QUARTERLY REVIEWS

THE PROPERTIES AND NATURE OF ADSORBENT CARBONS

By J. J. Kipling, B.Sc., M.A., D.Phil.
(The University, Hull)

Introduction and Nomenclature

Many materials, loosely referred to as carbons, have been used as adsorbents. This Review attempts to provide a comparative survey of their various properties, but not to deal with individual practical uses, which are described fully elsewhere.[1–3] It will also refer to carbon blacks, which are not made for use as adsorbents (though their surface properties are important, especially in rubber technology) but, having been investigated by the technique of adsorption, often provide results which throw light on the nature of the adsorbent carbons.

Both groups are among the materials frequently referred to in textbooks as " amorphous carbon ". As these substances are usually introduced together with diamond and graphite, it is often implied and sometimes stated that amorphous carbon, in this loose sense, is to be regarded as a third allotrope of the element. Some references to graphite will therefore be made with a view to assessing the status of these adsorbents, but without detailed comment on the various structural forms which carbon can take. This aspect of the subject was reviewed by Riley [4] and is being developed by his successors in the Northern Coke Research Laboratory and elsewhere.

Nomenclature.—The nomenclature on this subject is very unsatisfactory. Even active charcoal is " a poorly defined substance ",[5] partly because so little is generally known about its preparation and properties. The term " amorphous carbon " has been used to cover a much wider group of substances ; * those with which we are concerned are classified in Fig. 1. It

---

[1] Mantell, " Adsorption ", McGraw-Hill, New York, 2nd edn., 1951.

[2] *Idem,* " Industrial Carbon ", Van Nostrand, New York, 2nd edn., 1946.

[3] Hassler, " Active Carbon ", Chemical Publishing Co., New York, 1951.

[4] H. L. Riley, *Quart. Rev.*, 1947, **1**, 59.

[5] Steenberg, " Adsorption and Exchange of Ions on Activated Charcoal ", Almqvist and Wiksells, Uppsala, 1944.

[6] Gibson and H. L. Riley, *Fuel,* 1942, **21**, 36.

* " The names amorphous carbon, carbon black, retort carbon, acetylene black, coke, gas coke, metallurgical coke, pitch coke, petroleum coke, low temperature coke, charcoal, char, coal, anthracite, lamp black, bone black, electrode carbon, deposited carbon, soot, active carbon, vegetable black, channel black, natural graphite, vitreous carbon, carbonaceous matter, etc., all refer to more or less pure forms of carbon, and have a more or less precise significance." [6]

will be convenient to refer to the two most important groups as " charcoals " and " carbon blacks ". Each term refers to substances whose properties

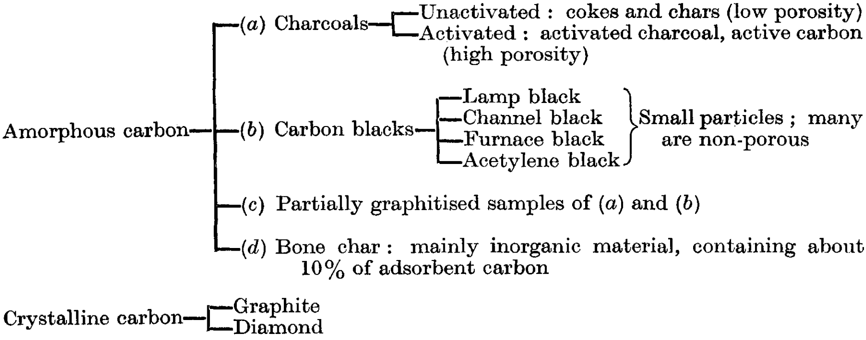


FIG. 1

(density, adsorptive capacity, etc.) vary over a wide range, in contrast to those of diamond and graphite.

" Charcoals " are always porous. The walls of the pores contribute most of the high surface area per unit weight (specific surface area) which is important in their use as adsorbents, as catalysts, and as catalyst supports. The adsorptive capacity can be varied (within limits) by the process of activation. The immediate product of carbonising the raw material, although porous, usually has a low or even negligible adsorptive capacity, and is referred to as an unactivated charcoal or " coke ". Activation converts it into an " activated charcoal " or " active carbon ". (An earlier use of the term " active carbon " to imply a special modification of the element has not been justified by subsequent investigations.[7])

The term " char " has sometimes, unfortunately, been used for unactivated charcoals, but usually refers to bone chars. These are pyrolysed bones which may contain 70—75% of calcium phosphate (which contributes to their effectiveness in sugar refining,[7] their main use) and only about 10% of carbon. It is also unfortunate that the term " animal charcoal " has been used in the literature to denote chars (of low carbon content) as well as charcoals of high carbon content such as blood charcoal.

" Carbon blacks " are mainly used as pigments and fillers (especially in rubber tyres) and many are non-porous. Their adsorptive capacity is derived from the high surface-weight ratio of the small particles in which they are prepared. The specific types and the relationship between particle size and use in rubber tyres are considered elsewhere.[8, 9]

---

[7] Deitz, " Bibliography of Solid Adsorbents, 1900—1942 ", National Bureau of Standards, Washington, 1944 ; supplement in preparation.

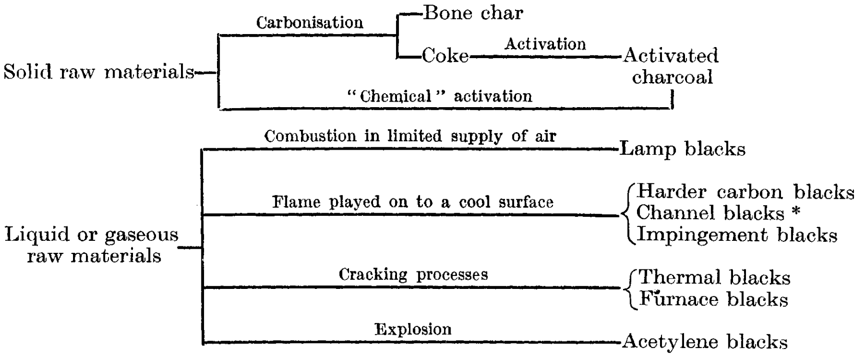
[8] Speedy, *Rubber Age, London*, 1943—4, **24**, 81, 114, 136, 162, 182, 206, 232, 260, 286 ; 1944, **25**, 14.

[9] Cohan and Steinberg, *ibid.*, 1945, **25**, 275 ; Parkinson, *Chem. and Ind.*, 1944, 325.

Methods of Preparation

The methods of preparation are summarised in Fig. 2.

(a) *Charcoals.* Details of the manufacture of commercial charcoals [1, 2, 3, 7, 10, 11] are relevant here only insofar as they are related to the properties of the products. The raw materials are always organic, and nearly always of biological origin, though a few experimental products have been made from synthetic polymers, *e.g.*, poly(vinylidene chloride) (Saran charcoals),[12, 13] and divinylbenzene copolymer.[14] Charcoals having the finest pores have been made from hardwoods,[15] nut-shells, and, in recent years, from various grades of coal. The suitability of coal varies with rank, and in order to achieve satisfactory mechanical as well as adsorptive properties, it is usual to blend a caking with a non-caking coal. These are ground to a fine powder, briquetted under high pressure without a binder, and carbonised at a low temperature (600°).[16–18] The open pore-structure of gas coke shows the need for preliminary treatment. A remarkable variety of other substances has been investigated.[3, 7]



* Named after the channel on which the flame impinges.

