in vacuum. Haber, and Böhm and Niclassen[16] could detect no crystalline structure in the freshly precipitated zirconium hydroxide nor in the hydroxide which had been precipitated and dried below 400°. No x-ray analyses of the aged sol have been reported, although Weiser[17] points out that aged sols usually assume micro-crystalline form while the corresponding hydrous oxides when first prepared are entirely amorphous.

The authors are indebted to Dr. C. Harvey Sorum and Dr. Fred Hazel for numerous suggestions during this investigation, and to Dr. Hazel also for valuable assistance in making the *P*H determinations.

Summary

1. Zirconium oxide hydrosols have been prepared and heated to temperatures up to 275°.

2. Measurements have been made on their relative viscosity, flocculation value, *P*H and intensity of scattered light.

3. High temperature was found to produce a decrease in viscosity, flocculation value and *P*H, and an increase in the intensity of scattered light.

4. The data presented indicate that the sols heated to higher temperatures are less hydrated than those heated to lower temperatures.

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[16] Haber, *Ber.*, **55**, 1717 (1922); Böhm and Niclassen, *Z. anorg. allgem. Chem.*, **132**, 1 (1924).

[17] Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., Inc., New York, 1926, p. 238.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Nature of the Sorption of Water by Charcoal

JAMES W. MCBAIN, J. L. PORTER AND R. F. SESSIONS

It is commonly supposed that water is not sorbed by charcoal but is taken up by capillary condensation of the liquid as such;[1] all ordinary estimates of the surface of charcoal are based upon this assumption. Our experiments appear to disprove this point of view. When activated sugar charcoal is exposed to water vapor, the charcoal undergoes linear expansion instead of the contraction that would be necessitated by the assumption of capillary columns with concave menisci. Part I of this communication describes experiments (by J. L. P.) on the expansion of charcoal caused by exposure to the vapors of water, benzene and heptane, respectively.

Part II describes isotherms for the sorption of water by charcoal. The sealed up sorption balance admits of far more rigorous evacuation than any hitherto employed. The result is that sorption of water vapor sets

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[1] For example, Lowry, THIS JOURNAL, **46**, 837 (1924); Cude and Hulett, *ibid.*, **42**, 391 (1920); Knudson, Dissertation, State University of Iowa (1924); Brown, *Phys. Rev.*, [2] **17**, 700 (1921); Lavine and Gauger, *Ind. Eng. Chem.*, **22**, 1226 (1930); Kreulen and Ongkiehong, *Brennstoff-Chem.*, **10**, 317 (1929).

in at relative humidity $p/p_s = 0.3$ and goes almost to completion at this pressure, the amount taken up being fully equal to that of any other liquid. The sorption of water is of a highly distinctive physical type occasioned by the development of mutual polarization of neighboring sorbed molecules. After eighteen months it is found that the charcoal has reacted chemically with the water. The "impurities" so introduced alter the sorption to higher relative humidities and to gradual instead of sudden taking up of water.

The conclusion is, therefore, that water sorbed by active charcoal exists as a continuous monomolecular film of liquid water extending throughout all the available structure of the charcoal as in typical cases of persorption. The specific heat of the sorbed water is in accordance with this interpretation.

Part I. The Expansion of Charcoal Caused by Sorption

The swelling of a non-rigid gel is a familiar occurrence, but the possibility of any effect on a rigid solid during sorption has been overlooked until recently. To test for it, Meehan[2] measured the expansion of a block of wood charcoal during sorption of carbon dioxide. It was thought desirable to extend the observations of Meehan to include the effect of vapors of organic liquids and to refine the method by using especially pure active charcoal and by employing more drastic evacuation of the charcoal, since sorption is greatly affected by impurities.

Activated sugar charcoal was made into coherent rods about 60 mm. long and 25 mm. in diameter by the following method. The powdered charcoal from pure sugar, carbonized at low temperature, was air-activated and then mixed with concentrated sugar solution to form a plastic mass which was compressed in a steel tube under high pressure, expelling most of the sirup, After drying, the charcoal was very gradually heated in a silica tube under low pressure to 1000° for three hours. After cooling, steam was passed through the tube as the temperature was raised to 1000° again for two hours.

