries which are filled at high relative pressure and which appear to be too wide to be filled completely by water. The saturation adsorption, measured after allowing the sample bulb to equilibrate with bulk liquid for many hours, amounts to about 0.35 cc. per gram for water and 0.94 cc. per gram for ethyl chloride.

Capillaries in Carbon Blacks.—The line of reasoning of the last section may be extended to an interpretation of the water isotherms of carbon blacks. The water isotherm for Spheron 6, Fig. 7, shows an upturn between 0.55 and 0.7 p_0, which we interpret as indicating the presence of small capillaries which fill with water in this region, since Graphon has in the same region practically no adsorption. The nitrogen isotherm and the ethyl chloride isotherm both fail to show the presence of these capillaries. Presumably the pores are so narrow that the carbophylic adsorbates fill them in the low-relative pressure region at which the first layer is formed on the exposed surface. If so, the point B adsorption includes the amount of vapor held in these narrow capillaries as well as that held as a monolayer on the surface not within the capillaries.

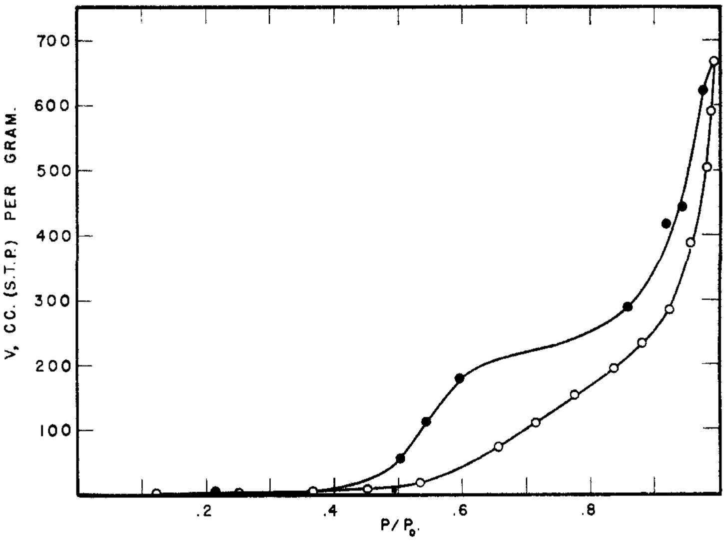

Fig. 8.—Water isotherms of Carbolac I at 28.6°: O, adsorption; ●, desorption.

Emmett and Anderson[14] have previously observed the same type of water isotherm for degassed Spheron 6 that we find, but their isotherm indicates about twice as much water adsorption as we find in the range 0.5 to 0.7 p_0. This is not disturbing, in view of the fact that their sample and ours were treated differently before the isotherm was determined. If we are correct in assuming that Spheron 6 particles have small cracks, the nature of the heat treatment will affect the porosity. After strong heating, in preparation of Graphon, all evidence of pores has disappeared.

For most of the Cabot carbon blacks that are thought to be essentially non-porous, the size of particles as computed from nitrogen areas is in good agreement with electron microscope values. Carbolac I is an exception. The electron-microscope arithmetic-mean diameter of the particles is 106 Å. The nitrogen area of about 1000 sq.m./g. gives a computed mean diameter of 26 Å. The discrepancy would correspond to a roughness factor of 4 for the nitrogen area.

The water isotherm for Carbolac I, Fig. 8, and the previously published water isotherm determined by Emmett and Anderson[14] both show the type of rise we have attributed to the effects of capillaries. Comparison of the Carbolac I isotherm with that for Spheron 6 shows however an important difference. The rise for both starts at about 0.55 p_0 but for Carbolac I there is no flattening at or about 0.7 p_0 as is the case for the Spheron isotherm. This suggests that the capillaries to which we ascribe the rise are wider in the Carbolac particles than in the Spheron particles, and that there is a greater range of capillary widths. If these capillaries are filled by nitrogen at point B they may account for the large roughness factor.

An alternative explanation might be made for the capillary-like nature of the water adsorption by Carbolac I. This is that the capillaries might not be within the rather small granules but that they might be in the spaces between the granules. The ultimate particles of Carbolac I are very small and it might be that they fit closely enough together that the voids between particles are sufficiently narrow to act as capillaries in which vapor may condense. There is some indication for such condensation of vapor. When the sample bulb is removed for weighing after equilibration at high relative pressure with any of the vapors we have studied, it has been noted that the particles are agglomerated and stick together as a solid ball. This must be due to a film of liquid between the particles which acts as a binder. As soon as the relative pressure is lowered this clumping disappears.

Desorption Hysteresis.—When water vapor is desorbed from a carbon surface there is always a pronounced hysteresis, regardless of whether the sample is porous or not. Some speculation regarding the possible source of hysteresis in absence of pores has been previously published.[9]

In addition to "reversible hysteresis" in which the isotherm loop closes at a relative pressure near 0.4 p_0 water desorption isotherms also sometimes fail to rejoin the adsorption branch, even at zero pressure. This is, we believe, due to chemisorption or reaction with water during the period in which the vapor is in contact with carbon. Such an effect seems to be more pronounced when one starts with a surface which has some oxygen complex than with an initially clean surface.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. LIII. Molecular Weight of Salts in Benzene by the Cryoscopic Method[1]

BY DAVID T. COPENHAFER[2] AND CHARLES A. KRAUS

The molecular weights of triisoamylammonium picrate, *n*-amyltri-*n*-butylammonium iodide, *n*-octadecyltri-*n*-butylammonium formate, tetraisoamylammonium thiocyanate and tetra-*n*-butylammonium thiocyanate have been determined in benzene up to the limit of their solubilities by a cryoscopic method. The molecular weights of equimolar mixtures of the last two salts have likewise been determined.

All these salts exhibit marked association in benzene solution, the degree of association being dependent on structural and constitutional factors. For the two thiocyanates and the iodide, the association number, *n* (ratio of observed molecular weight to formal weight) passes through a maximum at concentrations ranging between 0.12 and 0.28 molal; the association numbers, at the maximum, range between 21.9 and 31.9. The association number of tri-isoamylammonium picrate varies between 1.01 at 0.001 *m* and 1.58 at 0.1 *m*. Of the salts measured, octadecyltri-*n*-butylammonium formate exhibits the highest degree of association; at 0.001 *m*, $n = 10.7$; at 0.0033 *m*, $n = 21.5$.

The association number for the mixture of the two thiocyanates at a given total concentration is the mean of the value for the two components alone at the same concentration. The results of this investigation are discussed and correlated with the results of conductance measurements.

I. Introduction

Cryoscopic measurements by Kraus and Vingee[3] with solutions of salts in dioxane and by Batson[4] and Rothrock[5] with solutions of salts in benzene have shown that, in these solvents of low dielectric constant, association of ion pairs takes place to a measurable extent at concentrations as low as 0.001 *m*. At higher concentrations, the degree of association increases markedly, particularly with salts of large cations. However, these earlier measurements were not carried to concentrations above a few hundredths molal. It seemed of interest,

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(1) This paper is based on a portion of a thesis submitted by David T. Copenhafer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1942. Paper LII, THIS JOURNAL, **73**, 3293 (1951).

(2) University Fellow in Brown University, 1940–1941. Metcalf Fellow, 1941–1942.

(3) C. A. Kraus and R. A. Vingee, THIS JOURNAL, **56**, 511 (1934).

(4) F. M. Batson and C. A. Kraus, *ibid.*, **56**, 2017 (1934).

(5) D. A. Rothrock, Jr., and C. A. Kraus, *ibid.*, **59**, 1699 (1937).