FIG. 2

Two stages may be recognised in the production of an activated charcoal. In " carbonisation " the original material is pyrolysed in the absence of air to remove most of the elements other than carbon as volatile compounds.[19]

---

[10] " Thorpe's Dictionary of Applied Chemistry ", Longmans, Green and Co., London, 4th edn., 1938.

[11] Kirk and Othmer, " Encyclopedia of Chemical Technology ", Interscience, New York, 1949, Vol. III.

[12] Pierce, R. N. Smith, Wiley, and Cordes, *J. Amer. Chem. Soc.*, 1951, **73,** 4551.

[13] Dacey and Thomas, *Trans. Faraday Soc.*, 1954, **50,** 740.

[14] Winslow, Baker, Pape, and Matreyek, *J. Polymer Sci.*, 1955, **16,** 101.

[15] Chaney, Ray, and St. John, *Ind. Eng. Chem.*, 1923, **15,** 1244.

[16] Horton, Randall, and Aubrey, *Fuel*, 1944, **23,** 65, 100.

[17] Kipling, *ibid.*, 1950, **29,** 42.

[18] Fuel Research Board Technical Paper No. 47, " The Production of Active Carbon from Bituminous Coal ", London, 1938; Williams, *Mining J.*, 1946, **227,** 1026.

[19] Child, *Tropical Agriculturalist*, 1940, **94,** 99, describes the carbonisation of coconut-shell.

For a given material the fundamental structure of the carbon residue, in particular its potential pore-structure, is determined by the precise conditions used in the carbonisation process, especially in the case of coal.[16, 17, 20] In activation the relatively small pore-structure of the coke is developed by burning away some of the remaining material to create new pores and enlarge others. The reagents used are gaseous (air, oxygen, chlorine, sulphur vapour) and most give rise to an exothermic process. The reaction with steam, however, is endothermic, which makes for easier control of temperature (especially on the industrial scale) and hence for reproducibility of the product, a factor to which little attention seems to have been paid in most early work.*

Both the activating agent and the temperature of activation affect the properties of the product, as will be seen later. The endothermic processes usually need a higher working temperature than the exothermic processes ; air [11] and sulphur vapour [21] react readily at 300—600°, whereas steam and carbon dioxide need a temperature of 700—1000°, depending on the type of coke being activated.[22, 23] Lower temperatures are possible if the reaction is catalysed, and some catalysts, such as potassium carbonate, may occur in the coke as ash. There is a considerable literature on this subject, of which only a few papers can be quoted.[23–27] The kinetics and reaction mechanisms of these processes have been discussed [28] and reviewed [29] recently.

Several processes have been devised in which carbonisation and activation are carried out in one operation ; they are sometimes termed, rather unsatisfactorily, " chemical " activation. The raw material is intimately mixed with a dehydrating and/or oxidising agent such as zinc chloride, phosphoric acid, or potassium sulphide, and heated in the absence of air. In many cases, the activating agent liberates a gas which assists the development of an extensive pore system. The advantage of a one-stage process is somewhat offset by the need (in most cases) to remove the inorganic material left in the charcoal. This is not always completely successful ; a typical zinc chloride-activated wood charcoal was found to contain 6·38%

[20] Kipling, *Sci. Prog.*, 1949, **37,** 657.

[21] Lewis and Metzner, *Ind. Eng. Chem.*, 1954, **46,** 849.

[22] Gadsby, Hinshelwood, and Sykes, *Proc. Roy. Soc.*, 1946, *A*, **187,** 129.

[23] Gadsby, Long, Sleightholme, and Sykes, *ibid.*, 1948, *A*, **193,** 357.

[24] Lewis, Gilliland, and Hipkin, *Ind. Eng. Chem.*, 1953, **45,** 1697.

[25] Holmes and Emmett, *J. Phys. Colloid Chem.*, 1947, **51,** 1276.

[26] Long and Sykes, *Proc. Roy. Soc.*, 1952, *A*, **215,** 100 ; Arthur and Bowring, *J. Chim. phys.*, 1950, **47,** 540 ; Patai, Hoffman, and Rajbenbach, *J. Appl. Chem.*, 1952, **2,** 306, 311 ; Blayden, H. L. Riley, and Shaw, *Fuel*, 1943, **22,** 32, 64 ; Wynne-Jones, Blayden, and Marsh, *Brennstoff-Chem.*, 1952, **33,** 238 ; Sabo and Akamatu, *Fuel*, 1954, **33,** 195.

[27] Frey, *Proc. Roy. Soc.*, 1955, *A*, **228,** 510.

[28] Bangham and Townend ; Strickland-Constable ; Meyer ; Audubert and Busse ; Duval ; Jones and Townend ; Mertens ; Long and Sykes, *J. Chim. phys.*, 1950, **47,** 315.

[29] Blackwood, *Rev. Pure Appl. Chem. (Australia)*, 1954, **4,** 251.

* The very valuable bibliography compiled by Deitz [7] gives extensive reference to early work in most parts of the subject of this Review.

of zinc oxide.[30] As with raw materials, a considerable number of activating agents has been investigated, but only a few have found wide acceptance.[3]

The " activation " which is sometimes applied to charcoal used to remove impurities from organic preparations consists in heating the charcoals to about 120° for 1—2 hours. This simply drives off physically adsorbed gases (mainly moisture) ; it leaves the surface free for further adsorption, but it is not activation in the sense defined above.

" Re-activation " as applied to bone chars involves the burning away of adsorbed material with an activating gas, so that the carbon can be used again. The process inevitably removes some of the original carbon, thus tending to increase, with each cycle, the mineral content of the char.

" Outgassing " under vacuum is a preliminary to many adsorption experiments. It may be carried out at room temperature to remove physically adsorbed material, or at much higher temperatures to remove chemisorbed material ; if the latter process is carried too far, charcoals may suffer permanent change, amounting to further activation.[31] On the other hand, outgassing of carbon blacks at temperatures of 1000° and above leads to a decrease in surface area as the pseudo-graphitic crystallites grow.[32, 33]

(b) *Carbon blacks.* Carbon blacks are usually prepared by the incomplete combustion or thermal decomposition of materials such as acetylene, natural gas, oil, tar, and resins.[2, 8, 11] As these processes are carried out in the gas phase, they seem at first sight to differ fundamentally from the carbonisation of solids. The pyrolysis of hydrocarbons, however, involves the intermediate formation of polymers which may condense to form droplets from which the " carbon " is then derived.[34, 35] It is therefore suggested that there is only a quantitative and not a qualitative difference between such pyrolyses and the carbonisation of solids.[35] The solids, of course, have a much more definite structure, some of which is preserved in the charcoal.

(c) *Graphite.* Native graphite usually contains considerable impurities (Table 1), and for many purposes artificial graphite is preferred. This can readily be made with 98·8—99·5% of graphitic carbon.[2] The manufacturing process consists essentially in heating amorphous carbon to 2200—2700°, and involves two changes. The first is the graphitisation of the carbon which, after removal of the oxygen and hydrogen, shows itself in, for example, an increase in electrical resistivity.[33] The second is the volatilisation of compounds of silicon and of any metals present. A wide variety of materials is graphitised, partially or completely, and the physical properties of the product vary accordingly.