The extensometer resembled that of Meehan and was mounted in a bell jar placed on a thick metal base as shown in Fig. 1. The ground joint A at the top provided connections B to a Cenco Hyper-Vac pump capable of reducing the pressure to a few microns of mercury in a few minutes in spite of the gas being evolved from the charcoal. Another connection C led to the reservoir of liquid D to be sorbed and a third E carried the wires leading to the electric heater. The vessel was made vacuum tight with a white wax.[3]

Since the charcoal was heated to above 600°, the surroundings remaining at room temperature, the extensometer was set on two glass plates F separated by microscope slides, and the charcoal and heater rested on a plate of fused silica G. A metal cap H placed on the top of the charcoal J made connection to the extensometer with a small piece of fused silica K. Finally, a metal rod L extended from the adjustable screw head of the extensometer out through a waxed joint M, allowing adjustments to be made during the experiment.

The apparatus was calibrated by observing the mirror with a scale and telescope

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[2] Meehan, *Proc. Roy. Soc.* (London), **A115**, 199 (1927).

[3] Vacuum wax obtained from Firma Liliendahl, Thüringen, Germany.

several meters away and noting the change in scale reading when the screw head of the extensometer was turned by a known amount. The thread gave 50 turns to the inch, and one-tenth of a division was a vertical movement of 0.0001 inch. Calibration was made for each measurement at the range in use. The charcoal was evacuated for a day or two at 10^{-4} cm. of mercury with the charcoal at a red heat. The rod expanded on heating and contracted by about 0.3% on cooling, being then distinctly shorter than before evacuation, and the pressure fell to 10^{-6} cm. of mercury.

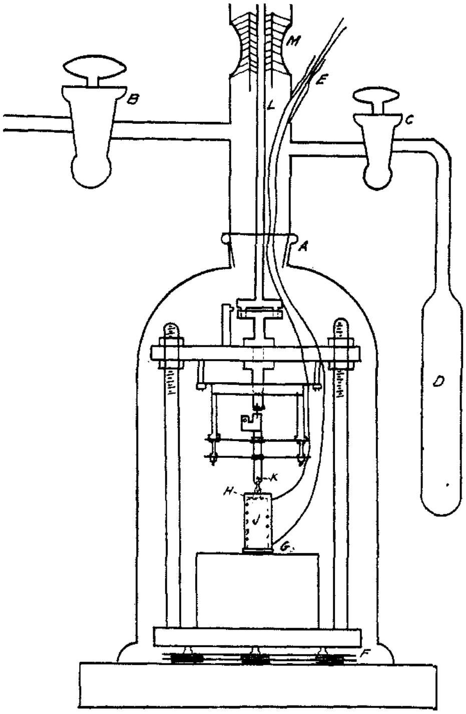

Fig. 1.—Extensometer in evacuable vessel with arrangement for heating the charcoal.

Vapor was admitted through a mercury-sealed stopcock from the reservoir D containing a liquid at the desired temperature and jacketed with a Dewar flask. Frequent readings were taken until constancy was attained. The movement was rapid during the first few minutes but was not completed for many days. The initial rate was greatest when the charcoal was most completely evacuated. The use of a fairly large dense rod necessarily interfered with the usually rapid attainment of sorption equilibrium. For some experiments a box was built around the vessel with an electric heater and fan to form a thermostat which could be regulated from 25 to 60°.

With benzene the following results were obtained upon exposure of the charcoal at 20° to the vapor of liquid benzene maintained at 0 and at 20° successively. The total expansion with the benzene at 0° and hence with a relative pressure of the benzene vapor p/p_s = 0.35 was 0.124 mm. or 0.191% expansion in length of the charcoal rod. Since the rod was homogeneous, a similar linear expansion must have occurred in each direction. The total linear expansion for p/p_s = 1 was 0.179 mm. or 0.274%. When the benzene was at −78° and the charcoal at room temperature, no expansion was observed.

