A STUDY OF THE FINE STRUCTURE OF CARBONACEOUS SOLIDS BY MEASUREMENTS OF TRUE AND APPARENT DENSITIES

PART I. COALS

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The true density of a series of coals was measured with helium gas and apparent densities were measured with methanol, water, n-hexane and benzene liquids. From the results obtained, the following conclusions were drawn.

Helium fills rapidly and completely the pore space of coals ground to pass a 72 B.S. sieve, and measures the true density of the coals. The pore space of coals ground to pass a 72 B.S. sieve is filled by methanol almost completely in a few hours. There is a contraction of $2 \cdot 6 \times 10^{-8}$ cm.^{3} for each cm.^{2} of surface covered by methanol. Water, n-hexane and benzene fill the pores space of some low rank coals practically completely. The apparent densities of such coals in these liquids are high owing to the contraction which accompanies adsorption. n-Hexane and benzene penetrate only very slowly into the pore space of some coals owing to the relatively large diameters of the molecules of these liquids. There is no appreciable volume of closed pores in coals.

The accessibility of the pore space of a coal to liquids and gases varies with rank in a manner similar to the porosity and adsorptive properties. Coals of high porosity have the most open pore structure. The pores in coals contain numerous fine constrictions, and the variation in the accessibility of the pore space from one coal to another is related to a variation in the width of these constrictions rather than in the mean diameter of the pores. The width of the constrictions is of the same order as the diameters of simple molecules and is smallest in coals containing between 89 % and 93 % carbon.

The Apparent Density of Porous Solids.—It is well known that the apparent density of finely porous solids and of solids possessing large specific surfaces is highly dependent on the method of measurement. The variation may be attributed in the main to two factors which influence the results in opposite directions. Values greater than the true density of the solid may result from the decrease in volume which accompanies adsorption of the filling fluid; alternatively, slow or incomplete penetration of the pores by the fluid may lead to low apparent density values. In the latter case a density drift (or increase of apparent density with time) is frequently observed. These considerations apply to a wide range of organic and inorganic colloidal materials and are well illustrated by the many measurements which have been made on charcoals. A selection of these is given in Table I; it is clear that very varied results may be obtained with a single charcoal, and also that the values obtained with a given series of liquids may fall into different order when different charcoals are used.

The results quoted in Table I show that both incomplete penetration of the pores and the contraction due to adsorption may be important. Thus the apparent density values are intimately related to the fine structure of the solid investigated; they depend not only on the properties of the liquid and the density of the solid, but also on the nature and extent of the surface of the solid, the size and accessibility of the pores, and the extent to which the accessibility of the pores and inner surfaces may be influenced by deformation of the solid resulting from interaction with the liquid.

The object of the present work was to use measurements of true and apparent densities to investigate the inner structure of coals, the variation of structure with rank (see later), and the nature of the interaction between coal surfaces and certain liquids.

TABLE I.—Apparent Densities of Charcoals in Liquids

Liquid	Harkins and Ewing [1]	Firth [2]		Cude and Hulett [3]	Culbertson and Weber [4]	Corriez [5]
	Activated coconut charcoal	Coconut charcoal	Sugar charcoal	Coconut charcoal	Active charcoal	Sugar charcoal
Water . . .	1·84	1·90	1·79	1·85	1·86	1·88
Chloroform . .	1·99	2·18	2·22	—	—	—
Benzene . . .	2·01	1·96	1·98	1·80	2·01	1·65
Carbon disulphide .	2·06	—	—	1·98	2·03	1·97
Acetone . . .	2·11	—	—	—	2·05	—
Ethyl alcohol . .	—	2·00	1·96	—	2·01	—

Significance of Density Measurements made with Helium.— The choice of helium for the measurement of the " true " density of a number of porous solids has been dictated by its small molecular diameter which should enable it to penetrate into very fine pores, and by its small van der Waals' field resulting in negligible adsorption on solids at room temperature. It is not, however, self-evident that a " true " density can be assigned to a complex and fine-structured material such as coal. If the solid contains closed pores which are inaccessible to all fluids including helium, then it may be necessary to define arbitrarily whether or not such spaces are to be included in the " true " volume of the material. Further, as has been well emphasised by Hermans,[6] density is essentially a macroscopic property, and irregularities of molecular dimensions cannot be measured by attempting to pack molecules into the available space. Thus, if the structure of the solid is such that " pores " of a few Ångströms diameter occupy an appreciable fraction of the total volume, then measurements made with helium (molecular diameter 2Å) will give an apparent density which has no precise or fundamental significance. Hermans considers that in the case of cellulose " there is no longer a conclusive reason to believe that any special preference should be given to the density found in helium, or that it would have any particular physical meaning." All the evidence resulting from the present work, however, tends to show that for coals helium may be used to measure a well-defined property which may reasonably be called the true density. In particular it may be mentioned here that although the fine structure and micro-pore volume are known to vary widely from one coal to another, the density measured in helium is a function of chemical composition only. Further evidence that helium measures the true density of coals is given in later sections of this paper.