Particle Size.—The form of the carbon is varied to suit its purpose. Active charcoals may be prepared as powders, especially for use with

---

[30] Anderson and Emmett, *J. Phys. Colloid Chem.*, 1947, **51,** 1308.
[31] Driver and Firth, *J.*, 1922, **121,** 2409.
[32] Polley, Schaeffer, and W. R. Smith, *J. Phys. Chem.*, 1953, **57,** 469.
[33] Schaeffer, W. R. Smith, and Polley, *Ind. Eng. Chem.*, 1953, **45,** 1721.
[34] Parker and Wolfhard, *J.*, 1950, 2038.
[35] Grisdale, *J. Appl. Phys.*, 1953, **24,** 1082.

solutions, or as granules for adsorption of gases. Carbon blacks are always powders, but with a wide range of particle size. Graphite for adsorption experiments is almost always powdered. The internal surface area of active charcoals is so high that the total adsorbing surface is almost independent of the granule size, whereas particle size is of great importance in determining the specific surface area of carbon blacks. Granule size of charcoals may, however, affect adsorption in non-equilibrium conditions, *e.g.*, when the charcoal is used in columns for adsorption from a stream of liquid or gas.[36–38]

Chemical Nature of the Product

Chemical Analyses.—Table 1 gives chemical analyses (percentages) of a representative selection of " carbons ". Some of the carbon blacks are almost pure elementary carbon, but the remaining materials contain significant percentages of other elements. The latter are often no more fully " carbon-ised " than anthracite, and as they are not pure carbon cannot be regarded as an allotropic modification of the element, particularly because small percentages of some elements can modify the physical and chemical properties of carbon appreciably.

There are two kinds of impurity, both of importance in adsorption. Combined hydrogen and oxygen nearly always remain from the organic raw material or the activating agent (*i.e.*, " carbonisation " is usually incomplete), and other elements may remain in individual carbons, *e.g.*, nitrogen in blood charcoal,[44] chlorine in charcoals activated by chlorine,[49] and sulphur in some commercial charcoals and carbon blacks.[50] These elements may considerably affect the characteristics of the surface as is discussed on p. 21.

Ash.—The second type of impurity is the ash, or uncombined inorganic matter. In the absence of residues from activating agents, the ash is usually alkaline. Thus a careful analysis of uncarbonised coconut-shell shows the presence of K_2O (0·226), Na_2O (0·127), CaO (0·017), MgO (0·016), $Fe_2O_3 + Al_2O_3$ (0·011), P_2O_5 (0·030), SO_3^{2-} (0·139), and Cl^- (0·324%).[43] The ash content naturally rises as carbonisation and activation remove volatile matter, and a typical activated coconut-shell charcoal has 3·5%

---

[36] Danby, Davoud, Everett, Hinshelwood, and Lodge, *J.*, 1946, 918.

[37] Barrow, Danby, Davoud, Hinshelwood, and Staveley, *J.*, 1947, 401.

[38] Kipling, *J.*, 1948, 1487.

[39] Garten and Weiss, *Austral. J. Chem.*, 1955, **8,** 68.

[40] Blayden, H. L. Riley, and Taylor, *J.*, 1939, 67.

[41] Deitz and Gleysteen, *J. Res. Nat. Bur. Stand.*, 1942, **28,** 795.

[42] Raistrick and Marshall, " The Nature and Origin of Coal and Coal Seams ", English Universities Press, London, 1948.

[43] Tendolkar and Thakoor, *J. Sci. Ind. Res., India*, 1952, **11,** *B*, 501.

[44] Honig, *Kolloid-Beih.*, 1926, **22,** 345.

[45] Kraus, *J. Phys. Chem.*, 1955, **59,** 343.

[46] Walker and Rusinko, *ibid.*, p. 241.

[47] Majumdar, *J. Sci. Ind. Res., India*, 1950, **9,** *B*, 22.

[48] Franklin, *Trans. Faraday Soc.*, 1949, **45,** 668.

[49] Alekseevski and Likharev, *J. Gen. Chem.* (*U.S.S.R.*), 1942, **12,** 306, 319.

[50] R. N. Smith, Pierce, and Joel, *J. Phys. Chem.*, 1954, **58,** 298.

TABLE 1*a*

	C	H	O	N	S	Cl	Ash	Ref.
Sugar charcoal, activated at 400° with oxygen	75·7	3·2	19·0	—	—	—	0·7	39
,, ,, ,, ,, 550° ,, ,,	85·2	2·1	10·4	—	—	—	1·33	39
,, ,, ,, ,, 800° ,, ,,	94·3	1·5	3·2	—	—	—	1·23	39
,, ,, ash extracted before activation	95·7	1·1	2·2	—	—	—	0·27	39
Cellulose coke, carbonised to 700° *	95·59	1·96	2·45	—	—	—	—	40
,, ,, ,, ,, 900°	97·26	1·07	1·67	—	—	—	—	40
Petroleum coke	99·70	0·11	—	—	—	—	—	41
Anthracite	92·5	3·5	1·9	1·2	0·9	—	—	42
Coconut-shell, unactivated	51·58	5·83	41·58	0·14	0·06	0·32	0·49	43
,, ,, after carbonisation to 29·72% yield	90·05	1·83	8·12	—	—	—	—	43
Typical coconut-shell charcoal, steam activated	86·7	1·8	9·5	—	—	—	2·0	†
Willow charcoal	87·89	2·46	7·47	0·17	0·08	—	1·93	2
Blood charcoal	82·97	0·95	4·95	3·12	0·69	—	8·02	44
Bone char (animal charcoal)	8·99	0·47	3·53	1·10	0·06	—	85·85	2
Carbon black	91·05	0·57	8·26	0·04	0·06	—	0·02	2
Channel ,,	95·84	0·71	3·40	—	0·02	—	0·03	45
Furnace ,, (gas)	97·52	0·32	0·42	—	0·09	—	1·65	45
,, ,, (oil)	98·22	0·30	0·83	—	0·41	—	0·24	45
Thermal ,,	99·22	0·48	0·24	—	—	—	0·06	45
Acetylene ,,	99·78	0·07	0·07	—	0·03	—	0·05	45
Spectroscopic graphitised carbon	99·99	0·00						42
Carbon graphitised at 2500°	99·77	0·08	0·06				0·07	46

* For analyses of cokes produced by carbonising coals to different temperatures, see ref. 48. † Analysed by Drs. Weiler and Strauss.

TABLE 1*b*

	Fixed C	Volatile matter	Ash	Ref.
Lamp black	94·1	5·9		8
Natural graphite (Ceylon)	94·98	1·40	3·62	47
,, ,, (Mysore)	64·55	2·50	32·93	47
Colourless diamond			0·02—0·05	10
Black ,,			Up to 4·8	10

of total ash, including K_2O (0·84), Na_2O (0·23), Fe_2O_3 (0·21), Al_2O_3 (0·68), CO_2 (0·05), and SiO_2 (0·26%).[51] Coal charcoals contain higher percentages of iron and sulphur.[52] Further inorganic materials may be added in " chemical " activation and in the impregnation of charcoals for special purposes, for example, platinised charcoals and whetlerites.[53] Similar analyses of ash from natural graphites are available.[54]

The ash, even if present to the extent of only a few units per cent., can profoundly alter the adsorbing characteristics of the carbon. This is not always sufficiently recognised, but it is especially evident in the adsorption of strong electrolytes (possibly by ion exchange) ; the ash also affects adsorption of non-electrolytes from solutions in water and some organic liquids, and even adsorption from the vapour phase.[55] Many years ago attention was drawn to chemical reactions which might take place between an organic preparation and the ash present in the charcoal used for its purification ; this is particularly important when animal charcoal is used.[56] Ash may also have specific catalytic effects on activation, as previously mentioned.