With heptane at 28° and charcoal at 55, 45 and 38° and with both at 27° the following linear expansions were observed.

p/p_s	0.30	0.46	0.61	1
Linear expansion, mm.	0.095	0.101	0.148	0.165
Linear expansion, %	0.175	0.187	0.273	0.306

With water, both water and charcoal being at 27°, the expansion at twenty-eight hours was twice that at six hours and amounted to 0.083 mm. or 0.13% linear expansion for p/p_s = 1.

With the charcoal at various temperatures, t, the final linear expansion with water vapor was as follows

t	61	41	38	37	31	30	28.6	28.5	27
p/p_s	0.21	0.51	0.60	0.64	0.89	0.94	0.97	1	1
Exp., %	0.02	0.04	0.06	0.07	0.08	0.09	0.11	0.13	0.13

Discussion.—Expansion of the solid would appear to be a necessary accompaniment of sorption.[4] This is reflected in the substantial expansion of charcoal when exposed even to low relative pressures of the organic vapors, for these are largely sorbed at low pressures.[5] Most of the expansion with water vapor takes place at higher relative pressures as would be expected from the form of the isotherms shown below in Part II, Fig. 2. This accounts for the curious fact that with the water reservoir at room temperature the charcoal contracts when heated to a few degrees above room temperature and expands again when cooled. The expansion caused by sorption is much greater than that caused by a few degrees change in temperature, and the sorption of water is greatly affected by such a change while the sorption and expansion with heptane is not.

Bangham[6] ascribed the expansion of his willow charcoal on sorption of gases to the action of the sorbed molecules being a two-dimensional gas acting as wedges to force the charcoal particles apart. He observed a time effect in that after a period the expansion was less, as if the sorbed molecules had forced the grains apart to enter the inner recesses of the solid, and then on equilibrium the tension was relaxed. We found no such relaxation, and at saturation it hardly seems probable. The total final volume must be greater if the solid is made up of small particles which may take up a layer of sorbed molecules. A solid piece of active charcoal formed from the charring of an organic substance, like a scrap heap of carbon chains and broken space lattices, is not in a state of internal equilibrium as is a crystal. The solid must be in a state of tension, and as the unsatisfied forces at the surface and in the irregular interstices act on the sorbed molecules there must be a shift in this internal tension which allows the solid to expand. The exposed atomic groups of the charcoal may also be distorted by the sorbed molecules.

Evans[7] cites Bangham's observation on the slight decrease of expansion with time as evidence for a change in type of sorption binding from one in which the molecules may move on the surface and force apart the grains to one in which the molecules are more firmly held. Our observations

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(4) For a connected account with numerous references, see J. W. McBain, "The Sorption of Gases and Vapours by Solids," Chapter XIII, pp. 390–399, also p. 356 (George Routledge and Sons, Ltd., London, 1932).

(5) McBain, Jackman, Bakr and Smith, *J. Phys. Chem.*, **34**, 1439 (1930); McBain, Lucas and Chapman, THIS JOURNAL, **52**, 2668 (1930); McBain and Sessions, unpublished.

(6) Bangham and Fakhoury, *Proc. Roy. Soc.*, (London), **A130**, 81 (1930); *J. Chem. Soc.*, 1324 (1931).

(7) Evans, *Trans. Faraday Soc.*, **28**, 440 (1932).