The Physical Structure of Coal.—Coals of different rank form a series of related materials representing different (though not necessarily

Harkins and Ewing, *J. Amer. Chem. Soc.*, 1921, **43**, 1787.
Firth, *Trans. Faraday Soc.*, 1923, **19**, 444.
Cude and Hulett, *J. Amer. Chem. Soc.*, 1920, **42**, 391.
Culbertson and Weber, *ibid.*, 1938, **60**, 2695.
Corriez, *Thesis* (Paris, 1937).
Hermans, *Contribution to the Physics of Cellulose Fibres* (Elsevier Publishing Co., 1946), p. 62.
Franklin, *Fuel*, 1948, **27**, 46.

successive) stages in the process of " coalification " which started with the decay of plant material in a peat-bog and led to the formation of lignites, sub-bituminous coals, anthracites and peranthracites. Investigations of the colloidal structure of coals are described in a series of papers presented to a Conference on the " Ultra-fine Structure of Coals and Cokes," and the subject has also been reviewed by Bangham.[8] Griffith and Hirst [9] measured the heat of wetting in methanol of some two hundred coals, and, with the aid of adsorption data due to Maggs,[10] gave evidence that the *surface area* of coals accessible to methanol varies from about 20 to 200 m.²/g. The relation between the surface area and rank of coals is shown in Fig. 1, where the heat of wetting in methanol is plotted against the volatile content of the coal.*
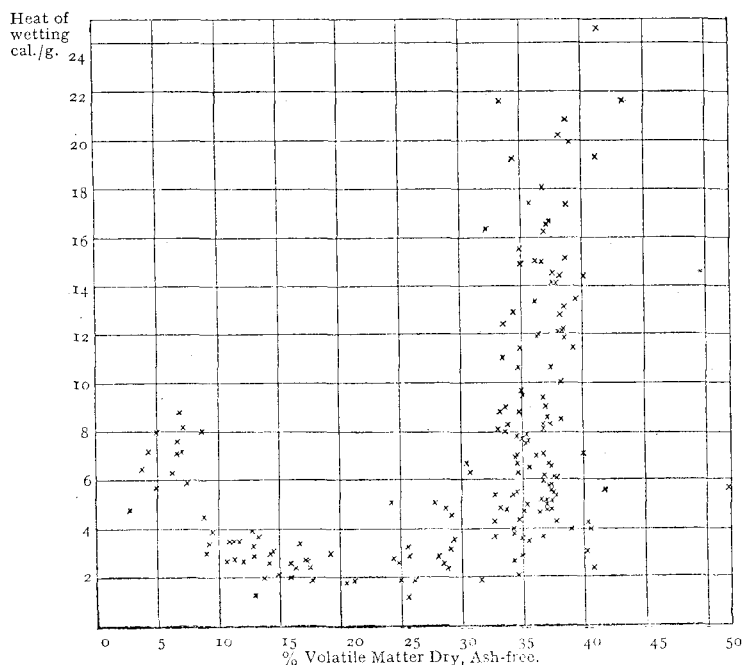

FIG. 1.—The heat of wetting–volatile matter classification.

The *porosity* of a large number of coals was measured by King and Wilkins,[11] who used mercury to measure the lump density and water for the " true " density. Porosity values ranged from about 2 % to 20 %, the variation of porosity with rank being similar to that of the heat of wetting in methanol. The highest porosities were found among the low rank coals, and the lowest in coals of about 89 % carbon content. Measurements by Duningham [12] again reveal a similar relationship between *inherent moisture content* and rank.

[8] Bangham, *Ann. Reports*, 1943, **40**, 29.
[9] Griffith and Hirst, *Conference on the Ultrafine Structure of Coals and Cokes* (B.C.U.R.A., 1944), p. 80.
[10] Maggs, *ibid.*, (B.C.U.R.A., 1943), p. 95.
* The volatile content of a coal is closely related to its rank, and 1 cal. of heat of wetting in methanol is equivalent to approximately 10 m.² of surface (see ref. 8).
[11] King and Wilkins, *Conference on the Ultrafine Structure of Coals and Cokes* (B.C.U.R.A., 1943), p. 46.
[12] Dunningham, *ibid.*, p. 57.

Bangham [8, 13] has postulated that coals have a micellar structure, the micelles being bound to one another principally by van der Waals' forces. Evidence of this is drawn from the behaviour of coal in solvents,[14] from adsorption and surface area measurements,[9, 10] from the rheological behaviour of coal [13] and from the low-angle scattering of X-rays.[15] The decrease in surface area and porosity with increasing rank (up to about 89 % carbon content) is attributed to a process analogous to syneresis. In the present work, measurements of true and apparent densities have yielded further information concerning the size and distribution of the pores in coals, and, on the basis of the results, the micellar theory is further developed.