Ash-free carbons.—While ash is beneficial for a few special purposes (*e.g.*, in the adsorption of calcium from sugar liquors by bone chars) its presence is normally undesirable in fundamental studies of adsorption, and attempts have been made both to remove it from commercial carbons and to prepare carbons initially ashless. For the latter purpose charcoals are usually made from sucrose, which can be obtained very pure.[57, 58] The product, though substantially free from ash, may contain much combined oxygen, as oxygen is usually the activating agent (Table 1).

To remove ash from commercial charcoals, hydrochloric and hydrofluoric acids are used, followed by very careful washing with water ; [51, 59–62] a very simple procedure uses cold 35—40% hydrofluoric acid.[27, 55, 63] The use of hydrofluoric acid is often regarded as a standard method of removing ash, but recent evidence suggests that it may also alter the chemical nature of the surface ; [27] care must therefore be exercised in its use, particularly if the charcoals are to be used with acids or bases.

For many purposes it suffices to remove only some components of the ash, and less active reagents such as water or acetic acid can be used ; these are particularly suited to Soxhlet extraction.[55, 64, 65] Alternatively,

---

[51] Long and Sykes, *J. Chim. phys.*, 1950, **47**, 361.

[52] Kipling, *Fuel*, 1950, **29**, 62.

[53] Emmett, *Chem. Rev.*, 1948, **43**, 69.

[54] Mackles, Heindl, and Mong, *J. Amer. Ceram. Soc.*, 1953, **36**, 266.

[55] Blackburn and Kipling, *J.*, 1955, 4103.

[56] Caspe, *J. Chem. Educ.*, 1932, **9**, 907.

[57] Bartell and Miller, *J. Amer. Chem. Soc.*, 1922, **44**, 1866.

[58] Fernelius (ed.), " Inorganic Syntheses ", Vol. II, McGraw-Hill, New York, 1946.

[59] Miller, *J. Phys. Chem.*, 1926, **30**, 1031.

[60] Dobine, *Compt. rend.*, 1941, **212**, 790.

[61] Coolidge, *J. Amer. Chem. Soc.*, 1927, **49**, 708.

[62] R. N. Smith, Geiger, and Pierce, *J. Phys. Chem.*, 1953, **57**, 382.

[63] Korver, *Chem. Weekblad*, 1950, **46**, 301.

[64] Blackburn and Kipling, *J.*, 1954, 3819.

[65] *Idem*, *J.*, 1955, 1493.

ash can be removed from the raw material before carbonisation. Thus if coconut-shell is submitted to Soxhlet extraction with water, alcohol, and ether successively, only silica is left.[66]

Apart from carefully prepared sugar charcoals, the materials lowest in ash content are probably the synthetic graphites, especially those made for spectroscopic use. The manufacture of a graphite containing less than 0·004% of ash has been recorded.[67]

Physical Properties

A valuable critical review of methods used to determine surface area, pore distribution, and particle size of solids in general is given by Jacobs and Tompkins.[68a]

Adsorptive Properties.—*Charcoals.* There are two important methods of measuring the adsorptive capacity of charcoals which are to be used for the physical adsorption of gases and vapours.

Volume activity and weight activity. As charcoal is often used in columns (for solvent recovery, in gas masks, etc.) the *service time* or *breakdown time* is used to specify the time for which a given product will completely remove vapour from a stream of an inert carrier (usually air) passing through a standard column at a standard rate. For the assessment of respirators, official tests [1] specify the standard conditions for measuring the breakdown to carbon tetrachloride vapour. The results may also be expressed in terms of *volume activity,* defined as the weight in grams of carbon tetrachloride adsorbed by 100 bulk c.c. of charcoal under these conditions, or *weight activity,* measured in the same way for 100 g. of charcoal. Adsorption is so fast that these conditions approximate very closely to equilibrium.[37, 68b] Volume and weight activity are therefore close measures of the equilibrium saturation capacity, and (somewhat less closely) of specific surface area.

Monolayer capacity. The second important method is the estimation of the monolayer capacity by using Brunauer, Emmett, and Teller's (B.E.T.) equation.[69] The standard method [70] involves determining the adsorption isotherm for nitrogen at − 195·8° or − 183·0°. Other adsorbates have also been used, and a simplified apparatus has been devised to avoid the need for a vacuum system.[71] The B.E.T. method, though more fundamental as a measurement of surface area, has not been applied to an activation series as fully as has the volume activity test.

Several other important methods of determining surface areas of solids [69, 72, 73] have been used less significantly for charcoal than the above

[66] Reyerson, *Ind. Eng. Chem.*, 1925, **17**, 1114.

[67] Harkins, Jura, and Loeser, *J. Amer. Chem. Soc.*, 1946, **68**, 554.

[68] (*a*) Jacobs and Tompkins, in " Chemistry of the Solid State ", ed. Garner, Butterworths, London, 1955 ; (*b*) de Boer, " The Dynamical Character of Adsorption ", Clarendon Press, Oxford, 1953.

[69] Brunauer, " The Physical Adsorption of Gases and Vapours ", Oxford Univ. Press, London, 1944.

[70] Emmett in " Advances in Colloid Science, Vol. I ", Interscience, New York, 1942.

[71] Loebenstein and Deitz, *J. Res. Nat. Bur. Stand.*, 1951, **46,** 51.

[72] Gregg, " The Surface Chemistry of Solids ", Chapman and Hall, London, 1951.

[73] Emmett in " Catalysis, Vol. I ", Reinhold, New York, 1954.

methods. In all cases it is important to use samples large enough to avoid the remarkably varied adsorptive capacities which can be found for different granules from the same batch.[74]

Carbon Blacks.—Adsorptive capacity. The adsorptive capacity of carbon blacks is closely related to the particle size. If it is assumed that the particles are spherical, measurements of surface area can sometimes be used to determine particle size, and *vice versa*. In fact, electron micrographs show that the particles are roughly spherical, but shadow casting has enabled deviations to be detected.[75, 76]

The only important adsorption work has been done by the B.E.T. method. Measurements of adsorption from solution (for instance of dyestuffs or iodine) have an uncertain theoretical foundation [77] and give rise to conflicting claims in practice.[78, 79]

Particle size. Carbon-black particles are not of uniform size, and it is therefore usual to quote mean diameters based on size distributions estimated from electron micrographs.[80, 81] Particle sizes have also been estimated from the low-angle scattering of *X*-rays. Small particles, whether crystalline or amorphous, scatter *X*-rays through small angles. The intensity of the scattered radiation can be related to particle size on the assumption that the particles are spheres.[82]

TABLE 2

	Area (m.^{2}/g.)	Ref.
Nut-shell charcoals, various activations	644—1136	83
Lampblack	28	78
Acetylene black	64	78
Grade 6 rubber black	114	79
,, ,, ,, ,, after graphitisation at 2000° . .	90	79
Colour black	198	8
Mogul ink black	350	78
Carbolac I	947	78
,, ,, ...	936	84
Natural graphites	0·3—26·5	54
Synthetic graphite	8—110	85
Crushed diamonds (2μ diameter)	9	85

---

[74] Coffin and Long, *Canad. J. Res.*, 1947, **25**, *B*, 502.