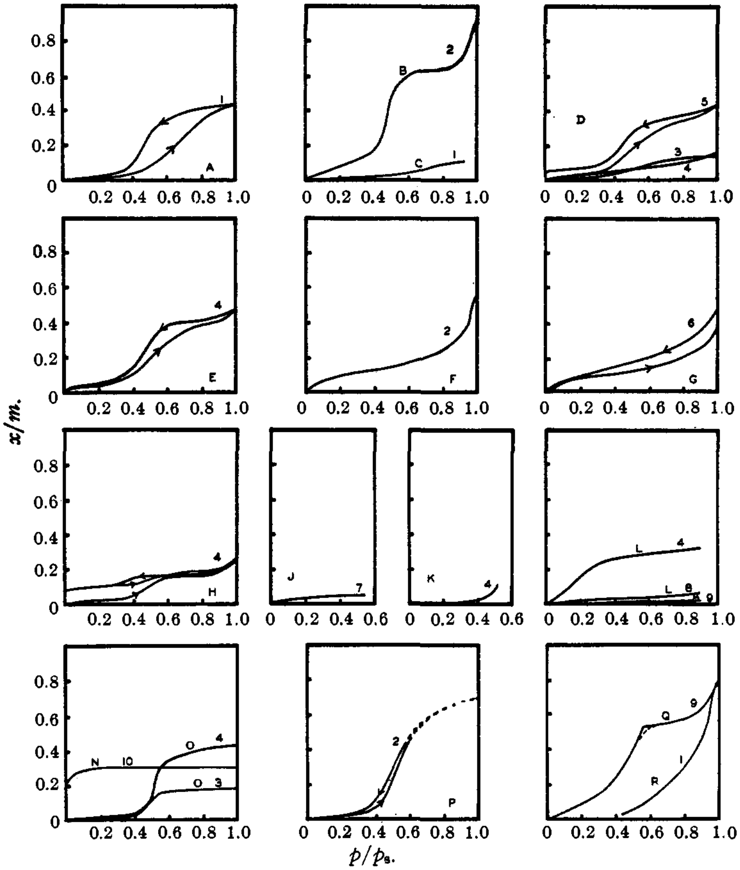

Fig. 2.—Collection of existing isotherms[1] of the sorption of water by charcoal.[2]

[1] (A) Berl and Andress, *Z. angew. Chem.*, **34,** 369 (1921); (B) Katz, *Proc. Acad. Sci. Amsterdam*, **26,** 548 (1923); (C) Bangham and Fakhoury, *J. Chem. Soc.*, 1324 (1931); (D) Rakovskii, *J. Russ. Phys.-Chem. Soc.*, **49,** 371 (1917); (E) Allmand, Hand, Manning, and Shiels, *J. Phys. Chem.*, **33,** 1686 (1929); (F) Hällström, Dissertation, Helsingfors (1920); (G) Lavine and Gauger, *Ind. Eng. Chem.*, **22,** 1229 (1930); (H) Bachmann, *Z. anorg. allgem. Chem.*, **100,** 34 (1917); (J) Schmidt and Hinteler, *Z. physik. Chem.*, **91,** 119 (1916); (K) Knudson, Dissertation, State University of Iowa (1924); (L) Wilson and Fuwa, *Ind. Eng. Chem.*, **14,** 917 (1922); (M) Selvig and Kaplan, *Ind. Eng. Chem.*, **12,** 783 (1920); (N) Woodhouse (quoted by Coolidge, THIS JOURNAL, **49,** 712 (1927)); (O) Coolidge, *ibid.*, **49,** 708 (1927); (P) Gustaver, *Kolloidchem. Beihefte*, **15,** 251 (1921); (Q) Lowry, THIS JOURNAL, **46,** 837 (1924); (R) Lowry and Hulett, *ibid.*, **42,** 1393 (1920).

[2] (1) Wood charcoal; (2) animal charcoal; (3) sugar charcoal; (4) coconut charcoal; (5) blood charcoal; (6) lignite; (7) bone charcoal; (8) carbon black (also lampblack); (9) coke; (10) chabasite.

and the fact that Bangham's charcoal was not adequately evacuated and air thoroughly excluded during the course of his experiment throw serious doubt on the evidence for this relaxation effect.

The fact that charcoal is distended through sorption of water vapor is irreconcilable with the hypothesis that the water merely condenses as bulk liquid in the pores owing to capillary condensation with concave menisci.[8] It is a proof that there is specific interaction between water and charcoal and that the water is adsorbed, or rather persorbed in the charcoal.

Density Measurements.—As is well known, the density of a given specimen of charcoal determined by the displacement of a wetting liquid depends greatly upon the liquid used. For example, one of us (J. L. P.) determined the density of the air-activated sugar charcoal "Air and Vacuum B,"[9] using the technique of Cude and Hulett.[10] The charcoal was evacuated at 500° at 10^{-5} cm. of mercury for two days. A pressure of 300 atmospheres was employed to eliminate "drift." The density thus determined was 1.694 as measured in benzene, 1.82 in ether and 1.546 in heptane.

