[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Pore Structure in Activated Charcoal. II. Determination of Macro Pore Size Distribution

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Theoretically it should be possible from water adsorption data to calculate with the Kelvin equation the pore size distribution of macro pores. If given enough time water should fill all the pore space at a relative vapor pressure very close to unity, but, as is the case with most activated charcoals, the relative vapor pressure is already above 0.99 when only a little over one-half of the pore volume is filled. The remainder of the pore space is in pores having diameters corresponding to relative vapor pressures above 0.99. To determine the latter with the necessary accuracy would be extremely difficult.

A more rapid, convenient, and accurate way to determine the size distribution in the large pore range is by the mercury penetration technique suggested by Washburn[2] and used by Ritter and Drake.[3] This technique was first applied to the determination of diameters of large pores in charcoals by Emmett[4] and his co-workers. By assuming the validity of the capillary rise equation or, as is the case with mercury, the capillary depression equation, it is possible to calculate pore diameters, D, from the pressures necessary to force mercury into the pores.

$$gdh\ \pi \frac{D^2}{4} = \pi D\sigma \cos \theta$$

$$D = \frac{4\ \sigma \cos \theta}{gdh} = \frac{4\ \sigma \cos \sigma}{P}$$

Here σ is the surface tension of mercury, g the gravitational force per gram, d the density, h the height of the mercury column, and θ the contact angle of the mercury with the capillary wall. The product gdh has the dimensions of force per sq. cm. and may therefore be designated as pressure, P.

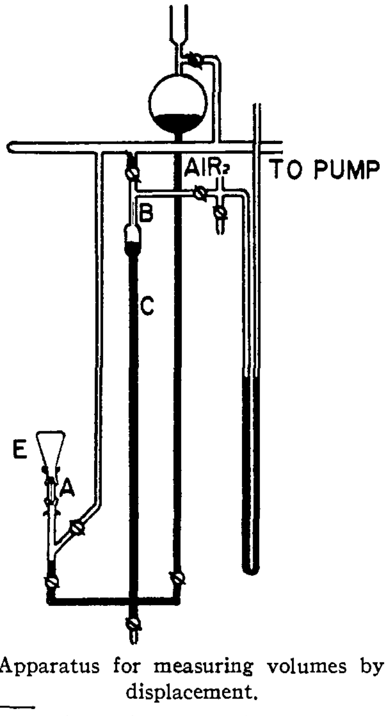

Fig. 1.—Apparatus for measuring volumes by mercury displacement.

Experimental

Materials.—The charcoals investigated were N-291-AY-1, Darco G-60 and PN-439, the same ones for which micro pore size distributions were determined.[5]

Determination of Total Pore Volume.—Measurements of the macro pores by mercury penetration begins with the largest pores and progresses toward the smaller ones, hence it is necessary to know the total pore volume to locate the starting point of the distribution curve. The total pore volume is the difference in volume of the charcoal by helium displacement and by mercury displacement.

Mercury Displacement Measurements.—If charcoal is placed in a flask of known volume, the flask evacuated, and then filled with mercury at about one atmosphere pressure, the mercury, due to its large surface tension, will not penetrate into the pore structure but will only fill the space between the particles. This volume of mercury when subtracted from the volume of the empty flask gives the volume of charcoal by mercury displacement.

In Fig. 1 is a diagram of the apparatus used for making these measurements. A weighed amount of charcoal is placed in calibrated flask E and the system evacuated. The mercury levels are adjusted so that the lower level is at a mark on capillary A and the upper one at a mark on capillary B. The mercury is allowed to rise into flask E and its pressure is adjusted to 900 mm. by means of compressed air. The volume of mercury entering E is measured by the calibrated buret C.

This pressure was adopted as the standard pressure in these measurements because it was found from studies with non-porous solids, presented graphically in Fig. 2, that the particles are not completely outlined by mercury at lower pressures. Curve 2 is for 6 to 8 mesh glass beads which, due to their smooth surfaces, are already well outlined by the mercury at 300 mm. pressure. Curves 4 and 5 are for 20 to 30 mesh and 30 to 40 mesh non-porous crushed coal. The volumes for these two samples approach a constant value at about 700 to 900 mm., indicating that a pressure of at least 700 mm. is necessary to force mercury into the rough surface of these particles. These two curves should be compared with the two similar curves 1 and 3 which are for the 12 to 30 mesh activated charcoals. Curves 1 and 3 level off at pressures between 800 to 1100 mm., indicating that these pressures are sufficient to cause the mercury to completely outline the particles but insufficient to cause penetration into the pores.

Mercury Penetration Measurements.—The apparatus (Fig. 3) for making these measurements is a modification

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[1] From a thesis submitted to the Graduate School of the University of Rochester in partial fulfillment of the requirements of the degree Doctor of Philosophy.

[2] Washburn, *Proc. Nat. Acad. Sci.*, **7**, 115 (1921); Washburn and Bunting, *J. Am. Ceramic Soc.*, **5**, 48 (1922).