[75] Watson, *J. Appl. Phys.*, 1949, **20**, 747.

[76] Cohan and Watson, *Rubber Age* (*New York*), 1951, **68**, 687.

[77] Kipling, *Quart. Rev.*, 1951, **5**, 60.

[78] W. R. Smith, Thornhill, and Bray, *Ind. Eng. Chem.*, 1941, **33**, 1303.

[79] Watson and Parkinson, *ibid.*, 1955, **47**, 1053.

[80] "Columbian Colloidal Carbons", Volumes I to III.

[81] Leigh-Dugmore, *Trans. Inst. Rubber Industry*, 1953, **29**, 92.

[82] D. P. Riley, Proceedings of Conference on the Ultra-fine Structure of Coals and Cokes, British Coal Utilisation Research Association, London, 1944.

[83] Fineman, Guest, and McIntosh, *Canad. J. Res.*, 1946, **24**, *B*, 109.

[84] Emmett and Cines, *J. Phys. Colloid Chem.*, 1947, **51**, 1329.

[85] Bartell and Dodd, *ibid.*, 1950, **54**, 114.

Surface area, and hence both adsorptive capacity and particle size, can be measured in permeability experiments. The flow of a gas or liquid through a column packed with fine particles is dependent on the external surface area of the particles.[72]

Typical Results.—Table 2 summarises typical values. Higher values have been quoted for some charcoals—even approaching the theoretical value for an extended single layer of graphite (2630 m.^{2}/g.)—though some downward revision has recently occurred, *e.g.*, Darco G from 2123 m.^{2}/g.[69] to 1295 m.^{2}/g.[71]

Effect of activation on adsorptive capacity of charcoals. The literature on charcoals has not sufficiently stressed that the adsorptive capacity (*a*) depends on the nature of the raw material and (*b*) varies continuously with the extent (time, temperature, concentration of activating agent) of activation,[15, 86, 87, 88] *i.e.*, charcoals are not simply " active " or " inactive ". Both points are illustrated in Fig. 3.[89]

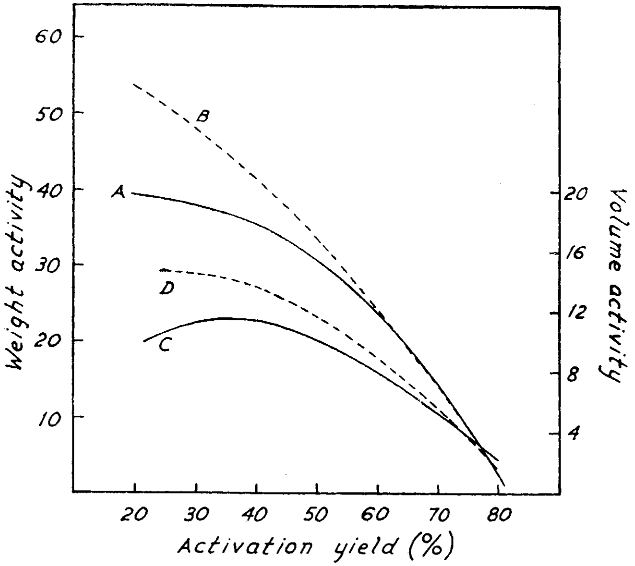


FIG. 3

Effect of steam activation on volume activity and weight activity of charcoals.

A, Volume activity ; nut-shell charcoal
B, Weight activity ; nut-shell charcoal
C, Volume activity ; unblended coal charcoal
D, Weight activity ; unblended coal charcoal

The extent of activation was early defined in terms of the loss of weight

---

[86] Lamb, Chaney, and Wilson, *Ind. Eng. Chem.*, 1919, **11**, 420.
[87] Burrage, *Trans. Faraday Soc.*, 1933, **29**, 564.
[88] Wiig and S. B. Smith, *J. Phys. Chem.*, 1951, **55**, 27.
[89] Hinshelwood *et al.*, " The Process of Charcoal Activation in Relation to the Properties of the Product ", unpublished report to the Ministry of Supply, 1942.

on activation,[90] though attempts to relate the properties of charcoals to this quantity were unfortunately not adopted for some years. The " activation yield " is simply the yield of activated charcoal expressed as a percentage of the weight of coke taken. Most physical properties (*e.g.*, density and particle strength, as well as adsorptive capacity) of charcoals are smooth functions of the activation yield. In Figs. 3 and 5, the activation yields are based on the weight of coke as directly prepared in the carbonisation process.[89] The coke may, however, suffer considerable loss in weight, even in the absence of an activating agent, between the temperature of its preparation (say 600—700°) and the temperature of activation (say 850—900°).[17] It has therefore been proposed that the activation yield should be based on the weight of coke after it has been heated in nitrogen to the higher temperature.[91] To refer to this loss of weight, which may take place in a stream of nitrogen or helium, as activation by inert gases [21] is hardly helpful.

The curves in Fig. 3 are reproducible for a given coke. This goes some way towards removing one of the greatest difficulties in adsorption studies, that of being unable to use the same material for repetition or extension of earlier work, or even to compare quantitatively two sets of results obtained on different charcoals.

Every volume-activity curve reaches a maximum, as there must be a point at which the removal of further material destroys more adsorption sites than it creates. Each maximum represents the limits of " activat-

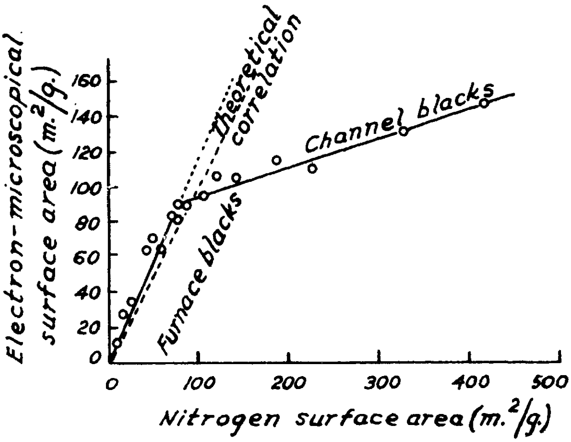


FIG. 4

Surface areas of carbon blacks ; comparison of values from electron microscope and nitrogen adsorption determinations.

[Reproduced, by permission, from Dannenberg and Collyer, *Ind. Eng. Chem.*, 1949, **41**, 1607.]

---

[90] Ray, *Chem. Met. Eng.*, 1923, **28**, 977 ; Bruns and Zarubina, *Kolloid Z.*, 1933, **64**, 279.