Interpretation of these data in accordance with the compression theory of Williams, Briggs, Harkins and Polanyi, who assume that the charcoal really displaces equal volumes of all the liquids and, therefore, compute the compression which would be necessary in the neighborhood of the charcoal to equalize the volumes of the different weights actually displaced, would force a revision of the postulated true density far below the 1.45 of Williams[11] and Polanyi with a corresponding increase in the postulated pressure and, therefore, would cause their results to diverge again. The interpretation of Howard and Hulett,[12] based directly upon the densities approaching graphite which they obtained with the non-sorbed gas of minute molecular size, helium, is much more convincing. According to this, if the true density be 2.25, the value 1.7 obtained with benzene would indicate that in each gram of charcoal there is a free space equal to 0.144 cc. or 32% of the volume occupied by the carbon structure itself which is inaccessible to the disk-like molecules of benzene which are 5 Å. in diameter.

However, it seems very probable that the sorbed liquid is actually

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(8) For example, McGavack, Jr., and Patrick [THIS JOURNAL, **42**, 946 (1920)] estimate the negative hydrostatic pressure, or tension, for liquid condensed in the pores, considered to exist in their silica gel, as 500 atmospheres in accordance with the classical laws of capillarity.

(9) McBain, Lucas and Chapman, THIS JOURNAL, **52**, 2668 (1930); McBain, Jackman, Bakr and Smith, *J. Phys. Chem.*, **34**, 1439 (1930).

(10) Cude and Hulett, THIS JOURNAL, **42**, 391 (1920).

(11) Williams [*Proc. Roy. Soc.* (London), **A98**, 223 (1920)] observed 2.17 with chloroform and 1.96 with water, and in other experiments found that one gram of a sample of charcoal exposed to saturated vapor took up 0.85 cc. of chloroform and 0.75 cc. of water. He, therefore, deduced 1.45 as a correct result, necessitating 11,000 atmospheres of sorption pressure. However, the basis of Williams' calculation (0.85/0.75) is fortuitous, since other investigators have obtained various ratios between water and organic liquids, 5/1 being obtained, for example, by J. Driver and J. B. Firth with similar charcoal [*J. Chem. Soc.*, **119**, 1126 (1921)].

(12) Howard and Hulett, *J. Phys. Chem.*, **28**, 1082 (1924).

denser[13] than ordinary liquid in bulk and that, therefore, both this decrease in volume and comparative inaccessibility of micropores play a part in producing the low densities obtained by Archimedes' method.

Part II. The Distinctive Behavior of Water on Charcoal

We are indebted to Miss Margaret McDowell for preparing Fig. 2, which comprises all the isotherms that have been obtained by previous authors for the sorption of water by charcoal. They are plotted upon identical scales for ready comparison and they exhibit an extraordinary variance, part of which may be interpreted by comparison with our own results. High initial irreversible sorption may commonly be ascribed to solid impurity such as CaO. A gradual slope where the main sorption sets in and a displacement of the curve toward high relative pressures is due to impurities of a gaseous nature; low absolute values are due to inactivity of the charcoal, etc.

Coolidge's diagram includes for contrast and comparison the isotherm which he quotes from the Harvard laboratory for the sorption of water by chabasite. It serves to illustrate the form that isotherms for organic vapors and charcoal assume with drastic evacuation in a sealed up McBain–Bakr sorption balance, showing that sorption goes largely to completion at low relative pressures. In complete contrast to this is the position and form of the isotherm now obtained by one of us (R. F. S.), using unusually rigorous evacuation, Figs. 3 and 4.