Experimental

Materials.—COALS. A list of the twelve coals used, together with their carbon contents and heats of wetting in methanol is given in Table II. All the samples were of " bright " coals (i.e. they contained a preponderating amount of vitrain). Except where otherwise stated, all measurements were made on coals ground to pass a 72 B.S. sieve, precautions being taken to avoid an undue proportion of fines.

TABLE II.—ANALYSES OF COALS

Coal	Locality	Carbon %	Heat of Wetting in Methanol cal./g.
A	Ireland	95·2	6·2
B	S. Wales	94·7	7·7
C	S. Wales	94·2	7·6
D	S. Wales	91·7	2·8
E	Kent	90·9	2·5
F	S. Wales	89·7	2·0
G	Derbyshire	84·6	5·8
H	Yorkshire	83·5	8·8
J	Staffordshire	82·9	10·4
K	Northumberland	82·4	16·6
L	Nottinghamshire	81·3	11·8
M	Northumberland	80·6	17·1

HELIUM. " Spectroscopically pure " helium was supplied by British Oxygen Co. Ltd.

LIQUIDS. Water was freshly distilled ; methanol and benzene of A.R. grade and n-hexane boiling at 67°-69° C were used.

Measurement of Densities with Helium.—A diagram of the apparatus is given in Fig. 2. In essentials it was the same as that of Smith and Howard.[16] The operation consisted in (1) thorough evacuation of the apparatus, (2) measurement of the temperature and pressure of a quantity of helium in the calibrated bulb F, (3) transfer of the helium through the capillary tube G into the calibrated bulb A which contained the sample, and (4) measurement of the temperature and pressure of the helium in the bulb A. This gave the free volume in the bulb A and hence the volume of the sample. The sample was weighed after the bulb was removed from the apparatus at the end of the experiment.

The bulb F, at room temperature, was surrounded by a water jacket fitted with thermometer and stirrer ; the bulb A was in a water-bath supported on the platform P and maintained at 25 ± 0·01° C. During the preliminary evacuation the water bath was replaced by an electric oven. Pressure measurements were made by adjusting the mercury level to a fixed mark B (viewed through a

[13] Bangham, *Conference on the Ultrafine Structure of Coals and Cokes* (B.C.U.R.A., 1943), p. 18.
[14] Kiebler, *Ind. Eng. Chem.*, 1940, **32**, 1389.
[15] Riley, *Conference on the Ultrafine Structure of Coals and Cokes* (B.C.U.R.A., 1943), p. 232.
[16] Smith and Howard, *Ind. Eng. Chem.*, 1942, **34**, 43.

telescope) and observing the height of the mercury in the capillary tube G. The capillary tube was carefully selected for uniformity of bore (mean diam. 1·16 mm., maximum deviation 0·004 mm.) and mounted against an engraved steel scale which was read to 0·1 mm.
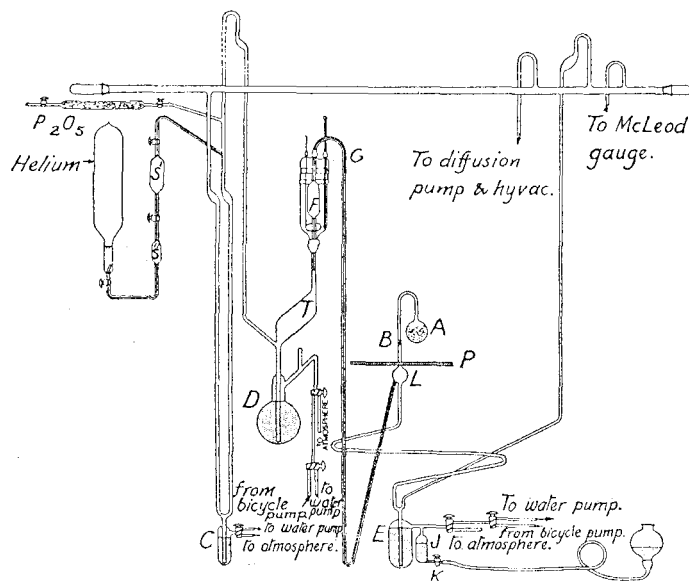

FIG. 2.

When coal is heated *in vacuo*, evolution of gas continues, at a steadily decreasing rate, for long periods of time. Further increase of temperature is always accompanied by further evolution of gas. It was therefore necessary to select arbitrarily an evacuation schedule which, whilst heating the coal sufficiently to ensure that measurable quantities of gas would not be disengaged subsequently at room temperature, yet would not cause significant structural changes. In practice, the sample was heated to 90°-100° C until a pressure of less than 10^{-4} mm. (with the pumps running) was obtained, the minimum period of heating being 16 hr. The sample was previously evacuated elsewhere in order to reduce its tendency to scatter when evacuated in the density apparatus. It was established that minor variations in the above procedure did not influence the results.