[91] Everett and Whitton, *Proc. Roy. Soc.*, 1955, **230** *A*, 91.

ability " imposed by the nature of the raw material,[89] and, as a secondary effect, its treatment in the carbonisation process.[17]

Particle size and surface areas of carbon blacks. Particle diameters of carbon blacks range from 33 to 2130 Å, giving surface areas of 947 to 15 m.^{2}/g.[78] Fig. 4 shows agreement between adsorption and electron-micrograph results for values up to about 100 m.^{2}/g. The change in slope at higher values is thought to show the development of pores in the carbons; [81, 92] it is marked in steam-activated carbon blacks known to be porous.[93] The burning of carbon spheres occurs not uniformly, but at specific sites from which pores can develop, thus considerably increasing the adsorbing area for a very small decrease in particle size.[94] Some of the higher values have also been criticised on the grounds that the cross-sectional area for the nitrogen molecule used in most calculations is too high,[95] and that, for some carbons, there is capillary condensation of nitrogen between the particles at high relative pressures.[96]

Density and Pore Volume.—Because many carbons are porous in nature, three types of density, bulk, granule, and material, can be defined.

Bulk density. The bulk, or apparent, density is the weight of material which can be packed into a given volume of container; [72] accurate results are quoted for particles of a specific grading. It was early used as an indication of the activity of charcoals. More recently it has been shown to decrease almost linearly with decreasing activation yield for charcoals from a given coke. Values between 0·3 and 0·7 g./c.c. are usual for gas-adsorbent charcoals.[17, 89] Each raw material gives its own range within these limits.

Granule density. The granule, or particle, density is the weight of a given (external) volume of granules, excluding the volume of free space between the granules. The free space can be determined by filling it with mercury, which does not penetrate the pores at atmospheric pressure.

Material density. This, the true density, is the weight of a given volume of the material comprising the granules, excluding the pore space. Its calculation requires a knowledge of the pore volume, which is useful in connection with the adsorptive capacity of the charcoals. Its determination simply involves a measurement of the volume of fluid, such as water, organic solvents,[69] liquid nitrogen,[97] or helium gas, required to fill the pores. The results show that there is an appreciable pore space in the unactivated coke which increases as activation proceeds,[89] and may in some cases exceed 1 c.c./g. The increase is not at all stages accompanied by an increase in adsorptive capacity; thus (Fig. 5) whereas the unactivated coke may adsorb substances with small molecules (*e.g.*, water), those with larger molecules (of which dyestuffs form a major group) are not adsorbed until

[92] Dannenberg and Collyer, *Ind. Eng. Chem.*, 1949, **41,** 1607.

[93] Turkevitch and Hubbell, *J. Amer. Chem. Soc.*, 1951, **73,** 1; Arnell and Henneberry, *Canad. J. Res.*, 1948, **26,** *A,* 29; Carman and Arnell, *ibid.*, 1948, **26,** *A,* 128.

[94] Dannenberg and Boonstra, *Ind. Eng. Chem.*, 1955, **47,** 339.

[95] Livingstone, *J. Colloid Sci.*, 1949, **4,** 447.

[96] Holmes and Emmett, *J. Phys. Colloid Chem.*, 1947, **51,** 1262.

[97] von Antropoff, *Kolloid Z.*, 1954, **137,** 105.

considerable activation has taken place.[98, 99, 100] This emphasises the importance of pore size in adsorption, which is considered in the next section.

The precise value obtained for the material density depends on the liquid used [69, 101] and has recently been shown to be directly proportional to the surface tension of the liquid.[102] The most accurate results are obtained with helium gas at 25° (at which temperature its adsorption is negligible),[103] giving values of 2·15 for coconut-shell charcoal, 2·26 for sugar charcoal, and 2·28 g./c.c. for Ceylon graphite.[104] During activation of coconut-shell, the value may rise from 1·98 to 2·07.[97] The similarity of these values to that of graphite is significant, as appears from X-ray work (p. 19). For a strict comparison, allowance should be made for the ash in charcoals, which is normally denser than the carbon and present in sufficient quantity to affect the density of the total material.

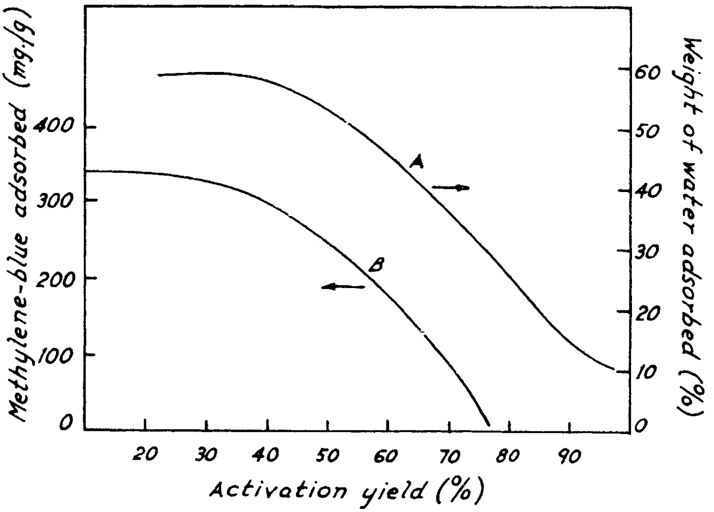


FIG. 5

Effect of activation on adsorption capacity of nut-shell charcoal.

A, adsorption of water vapour at saturation
B, adsorption of methylene-blue from aqueous solution

Pore Size.—For porous charcoals the adsorptive capacity for different adsorbates is related, not simply to the total pore volume, but to the volume available in pores of a specific size. The nature and size of these pores have been studied over many years, but many points remain on which there are differences of opinion. A recent Review by Dubinin gives

---

[98] Kipling, unpublished observations.

[99] Bell and Philip, *J.*, 1934, 1164.

[100] King, *J.*, 1934, 1975.

[101] Courty, " Charbons actives ", Gauthiers-Villars, Paris, 1952.

[102] Guest, McIntosh, and Stuart, *Canad. J. Res.*, 1946, **24**, *B*, 124.

[103] Franklin, *Trans. Faraday Soc.*, 1949, **45**, 274.

[104] Howard and Hulett, *J. Phys. Chem.*, 1924, **28**, 1082.

a very useful survey of Russian work on this problem.[105] It is proposed now merely to supplement this by reference to work done elsewhere. Early work is summarised by Brunauer,[69] and that done during the 1939—1946 war period by Emmett.[53] It will be useful to follow Dubinin's classification of pore sizes into the three groups of micro-pores, transitional pores, and macro-pores.

Macro- and transitional pores. These have been investigated by the " porosimeter " method. Mercury is forced into the pores under pressure, the pressure required being inversely proportional to the pore diameter.[106] Juhola and Wiig successfully calibrated their apparatus by using a hole of diameter $3{\cdot}8 \times 10^6$ Å (0·38 mm.), bored in coconut-shell charcoal [107] (cf. Emmett [53]), and then estimated pore sizes from 160,000 to 1200 Å diameter. For a zinc chloride-activated wood charcoal and an unactivated coke from briquetted coal, the macro-pore volume was a small fraction of the total, but the decolorising charcoal, Darco G, had a third of its internal volume in pores of diameter 40,000—160,000 Å. They estimated that for most charcoals having an adsorbing area of 1500 m.^{2}/g. the macro-pores contribute only about 3 m.^{2}/g.