Special care was taken to eliminate gas from the water used. The charcoal was Smith's air-activated sugar charcoal, "C,"[14] which is a highly active charcoal, measuring 80.6.[15] For Tube 2 (Fig. 3) it was evacuated for four hours at 412° and 10^{-5} mm., exposed twelve hours to pure water vapor, evacuated for one hundred and two hours at 412° and 10^{-5} mm. and then for one hour at 1010° and 10^{-5} mm. All the readings were taken on the sixteenth and seventeenth days, sorption and desorption being interspersed irregularly without noticeable hysteresis. For Tube 3 (Fig. 4) evacuation was four hours at 550° and 10^{-5} mm., exposure to water vapor twelve hours at room temperature, evacuation for one hundred hours at 550° and 10^{-5} mm. and finally one hour at 1010° and 10^{-5} mm. Sorption was measured up to $p/p_s = 0.28$ on the first and second days and for higher values on the seventh to twelfth days; desorption on the eleventh and twelfth days.

Nearly the whole of the water sorbed is taken up at a relative pressure of

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(13) It has been shown by E. Filby and O. Maass [*Can. J. Research*, **7**, 162 (1932)] for cellulose and by Ewing and Spurway [THIS JOURNAL, **52**, 4635 (1930)] for silica that the first portion of water sorbed (up to $x/m = 0.04$) has a density greater than that of liquid water.

(14) McBain, Lucas and Chapman, THIS JOURNAL, **52**, 2668 (1930); McBain, Jackman, Bakr and Smith, *J. Phys. Chem.*, **34**, 1439 (1930); McBain and Britton, THIS JOURNAL, **52**, 2198 (1930).

(15) One gram of 200-mesh charcoal sorbs in three minutes from 50 cc. of a 0.2 *N* aqueous solution of iodine in 0.27 *N* potassium iodide 80.6%; method of Chaney, Ray and St. John, *Ind. Eng. Chem.*, **15**, 1244 (1923).

0.3, where the sorption, x/m, rises from almost negligible values to nearly 40% of the weight of the charcoal. At the low relative humidity, 0.2, x/m was only 2.5 and 1%, respectively. The final values of x/m for water exceed those for organic solvents,[16] probably on account of the small size of water molecules. This is probably the more ideal form of isotherm for water with charcoal, just as the almost rectangular isotherm, with sorption largely taking place at very low relative pressures, is ideal for organic solvents on charcoal or for water or methyl alcohol on chabasite. The various forms of isotherm quoted in Fig. 2 are probably due to impurity.

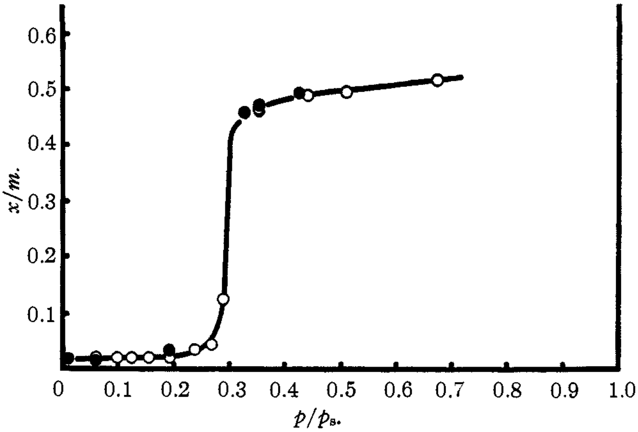

Fig. 3.—Isotherm for water with very active sugar charcoal at 120° after exceptional evacuation (Tube 2). Grams of water sorbed per gram of charcoal, x/m, are plotted against relative humidity, p/p_s. ○, sorption; ●, desorption.

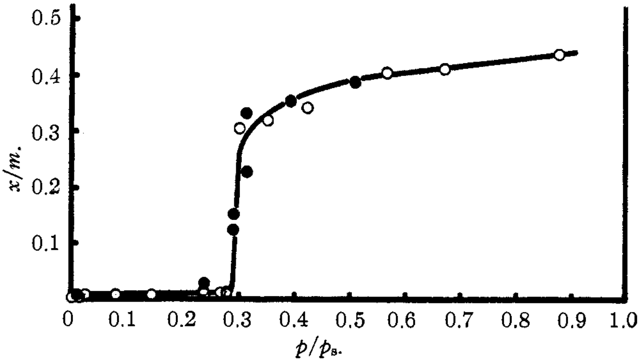

Fig. 4.—Isotherm for water with very active sugar charcoal at 120° after exceptional evacuation (Tube 3). ○, sorption; ●, desorption.