The first reading of the pressure of helium in the sample bulb was made as rapidly as possible ; it was generally completed 30-40 sec. after the gas first entered the bulb. Further readings were taken at intervals until no further change was observed in 24 hr. In general, coals showed no density drift in helium provided sufficient time was allowed for the sample to come to the temperature of the thermostat before the gas was admitted.

Duplicate determinations of the free-space in the bulb did not differ by more than 0·1 %. The recorded density values are therefore accurate to ± 0·2 %.

Measurement of Apparent Densities in Liquids.—The coal samples, contained in calibrated glass bulbs, were evacuated as described above. The bulbs were then sealed, the sealed tips were broken off while immersed in the liquid, and the bulbs placed in a thermostat at 25 ± 0·02° C before levelling the liquid and weighing. The density drift was often considerable, and in order to obtain comparative data it was necessary to make measurements after standard periods of immersion. Except where otherwise stated, all densities recorded were measured after 24 hr. immersion and all density drifts are given as the percentage difference between the density values obtained after 2 hr. and after 24 hr. immersion. Duplicate measurements did not differ by more than 0·5% even when large density drifts occurred.

Lump Density.—For the measurement of the lump density of coals, single lumps were dried to constant weight in an air-oven at 105° C, smeared with a

thin film of vaseline, and re-weighed rapidly in air and in water. The possi-
bility of errors due to large ash inclusions or other irregularities was eliminated
by making measurements on five or six different lumps of each coal.

Correction of Densities for Mineral Matter.—An approximate cor-
rection for mineral matter was applied to all the density values recorded.
Wandless and Macrae,[17] who made a detailed study of one coal, showed that
the error involved in correcting for mineral matter on the basis of *ash* density
and *ash* content is not appreciable so long as the ash content is small. The
corrected density is given by

$$d = \frac{ad'(100 - A)}{100a - Ad'} \, ,$$

where d' is the observed density, a the density of the ash and A the ash content
per cent. The correction amounts to less than 2 % for all the coals used in the
present investigation.

Measurement of Heat of Wetting.—Heats of wetting of coals in liquids
were measured by the routine method developed in the B.C.U.R.A. laboratories
by Griffith and Hirst.[9]

Results

Control Experiments with Helium.—Preliminary experiments showed
that under the conditions of the density measurements helium penetrates rapidly
and completely into the pores of all the coals investigated. Equilibrium was
always rapidly established, and, below a certain size limit, the density was in-
dependent of the particle size of the material (Table IV, column 3). Further,
the results were not altered when the period of evacuation at 90°-100° C was
extended from 16 hr. to 10 days.

TABLE III.—APPARENT DENSITIES OF THE COALS

Coal	Helium		Methanol		Water		n-Hexane		Benzene	
	Density (g./cm.³)	Drift (%)	Density after 24 hr. (g./cm.³)	Drift (% 2 hr. to 24 hr.)	Density after 24 hr. (g./cm.³)	Drift (% 2 hr. to 24 hr.)	Density after 24 hr. (g./cm.³)	Drift (% 2 hr. to 24 hr.)	Density after 24 hr. (g./cm.³)	Drift (% 2 hr. to 24 hr.)
A	1·645	0·0	1·700	0·3	1·630	0·0	1·497	0·8	1·518	1·5
B	1·517	0·0	1·556	0·1	1·488	0·0	1·433	1·9	1·450	2·9
C	1·497	0·0	1·549	0·1	1·475	0·0	1·425	2·0	—	—
D	1·361	0·4	1·374	0·4	1·318	0·0	1·300	0·3	1·293	0·3
E	1·337	0·0	1·352	0·2	1·305	0·0	1·297	0·3	1·299	0·6
F	1·311	0·0	1·333	0·6	1·291	0·0	1·286	0·3	1·297	0·3
G	1·293	0·0	1·334	0·6	1·297	0·0	1·276	0·7	1·286	1·3
H	1·301	0·0	1·357	0·6	1·307	0·0	1·262	1·8	1·276	2·5
J	1·302	0·0	1·402	0·7	1·333	0·0	1·297	0·8	1·292	1·3
K	1·305	0·0	1·387	0·4	1·326	0·0	1·329	1·8	1·342	1·4
L	1·317	0·0	1·387	0·5	1·328	0·0	1·272	2·2	1·321	2·6
M	1·341	0·0	1·327	0·3	1·370	0·0	1·374	2·9	—	—

The True and Apparent Densities of Twelve Coals.—The apparent
densities and density drifts of the twelve coals described in Table II were
measured in methanol, water, n-hexane and benzene, and true densities were
measured with helium. The results are given in Table III, and in Fig. 3 the
densities are plotted against the carbon content of the coals. The main feature
of the results are—

(1) The density in methanol is in every case the highest.