A limitation seriously affecting all estimates of pore size is that the shape of the pores is not known. The simplest and most generally adopted assumption is that the pores are cylinders closed at one end,[108] though this is likely, especially in view of the *X*-ray findings, to be an idealisation, a point which should be borne in mind as methods of estimation are refined. Various other shapes have been suggested, usually in connection with theories to explain hysteresis in the adsorption of vapours, *e.g.*, " ink-bottle " pores,[109, 110] wedge-shaped pores,[111] and cylindrical pores open at both ends.[104, 112, 113]

Micro-pores. Estimates of pore sizes in this region depend on theories of adsorption, the applicability of which often extends to the transitional-pore region. These theories are open to criticism and subsequent modification to an extent which makes the results based on them uncertain in detail, though there is a large measure of agreement in semi-quantitative terms and this itself is of considerable value.

If adsorption is essentially confined to a monolayer, the pore diameter may be assumed to be at least two but not more than four molecular diameters ; [114] the latter is the minimum figure for the inception of hysteresis.[113] For multilayer adsorption the B.E.T. equation gives the

---

[105] Dubinin, *Quart. Rev.*, 1955, **9**, 101.

[106] Ritter and Drake, *Ind. Eng. Chem. Anal.*, 1947, **17**, 782.

[107] Juhola and Wiig, *J. Amer. Chem. Soc.*, 1949, **71**, 2078.

[108] Foster, *Trans. Faraday Soc.*, 1932, **28**, 645.

[109] Kraemer, in Taylor, " A Treatise of Physical Chemistry ", MacMillan, 2nd edn., New York, 1931.

[110] Voigt and Tomlinson, *Canad. J. Chem.*, 1955, **33**, 215.

[111] Rao, *J. Phys. Chem.*, 1941, **45**, 506.

[112] Foster, *ibid.*, 1951, **53**, 638 ; *J.*, 1952, 1806.

[113] Cohan, *J. Amer. Chem. Soc.*, 1938, **60**, 433 ; 1944, **66**, 98.

[114] Foster, *Discuss. Faraday Soc.*, 1948, **3**, 41.

maximum number of layers of adsorbate formed. From a knowledge of the molecular size and, sometimes, of the orientation of the adsorbate, values between 10 and 100 Å have been obtained for the pore diameters.*

Hysteresis and Capillary Condensation.—In principle, the capillary condensation theory is of the greatest use, as it can lead to an analysis of the *distribution* of pore sizes. It was introduced to explain the hysteresis observed in some adsorption isotherms, but has been extensively modified to take into account the likelihood that monolayer or even multilayer adsorption takes place before liquid condenses in the capillaries. Its present standing is discussed by Ries,[115] Eley,[116] Foster,[112, 114] and others.[117, 118] Everett and Whitton have introduced a " domain " theory of hysteresis which may further modify our conception of adsorption in micro-pores.[119]

Quantitatively the theory uses the Kelvin equation [120]

$$r = \frac{2\gamma V \cos\theta}{RT \ln(p_0/p)}$$

to relate pore radius, r, to the relative pressure, p/p_0, at which condensation occurs ; V is the molar volume, γ the surface tension at temperature T, and θ the angle of wetting. Its application to the range of pressure in which hysteresis is observed gives a corresponding distribution of pore size. Unfortunately, there is uncertainty as to (*a*) the validity of using normal molar volumes and surface tensions with columns of liquids having a meniscus only a few molecular diameters wide, (*b*) whether the equation should be applied to the adsorption or desorption branch of the isotherm, and (*c*) the angle of wetting. On these grounds, some authors reject its use outright ; others consider its use to be justified if attention is paid to these points.

The pore-size distribution of steam-activated nut-shell charcoals calculated directly from the desorption branch of the benzene isotherm shows a sharp peak at a diameter of 30 Å for gas-adsorbent charcoals, with an additional peak at 60 Å for those used for adsorption from solution.[121] *X*-Ray studies give similar results.[122] Everett and Whitton, however, prefer to describe this system as showing " a phase-change from monolayer to multilayer adsorption ", rather than capillary condensation, as the pore diameters are only two or three times the molecular diameter of benzene. They discuss adsorption in the pores in some detail.[91]

Barratt, Joyner, and Halenda have used the low-temperature nitrogen isotherm. Desorption is considered to involve two processes : (i) liquid

---

[115] Ries in " Catalysis, Vol. I ", Reinhold, New York, 1954.

[116] Eley, *Ann. Reports*, 1952, **49,** 18.

[117] Carman, *J. Phys. Chem.*, 1953, **57,** 56.

[118] Pierce and R. N. Smith, *ibid.*, p. 64.

[119] Everett and Whitton, *Trans. Faraday Soc.*, 1952, **48,** 749.

[120] Thomson, *Phil. Mag.*, 1871, [4], **42,** 448.

[121] Davies, *Chem. and Ind.*, 1952, 160.

[122] Brusset, *Bull. Soc. chim. France,* 1949, **16,** 323.

* Pore sizes are sometimes quoted as diameters and sometimes as radii, even by the same authors.

which has been adsorbed by capillary condensation is progressively removed, leaving the capillary wall covered with " physically adsorbed " vapour in a multilayer, (ii) as the partial pressure is lowered, the thickness of this vapour film decreases as it would on desorption from a plane surface.[123] The thickness of the vapour film at any relative pressure is taken from data on adsorption of nitrogen by crystals.[124] Hence the amount of liquid held by capillary condensation can be calculated and used to deduce, from the Kelvin equation, the size of the central region of the pore. This, added to the thickness of the " physically adsorbed " vapour film, gives the total diameter of the pore.

Activated charcoal is thus shown to have a mean pore diameter of less than 20 Å. New bone char has a wide range of pores, between 20 and 200 Å in diameter, the smallest being lost in the re-activation process; the latter figures are confirmed by the porosimeter method.[125]

The Water Isotherm.—This isotherm has been used extensively because it has a much bigger hysteresis loop than most others. It was long thought that the shape of the adsorption branch of the isotherm indicated capillary condensation. It now seems clear, however, that it is due to the absence of strong forces between the surface and the water except where oxygen complexes provide centres of adsorption; from these, " islands " of water molecules can grow, held together by hydrogen-bonding.[45, 126] This theory is supported by the alteration in the shape of the isotherm which can be brought about by removing or augmenting the surface complexes,[127–129] and by the observation of the same shape of isotherm (but without a hysteresis loop) for non-porous carbon black.[130] Thus a hysteresis loop must be present before the capillary condensation theory can be applied. The shape of the water isotherm is also dependent on the ash content of the charcoal.[61, 128, 131] Adsorption is much higher if ash is present, presumably owing to the formation of a solution of the ash[67] as has been found for metals.[132] The contact angle (θ) of water with graphite is markedly dependent on the ash content;[133] the importance of ash in this respect has generally been overlooked.

It is now usual, though not universal, to apply the Kelvin equation to the desorption branch of the water isotherm. In the past, it was usually assumed that $\cos \theta = 1$, but values of 0·62—0·65 gave the same pore

---

[123] Barrett, Joyner, and Halenda, *J. Amer. Chem. Soc.*, 1951, **73**, 373.

[124] Shull, *ibid.*, 1948, **70**, 1405.

[125] Joyner, Barrett, and Skold, *ibid.*, 1951, **73**, 3155.

[126] Bering and Serpinsky, *Bull. Acad. Sci.* (*U.S.S.R.*), 1953, 851; McDermot and Arnell, *J. Phys. Chem.*, 1954, **58**, 492.