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[16] McBain, Lucas and Chapman, THIS JOURNAL, **52**, 2668 (1930); McBain, Jackman, Bakr and Smith, *J. Phys. Chem.*, **34**, 1439 (1930); McBain and Sessions, unpublished.

The hypothesis of capillary condensation would necessitate the assumption that the pores in the charcoal were all of uniform diameter, that is, equivalent to one long cylinder. It would leave unexplained the characteristic form as well as the position of the isotherms for organic vapors whose final x/m values are less, for it would assume that these substances which wet charcoal do not condense, whereas water which wets with difficulty would be condensed, filling a larger volume, the pores being much coarser than molecular dimensions. We reject the hypothesis of capillary condensation and assume adsorption or, rather, persorption in both cases. Still less can the classical compressed film theory reconcile the different behaviors of benzene and water on charcoal, the sorption of organic solvents being practically complete at a relative pressure of 0.1, whereas that of water is scarcely begun.

Neglecting a slight initial sorption, the question immediately arises as to why water is not sorbed before the relative pressure attains a definite, fairly large value. The only answer is in terms of Langmuir's theory. A molecule of water vapor striking the charcoal surface will evaporate after a very brief interval unless in the meanwhile other molecules have arrived on the adjacent surface. They are then held by mutual polarization[17] and the polarization of the underlying surface which they may affect. The latter polarization will, of course, disappear almost immediately after evaporation of the water. Sorption will not be complete; that is, it will increase with further increase of relative pressure because in accordance with the Langmuir theory some spots must be left vacant by evaporation at all pressures below saturation.

Specific heat determinations carried out by one of us (J. L. P.) in collaboration with Dr. S. B. Thomas show that at room temperature the specific heat of water sorbed in activated sugar charcoal is nearly that of liquid water and is, therefore, widely different from that of ice or water of crystallization or other constrained positions of water molecules.[18] It may be pointed out that there is an obvious analogy between the form of the water isotherm and the imperfect gas condensing to liquid, although the present case would be two-dimensional. It is well known[19] that the heat of sorption of water is nearly equal to the latent heat of condensation of water vapor to liquid water.

Interaction upon Long Standing.—This very active, exceptionally evacuated charcoal reacts with water or water vapor in the course of time. This was shown by Dr. S. B. Thomas, who demonstrated the evolution of hydrogen when the specific heat determinations were much prolonged,

(17) For references see J. W. McBain, "The Sorption of Gases and Vapours by Solids," p. 525.

(18) H. Ulich, *Z. Elektrochem.*, **36**, 503 (1930).

(19) Coolidge, THIS JOURNAL, **46**, 625 (1924); Lavine and Gauger, *Ind. Eng. Chem.*, **22**, 1226 (1930); Allmand, Hand, Manning and Shiels, *J. Phys. Chem.*, **33**, 1684 (1929). It would be of interest to know whether the changed form of isotherm observed by Coolidge at 218° is affected by interaction between water and his active charcoal.

and by one of us (J. L. P.), who redetermined the sorption isotherms of Figs. 3 and 4 after they had stood (still sealed) for fifteen months at room temperature. Tube 2 now assumes the form and position shown in Fig. 5.[20] When the tube was surrounded by liquid air, an electric discharge could be freely passed, giving the characteristic blue color of hydrogen. Isotherms for organic substances show no change even when the system has been standing for many years as will be shown in another communication.[21]

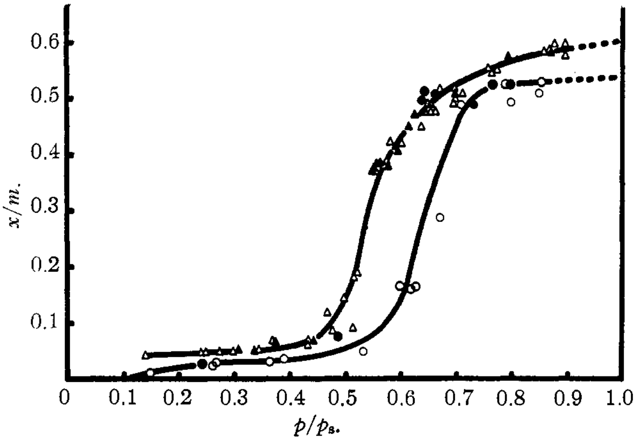

Fig. 5.—The 120° isotherm in Fig. 3 (Tube 2) redetermined at 60 and 120° after the water and charcoal had interacted during fifteen months and the water had to compete with the products. ○, 120°, sorption; ●, 120°, desorption; △, 60°, sorption; ▲, 60°, desorption.