(2) Densities in n-hexane and in benzene are in general lower than the true
density (measured with helium). Two low rank coals are exceptions.

(3) Where the apparent densities in n-hexane and in benzene differ appreciably,
the value given by n-hexane is the lower.

(4) Apparent densities in water are lower than the true density for high rank
coals and higher for low rank coals. The change occurs between 82 % and
85 % carbon content.

[17] Wandless and Macrae, *Fuel*, 1934, **13**, 4.

TABLE IV.—INFLUENCE OF PARTICLE SIZE ON APPARENT DENSITY

| Coal	Size	Helium		Methanol		Water		n-Hexane	
		Density (g./cm.^{3})	Drift (%)	Density after 24 hr. (g./cm.^{3})	Drift (%, 2 hr. to 24 hr.)	Density after 24 hr. (g./cm.^{3})	Drift (%, 2 hr. to 24 hr.)	Density after 24 hr. (g./cm.^{3})	Drift (%, 2 hr. to 24 hr.)
F	(1) Through 14 B.S. on 1/32 in. . . .	1·298	0·0	1·315	2·2	1·285	0·9	1·273	0·0
	(2) Through 72 B.S. on 100 B.S. . . .	1·299	0·0	1·331	1·1	1·283	0·0	1·271	0·4
	(3) Through 72 B.S. . . .	1·311	0·0	1·333	0·6	1·289	0·0	1·281	0·3
	(4) Through 240 B.S. .	1·307	0·0	1·335	0·2	1·285	0·0	1·291	0·6
K	(1) Through 14 B.S. on 1/32 in. . . .	1·292	0·0	1·373	0·4	1·311·	0·0	1·316	2·2
	(2) Through 72 B.S. on 100 B.S. . . .	1·294	0·0	1·371	0·6	1·318	0·0	1·318	2·1
	(3) Through 72 B.S. . . .	1·305	0·0	1·386	0·4	1·327	0·0	1·330	1·8
	(4) Through 240 B.S. .	1·305	0·0	1·380	0·5	1·336	0·0	1·339	1·8
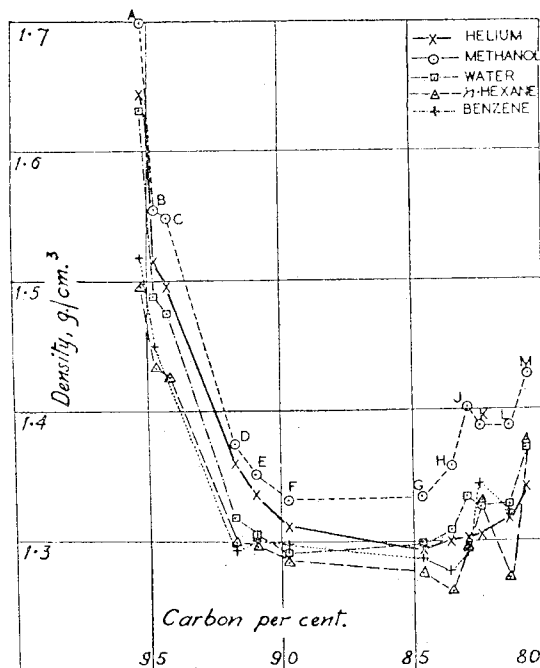
FIG. 3.

(5) (a) There is, in general, no density drift in helium.   One coal showed a small drift.

(b) There is no density drift in water.

(c) Density drifts in methanol are generally small (0·2–0·6 %).

(d) Considerable density drifts in n-hexane and benzene are observed with some coals.

(6) TRUE DENSITIES.—The significance of the values obtained for the true densities of coals is discussed elsewhere.[7]   It is shown that for all the coals investigated the true specific volume is a linear function of the hydrogen content, and extrapolation gives 1·85 g./cm.³ for the density of a " coal " of zero hydrogen content.   This relationship indicates that there is a characteristic molecular or atomic packing which is common to all coals and very different from that of graphite (density, 2·26 g./cm.³).

These measurements provide a general survey of the way in which the apparent densities of coals vary with rank and with the nature of the fluid used to make the measurement.   The following series of subsidiary measurements were made to assist in elucidating the results.

(1) To ascertain the significance of the low apparent densities of some coals in water, n-hexane and benzene, the lump densities of the coals C, D, F, H and K were measured as described above, and from the lump densities and the densities in helium the true porosities were calculated.   The results are given in Table IV.

(2) To investigate further the density drifts and low apparent density values, the dependence of the results on the particle size of the coal was studied. Results obtained with coals F and K prepared in four size grades are given in Table V.

TABLE V.—POROSITY OF COALS

Coal	Density * of Dry Lump (g./cm.³)	Porosity Calc. from Density in Helium (%)
C	1·364	10·1
D	1·313	4·7
F	1·301	3·2
H	1·214	7·7
K	1·151	12·3

* Densities not corrected for mineral matter.