[3] Ritter and Drake, *Ind. Eng. Chem., Anal. Ed.*, **17**, 782, 787 (1945).

[4] Emmett, Holmes and Mace, OSRD Formal Report, 1943.

[5] Juhola and Wiig, THIS JOURNAL, **71**, 2069 (1949).

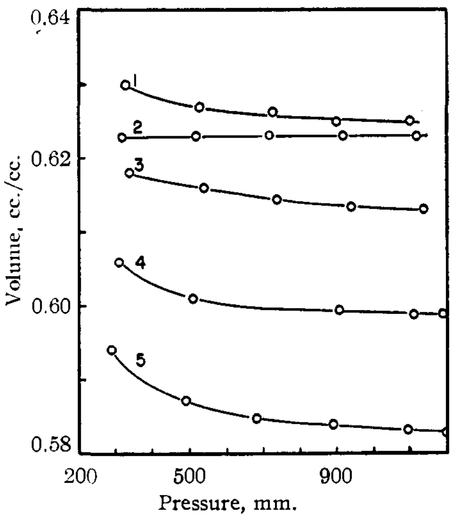

Fig. 2.—Effect of pressure on volumes by mercury displacement: 1 and 3, 12 to 30 mesh activated charcoals; 2, 6 to 8 mesh glass beads; 4 and 5, 20 to 30 and 30 to 40 mesh non-porous crushed coal,

of that used by Ritter and Drake[3] and Emmett.[4] A weighed quantity (about 2 cc.) of charcoal is placed in glass tube T and a small wad of glass wool placed over the charcoal to prevent it from floating on the mercury which is run in later. The calibrated glass capillary tube C, containing a platinum resistance wire, is attached to T. The tube assembly is evacuated and mercury run in until the level is near the top of the capillary. The mercury filled tube assembly is then raised into the steel tube L and the bottom cap screwed up tightly. By means of nitrogen from cylinder N the pressure on the mercury may be increased, usually in 20 to 300 lb. per sq. in. intervals, as measured on gage G. S contains two fine capillaries or orifices and serves as a protective device for the gage. The amount of mercury penetration into the charcoal is measured by the decrease in the mercury level in C. The spring and weight W on the lower end of the spring, the platinum resistance wire, the mercury in C and T, the tungsten wire sealed into the bottom of T, and the insulated bolt through the bottom cap make up part of an electrical circuit. By measuring the change in potential drop through this circuit it is possible to measure the change in mercury level in C since the resistances of the platinum wire and the mercury surrounding the wire are greatly different.

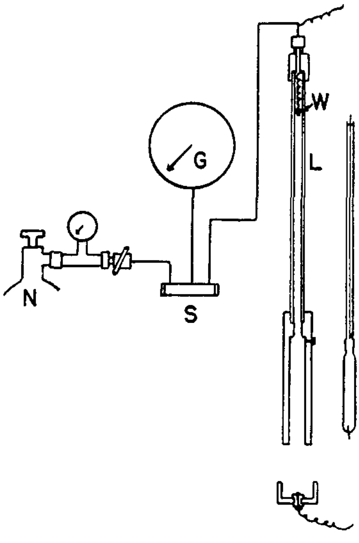

Fig. 3.—Apparatus for measuring pore diameters by mercury penetration.

Results and Discussion

In Fig. 4 are the macro pore size distribution curves by the mercury penetration technique, using cos θ equal to unity in the capillary rise equation, for the three charcoals studied. The largest diameter, 160,0000 Å., corresponds to a pressure of 900 mm., the standard pressure in the mercury displacement measurement. The volume of pores less than 160,000 Å. is therefore equal to the total pore volume. As the pressure is increased the mercury penetrates into smaller pores and at 2,400 lb. per sq. inch, the maximum obtainable from the nitrogen cylinder, the pore penetrated is 1,200 Å. in diameter.

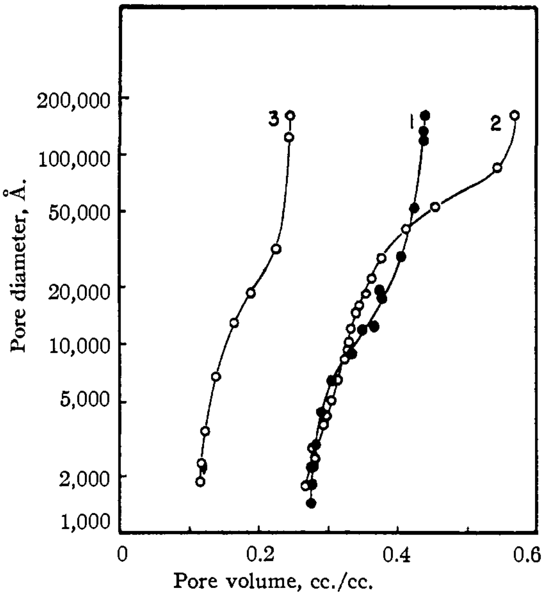

Fig. 4.—Pore size distribution in the macro pore range determined by the mercury penetration technique: 1-N-291-AY-1; 2 Darco G-60; 3-PN-439.