It will be noted from Fig. 5 that the heat of wetting of this charcoal must be positive in accordance with all direct measurements although not with the conclusions of Coolidge for the initial portions of the isotherms nor of Keyes and Marshall for the initial heat of sorption at 0°.[22]

Summary

Upon the basis of measurements of the expansion of charcoal when exposed to water vapor and of the highly distinctive isotherms obtained with rigorously evacuated charcoal, it is concluded that neither the hypothesis of capillary condensation nor that of high compression is applicable, but that water is adsorbed or persorbed as a two-dimensional liquid film permeating the accessible structure of the charcoal. The results are

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(20) Tube 3 gave an isotherm even more displaced and sloping than that of Tube 2 at 120°, passing almost linearly from the value of $x/m = 0.03$ for $p/p_s = 0.5$ to 0.35 for $p/p_s = 0.83$.

(21) McBain and Sessions, unpublished.

(22) For references see J. W. McBain, "The Sorption of Gases and Vapours by Solids," pp. 147, 415, 419, 423, 425.

in accordance with observations on density and on the specific heat of the sorbed water. Data for other liquids are adduced for comparison.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Action of Radon on Some Unsaturated Hydrocarbons. III. Vinylacetylene and Butadiene

BY G. B. HEISIG

The polymerization of acetylene by radon involves an abnormally large number of molecules reacting per ion pair formed, compared to the number of molecules of other unsaturated hydrocarbons condensing per ion pair formed ($-M/N$). An examination shows that the ratio of hydrogen and methane formed to the decrease of pressure of the hydrocarbon, $\Delta(H_2 + CH_4)/-\Delta HC$, is lowest for acetylene. Ethylene, on the other hand, has a relatively low value of the $-M/N$ and a comparatively high value for the $\Delta(H_2 + CH_4)/-\Delta HC$. The effect of alpha particles on a molecule containing both a double and a triple bond is, therefore, of interest. Both vinylacetylene ($H_2C{=}CHC{\equiv}CH$) and butadiene ($H_2C{=}CH{-}CH{=}CH_2$) are known to polymerize readily when heated,[1] and since therefore they might be expected to act readily under the influence of alpha particles, they were selected for this work.

The procedure and methods of calculation are similar to those used in a previous paper.[2]

The results of this investigation are summarized in Table I.

TABLE I

	P drop of HC, mm.	% of P drop used in calcn.	$\frac{\Delta(H_2 + CH_4) \times 100}{-\Delta HC}$	$-M/N$	Product
Vinylacetylene	302.8	100.00	2.4	10.8	White solid—yellow to orange
Butadiene I	507.0	79.9	3.5	9.1	Lt. colored, liquid becoming more viscous
Butadiene II	413.4	88.6	3.1	8.9	

Nieuwland, Calcott, Downing and Carter[3] state that under pressure with or without the usual polymerization catalysts, vinylacetylene is readily polymerized by heat to form viscous drying oils and finally hard resinous solids. In the present work, however, no liquid apparently was formed. The first product noted in the polymerization by alpha particles was a

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(1) Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, **53**, 4197–4202 (1931); Lebedev and Skrawonskaja, *Chem. Centr.*, I, 1440 (1912); *J. Russ. Phys.-Chem Soc..*, **43**, 1124–31 (1911); Lebedev, *Chem. Abstracts*, **9**, 799 (1915); *J. Russ. Phys.-Chem. Soc.*, **45**, 1373–88 (1913).

(2) Heisig, THIS JOURNAL, **53**, 3245–3263 (1931).

(3) Ref. 1, p. 4200.