The strong influence of the chemical character of the coal surface on the values of the apparent densities in liquids was confirmed by measurements made on oxidised coals.   Samples of coals F and K, ground to pass 72 B.S.S., were spread in thin layers in a well-ventilated air oven at 105° C for 36 days.   The densities and heats of wetting before and after oxidation are given in Table VI.

TABLE VI.—INFLUENCE OF OXIDATION ON APPARENT DENSITIES AND HEATS OF WETTING

Material	Helium		Methanol			Water			n-Hexane		
	Density (g./cm.³)	Drift (%)	Density after 24 hr. (g./cm.³)	Drift (% 2 hr. to 24 hr.)	Heat of Wetting (cal./g.)	Density after 24 hr. (g./cm.³)	Drift (% 2 hr. to 24 hr.)	Heat of Wetting (cal./g.)	Density after 24 hr.	Drift (% 2 hr. to 24 hr.)	Heat of Wetting (cal./g.)
Coal F	1·311	0·0	1·333	0·6	2·0	1·291	0·0	0·6	1·286	0·3	1·8
Coal F oxidised	1·359	0·0	1·400	0·7	3·4	1·357	0·1	3·5	1·321	0·0	2·3
Coal K	1·305	0·0	1·387	0·4	16·6	1·326	0·0	9·5	1·329	1·8	4·9
Coal K oxidised	1·427	0·0	1·577	1·1	22·6	1·479	0·4	12·3	1·371	1·4	1·5

Discussion

Apparent Densities in Methanol : Compression of the Adsorbed Liquid.—The apparent density in methanol exceeds the density in helium for all the twelve coals investigated. It has been shown above that helium penetrates rapidly and completely into the pores of coals ground to pass a 72 B.S. sieve. Moreover, measurements on the two widely different coals F and K (Table V) show that the pores of coals ground to pass a 72 B.S. sieve are also completely filled by methanol in 24 hr. ; density drifts in methanol are small and decrease with decreasing particle size, and density values after 24 hr. are practically independent of particle size. The difference between the density values obtained with helium and with methanol must therefore be attributed to the contraction which accompanies adsorption.

The contraction per g. of coal is given by $(V_{He} - V_{MeOH})$, where V_{He} is the specific volume in helium and V_{MeOH} the apparent specific volume in methanol. This function is found to be directly proportional to the heat of wetting of the coal in methanol, for eleven of the twelve coals investigated (Fig. 4), the contraction being 0·0026 cm.[3] per calorie heat of wetting. Only coal J is represented by a point lying well above the line, but the heat of wetting of this coal was liberated exceptionally slowly and the value recorded is known from other evidence to represent a gross under-estimate.*

Maggs [19] has shown that the heat of wetting of coals in methanol is 1 cal./10 m.[2] of surface, and this is the same as the figure obtained by

X COALS < 72 B.S.S
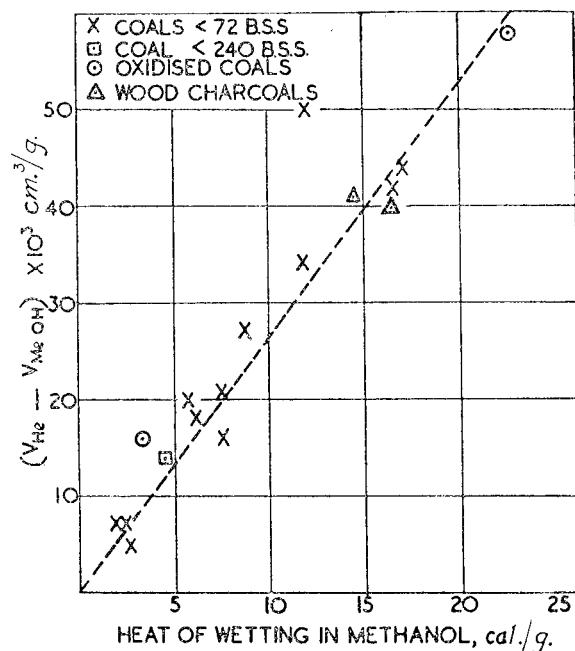□ COAL < 240 B.S.S.
⊙ OXIDISED COALS
△ WOOD CHARCOALS

FIG. 4.

Bangham [8] for charcoal. The heat of wetting in methanol may therefore be taken as a measure of the specific surface of the coals, modified coals

* Owing to the limitations of the calorimeter used, heats of wetting could only be measured during the first 10 to 20 min. after immersion. Specific volumes measured after 2 hr. immersion rather than after 24 hr., were therefore used in obtaining the values of $(V_{He} - V_{MeOH})$ shown in Fig. 4.

and charcoals discussed here. The linear relationship in Fig. 4 then shows that the contraction due to adsorption is proportional to the surface area covered. The fact that the line passes through the origin confirms that methanol and helium penetrate to an approximately equal extent into the pore structure.