Attempts have been made to test the validity of this method of measuring pore diameters. In one experiment the pressure was measured at which mercury would just penetrate a hole, 3.81×10^6 Å. in diameter, bored into a block of briquetted coconut charcoal. The calculated diameter agreed within experimental error with the true diameter, but as these diameters are of a different order of magnitude than those believed to exist in charcoals, the agreement cannot be accepted as proof but only as an indication that the capillary rise equation may apply to smaller pores.

In another experiment to test the validity of the method mercury was forced at known pressures into a fine calibrated glass capillary. The calibration was done by measuring the length of a

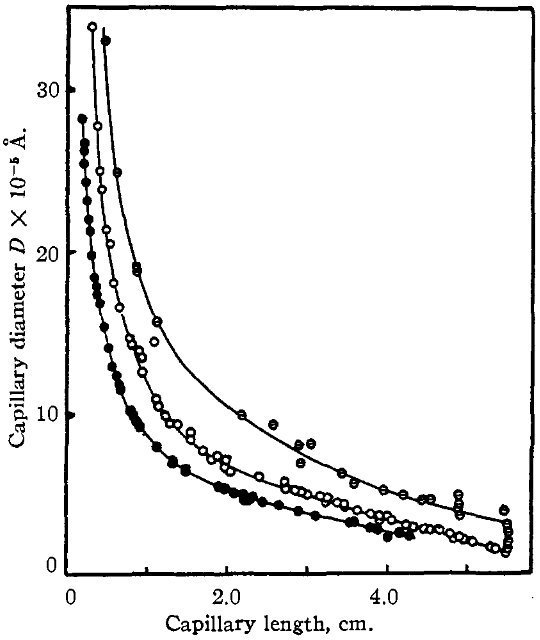

Fig. 5.—Diameter glass capillary determined by mercury penetration technique: ●, calibration, O, calc., increasing press.; ⊖, calc., decreasing press.

weighed drop of mercury at different positions in the capillary. In Fig. 5 are presented the calibration curve and the calculated capillary diameter curves when the mercury pressure was increased and again when decreased. The similarity between the curves indicates that the mercury penetration methods does measure diameters down to 100,000 Å., the upper limit of pore diameters in charcoal. However, the magnitude of the calibration curve is lower than the curve calculated for increasing pressures, the correction factor being 0.78. This difference in diameters may be attributed to cos θ being equal to 0.78 instead of unity, the value used in the calculation. A value of cos $\theta = 0.78$ corresponds to a contact angle of 140°, the same angle found by Ritter and Drake[3] for mercury on a variety of solids. Although the present results were obtained for a glass system they may apply to charcoal as well, since the behavior of mercury toward these two materials is very similar.

For some pore structure studies an approximate value for cos θ is satisfactory since the pore size distribution of the large pores need not be known with any great degree of accuracy. This is true of pore structure studies in relation to physical adsorption of gases in a monolayer or multilayers since the surface area associated with large pores is very small, being less than one square meter as compared to 400–500 sq. meters per cc. ($\sim$1500 sq. meters per g.) for the total surface area of a great many charcoals. In the study of the effect of pore structure on the efficiency of a charcoal as a catalyst carrier and in studying adsorption at relative pressures close to one, it may be desirable to know the pore size distribution of these large pores with a high degree of accuracy.

When the mercury penetration technique was first applied to the study of pore structure it was suspected that at the higher pressures the mercury might crush some of the pore structure. This possible effect was investigated by making three successive mercury penetration measurements on a charcoal which was known to be very soft and hence susceptible to crushing. Because of hysteresis, the mercury was removed from the charcoal after each penetration by distillation at elevated temperature and reduced pressure. The three successively determined distribution curves coincided, leaving no doubt that there was no destruction of the poor structure.

An observation made in the experiments with mercury penetration into the fine glass capillary may give the answer to the cause of hysteresis observed in the present penetration measurements and in those of Ritter and Drake.[3] Most activated charcoals retain about 93% of the mercury in the pore structure after the pressure has been released to the original pressure. The same degree of hysteresis was produced when two very small particles of grit became lodged in the glass capillary. When the pressure was released the mercury column broke at the grit particles, forming three segments which could be removed from the capillary only with great difficulty. Since charcoal is a very non-homogeneous material there are probably many constrictions in the pores which behave as the grit particles in the glass capillary by breaking up the mercury columns into many segments.

Acknowledgment.—The authors wish to thank the Chemical Corps Technical Division for its financial support of this investigation, especially for a fellowship held by (A. J. J.).

Summary

The pore size distribution in charcoal, in the pore diameter range 1,200 to 160,000 Å., may be determined by forcing measured quantities of mercury into the charcoal at known pressures. By the capillary rise equation the pore diameter can be calculated from the applied pressure and surface tension of mercury.

Received January 10, 1949