It is important to note that the contraction per unit area of adsorbing surface is found to be of equal magnitude for charcoals, anthracites, coals of low rank and highly oxidised coals in spite of the widely differing physical and chemical properties of these materials. The contraction cannot, therefore, be attributed either to incipient solution or to contraction in the solid substance.

Taking a heat of wetting of 1 cal. to represent 10 m.^{2} of surface the observed contraction is $2 \cdot 6 \times 10^{-8}$ cm.^{3} per cm.^{2} of surface, or about 60 % of the volume which would be occupied by a monolayer of methanol on the surface of the solid if no contraction occurred. Thus, even if the contraction were spread evenly throughout the absorbed material (coals absorb the equivalent of from 3 to 5 molecular layers of methanol at saturation pressure at 25° C), it is surprisingly large. Measurements involving charcoals and cellulosic materials indicate, however, that the large contraction observed when methanol is adsorbed on coals is not exceptional.

Several authors have calculated the hydrostatic pressure required to produce the observed contraction in the adsorbed film, but it seems that such calculations can have little meaning since the adsorbed film and the forces responsible for its formation are essentially anisotropic, and the structure and properties of the film differ from those of the bulk liquid. Direct measurements of the volume occupied by water vapour on cellulose [18] and by organic vapours on charcoal [19] have shown that the greatest contraction occurs for small quantities of vapour adsorbed, when the lateral film pressure is very small and the volume change must be attributed almost entirely to the close approach of the adsorbate molecules to the surface atoms of the adsorbent. It seems probable, therefore, that the greater part of the large contraction observed when methanol is adsorbed on coal occurs in the direction perpendicular to the adsorbing surface.

Apparent Densities in n-Hexane and Benzene.—The apparent densities of coals in n-hexane and benzene show considerable drifts, and the values obtained after 24 hr. immersion are lower than the corresponding densities in helium for all except two of the coals investigated. Penetration of the pores by these liquids is slow and incomplete, and the extent of penetration varies with the rank of the coal. In the coals D, E and F, the liquids are almost completely excluded from the pores : the drifts are exceptionally slow, and for coal D the apparent density in n-hexane after 2 hr. immersion is still very near the lump density. The densities of the anthracites in n-hexane are much lower than in helium, but comparison with the lump density shows that the liquids penetrate to a considerable part of the pore space. The coals K and M, for which the apparent densities in n-hexane are higher than in helium, are both law rank coals of high porosity. It appears, therefore, that the accessibility of the pores of coals to n-hexane and benzene is at a minimum for coals containing between 89 % and 93 % carbon, and increases for coals of higher or of lower rank, being greatest for low rank coals of high porosity. That is, the *accessibility* is closely related to the *porosity*.

n-Hexane and benzene readily wet the surfaces of coals, and the viscosity of n-hexane is very low. The poor penetrating power of the liquids cannot, therefore, be attributed either to a wetting angle greater than 90°

[18] Stamm and Seborg, *J. Physic. Chem.*, 1935, **39**, 133. Stamm and Hanson, *Ibid.*, 1937, **41**, 1007.
[19] Danforth and Devries, *J. Amer. Chem. Soc.*, 1939, **61**, 873.

or to high viscosity, but must be associated rather with the relatively large size of the benzene and n-hexane molecules. The molecule of n-hexane is considerably larger than that of benzene, and, where the apparent densities of a coal in the two liquids differ appreciably, the n-hexane value is the lower.

The above results therefore suggest that the width of the pores or of constrictions in the pore system in coals is of the same order as the diameters of the molecules used for the density measurements. These fine pores or constrictions are smallest in coals containing between 89 % and 93 % carbon. In the coal D the pores or constrictions are so narrow that even helium (molecular diameter 2 Å) penetrates somewhat slowly, a small density drift being observed.

It may be noted that the low apparent densities in n-hexane or benzene are always associated with long, slow drifts. This was observed also with other organic liquids of relatively large molecular size ; even the heavy oil supplied for a Hyvac rotary pump showed a prolonged density drift, indicating slow penetration. This behaviour may probably be attributed to slow distortion of the coal substance by the spreading pressure in the adsorbed films, and is in sharp contrast with that of carbonised coals ; the more rigid structure of the latter resists deformation by adsorbed films at 25° C, and, if the molecules of a given liquid are too large to enter the pores, then the liquid is totally excluded and there is no density drift.[20]

Apparent Densities in Water.—The apparent density in water is greater than the density in helium for coals of less than about 84 % carbon content. For high rank coals, on the other hand, it is intermediate between the values obtained with helium and n-hexane, being close to the low, n-hexane value for coals containing between 89 % and 93 % carbon, and nearly equal to the helium value for the highest rank anthracite (Fig. 3). Thus, as in the case of n-hexane and benzene, the accessibility of the pores and inner surfaces of coals to water is greatest for low rank coals of high porosity, passes through a minimum for coals containing between 89 % and 93 % carbon, and increases again with increasing rank among the anthracites.

The failure of water to fill completely the pores of high rank coals cannot be due to the size of the water molecule, since the molecule of methanol is larger, and apparent densities in methanol are high. Moreover, the absence of any density drift suggests that the cause of low apparent densities in water is different from that of the low values obtained with n-hexane and benzene. This difference is also revealed by the measurements made on samples of coals F and K ground to various sizes (Table V). Finer grinding increases the apparent density of both coals in n-hexane, and the drift for coal F is also increased. In water, on the other hand, the apparent density of coal F remains constant and that of coal K is increased, but in neither case is a density drift introduced.

It seems, therefore, that the low apparent densities of high rank coals in water is an effect associated with their poor wettability. That the external surfaces of coals D and F (91·7 % and 89·7 % carbon respectively) are not easily wetted by water was shown when attempts were made to measure their densities by immersing the sample (not previously evacuated) in the boiling liquid in a simple density bottle. The particles were not wetted even after prolonged boiling, and apparent densities as low as 0·7 g./cm.[3] were recorded.* With coals C and K, on the other hand, the

[20] Franklin, *Coal Res.*, 1946, p. 37.

* Striking proof of the way in which poor wettability (due to a large angle of contact) may influence apparent densities in water even after evacuation was obtained with a sample of the commercial carbon black P33. The material was evacuated at 90° C for three days, after which time the particles adhered to one another, and the substance could be shaken about in the glass bulb in the

results agreed well with the apparent densities measured in water after evacuation.

There is an apparent contradiction between these results and some later work by Maggs [21] who found that even high rank coals adsorb at saturation pressure, sufficient water vapour to fill all the pores. The discrepancy may perhaps be due to the fact that Maggs used water *vapour* whereas in the present work the coal was always placed in direct contact with the liquid. High rank coals contain adsorbed methane, the last traces of which are difficult to remove, and it may be that water vapour can replace the gas molecule by molecule, whereas the presence of liquid water impedes its escape.

Dimensions of the Pores in Coals.—Comparison of the porosity of coals as measured by King and Wilkins with the heat of wetting in methanol as measured by Griffith and Hirst suggests that the porosity is approximately proportional to the surface area. It follows that, for any given structural model, the mean diameter of the pores is approximately the same in all coals. Measurements of the porosity of the coals c, D, F, H, and K confirm this observation. Assuming that 1 cal. of heat of wetting in methanol corresponds to 10 m.^{2} of surface, then, if the pore space in coals consists in uniform, cylindrical, non-intersecting pores, the mean pore diameter in all coals is about 40 Å. Alternatively, if the solid consists of equally spaced cubes of coal substance, the distance of separation between the cubes would be about 12 Å. The dimensions of the regions of continuous coal substance would, of course, vary with the surface area of the coal.

It has been shown, however, that coals do not behave as if they all contain uniform pores whose size is independent of rank. The pores of coal containing between 89 % and 93 % carbon are the least easily penetrated by liquids and among both low rank coals and anthracites permeability increases with increasing porosity. Similar observations have been made by Graham [22] who has pointed out that the permeability to methane and to moisture varies widely from one coal to another, the permeability of many anthracites and some low rank coals being low whereas other low rank coals and also the highest rank anthracite have a high permeability.

Since the mean pore diameter in all coals is approximately equal while the permeability varies widely, it must be presumed that the pores are not uniform along their length but contain fine constrictions, and that the accessibility of the pore space to liquids and gases is determined by the size and frequency of these constrictions rather than by the mean pore diameter. On this hypothesis, the pores are most highly constricted in coals containing between 89 % and 93 % carbon, while low rank coals of high porosity have the most open pore structure.

The configuration of the fine pores must be intimately related to the way in which the coal micelles are bound together, and the variation of the pore structure with the rank of the coal must be associated with the changes in micellar structure which occur during coalification. If the decrease in surface area and porosity which occurs with increasing rank up to about 90 % carbon be attributed to an increase in the size of the micelles, then the decreasing accessibility of the pores is in no way explained. The results suggest, rather, that the changes in pore structure

form of a hemispherical lump with a partly shiny surface. Its density in helium was 1·80 g./cm.^{3}. When attempts were made to measure the density in water the solid floated, and approximate measurements gave values of about 0·8 g./cm.^{3}, showing that atmospheric pressure was not sufficient to force the water into the evacuated spaces between the loosely aggregated particles.

[21] Bond, Griffith and Maggs, *Faraday Soc. Discussions*, 1948, **3**, 29.
[22] Graham, *Conference on the Ultrafine Structure of Coals and Cokes* (B.C.U.R.A., 1943), p. 151.

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at this stage are due to a *closer compacting of the coal micelles*.   In a later paper a simple model based on this hypothesis is developed and is shown to be consistent with a wide range of experimental results in addition to those described above.

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