[127] King and Lawson, *Trans. Faraday Soc.*, 1934, **30**, 1094; Lawson, *ibid.*, 1936, **32**, 473.

[128] Burrage, *J. Phys. Chem.*, 1933, **37**, 1095.

[129] Emmett and Anderson, *J. Amer. Chem. Soc.*, 1945, **67**, 1492.

[130] Dubinin, Zaverina, and Serpinsky, *J.*, 1955, 1760.

[131] Allmand, Hand, Manning, and Shiels, *J. Phys. Chem.*, 1929, **33**, 1682; Allmand, Hand, and Manning, *ibid.*, p. 1694.

[132] Bowden and Throssell, *Proc. Roy. Soc.*, 1951, *A*, **209**, 297.

[133] Majumdar, *J. Sci. Ind. Res., India*, 1949, **8**, *B*, 232.

distribution [134, 135] as that calculated by Barrett, Joyner, and Halenda's method (p. 17). Similarly, Juhola and Wiig have found a value of 0·49 appropriate for the desorption branch, or 0·28 for the adsorption branch,[136] though the values may vary according to the nature of the surface.[135] These values were obtained by reference to an alternative method which involves the assumption that water is adsorbed by capillary condensation, but avoids the use of the Kelvin equation. Water is adsorbed in stages, and after each stage the remaining free surface is estimated by the usual low-temperature nitrogen method. If the pores are cylindrical, the surface area A of pores of diameter D having a total volume v, is given by $A = 4v/D$. The experimental data give a curve from which $\mathrm{d}v/\mathrm{d}A$ can be obtained and used in this equation to derive a curve of v against D. Thus the pore distribution is referred ultimately to the B.E.T. surface-area determination, the water being used to block the pores stage by stage in order of increasing size. Of the materials studied, an unactivated coke made from coal showed mainly monolayer adsorption, an activated charcoal had pores mainly of 10—40 Å in diameter, as did Darco G 60, which, however, also had a significant volume of pores of diameter 100—200 Å.

If a powder is compressed into a porous plug, the type of isotherm is changed by the introduction of capillary condensation at the higher relative pressures.[137] This leads to a further method for determining pore-size distributions [138] which is, however, unlikely to find wide use in this field, as it involves a knowledge of the adsorption isotherm on the free surface of the material, and this is usually not available.

Heats of Wetting.—A quite different method is based on the observation that for non-porous carbonaceous solids the heat of wetting is essentially constant at 400 ergs/cm.^{2} (or 1 cal./10 m.^{2}) for a group of organic liquids showing a nearly 8-fold range of molecular volume.[139] For porous carbonaceous solids this could be used to investigate the micro-pore distribution by relating the heats of wetting to the molecular volumes for this series of liquids.[140] If the surface orientations of the adsorbates were known it would be better to relate the heats of wetting to the adsorbed area. (At more polar surfaces, the nature of the wetting liquid becomes more important,[141] and ash content may also be significant.[142])

Distributions of pore volume with pore diameter usually approximate to the Gaussian distribution found originally by Kubelka for charcoals,[143] and by Foster for oxide gels.[108] The spread is considerable in many cases (cf. Dubinin [105]), though the new Saran charcoals have a very narrow range [53] and consequently show "molecular sieve" properties.[13] This doubtless

---

[134] McDermot and Arnell, *Canad. J. Chem.*, 1952, **30**, 177.

[135] Juhola, Palumbo, and S. B. Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 61.

[136] Juhola and Wiig, *ibid.*, 1949, **71**, 2069 ; Wiig and Juhola, *ibid.*, p. 561.

[137] Carman and Raal, *Proc. Roy. Soc.*, 1951, *A*, **209**, 59.

[138] Carman, *ibid.*, 1951, *A*, **209**, 69.

[139] Bond and Maggs, *Fuel*, 1949, **28**, 169.

[140] *Idem, ibid.*, p. 172.

[141] Chessick, Zettlemoyer, Healey, and Young, *Canad. J. Chem.*, 1955, **33**, 251.

[142] Basford, Jura, and Harkins, *J. Amer. Chem. Soc.*, 1948, **70**, 1444.

[143] Kubelka, *Kolloid Z.*, 1931, **55**, 129.

reflects the homogeneity of the polymer from which they were prepared, as contrasted with the inhomogeneous wood, coal, or nut-shell used for making most charcoals. The suitability of charcoals for adsorption of different substances is thus clearly determined in large measure by the pore-size distribution.

Effect of Activation.—It remains to discuss the way in which activation affects the distribution of pore size. In extensive steam activation of Saran charcoal, the width of the pores is reported to increase without the creation of any new pores.[144] Correspondingly the rate at which exchange takes place between adsorbed radioactive benzoic acid and non-radioactive benzoic acid in solution increases as activation proceeds.[62] Unactivated Saran chars are reported to have pores mainly of diameter 5—10 Å. Yet, even allowing for the increase in size on activation, the estimation of a mean pore diameter of " 12—15 molecular diameters " for the activated charcoals seems large, and certainly greater than is found for most of the charcoals discussed so far.

It is far from certain that other charcoals behave in this way, particularly as it has been shown that steam-activation can produce pores in previously non-porous carbon blacks,[145, 146] and that oxygen activation can increase the surface area of graphite, presumably by creating new pores.[147] The creation of new (small) pores, with simultaneous increase in the size of existing pores, is found with steam or hydrogen activation of charcoals [25, 53] and with carbon dioxide activation of petroleum cokes.[147] For steam activation, carried out over a wide range of activation, the mean pore diameter of coconut-shell charcoals remains almost constant (at no more than 30—40 Å),[98] and that of coal charcoals gives only a very small increase (from 14 to 20 Å), though there is a large increase in total micro-pore volume,[88] and probably a decrease in the fraction of macro-pore volume.[69]

These very narrow pores restrict multilayer adsorption very considerably as compared with that taking place on non-porous carbon blacks or even solids with wider pores such as the oxide gels. This applies both to vapour adsorption, in which the Type I isotherm typical of monolayer adsorption [148] is characteristic of charcoals, and to adsorption from solutions.[64, 149, 150]

***X*-Ray Analyses.**—*X*-Ray analysis of amorphous carbon and graphite has recently been reviewed by Riley [4] and Cameron.[151] Riley concluded that amorphous carbons may show two types of structure. The first contains very small turbostratic lamellae [152] which may be considered as

---

[144] Pierce, Wiley, and R. N. Smith, *J. Phys. Chem.*, 1949, **53**, 669.

[145] Anderson and Emmett, *J. Appl. Phys.*, 1948, **19**, 367.

[146] *Idem*, *J. Phys. Chem.*, 1952, **56**, 756.

[147] Gulbranson and Andrew, *Ind. Eng. Chem.*, 1952, **44**, 1039, 1048.

[148] Carteret and Imelik, *Bull. Soc. chim. France*, 1954, **21**, 65.

[149] Hansen, Fu, and Bartell, *J. Phys. Colloid. Chem.*, 1949, **53**, 769.

[150] Morrison and Miller, *Canad. J. Chem.*, 1955, **33**, 330.

[151] Cameron, *Gas and Coke*, 1950, 21.

[152] Biscoe and Warren, *J. Appl. Phys.*, 1942, **13**, 364 ; Warren in " Chemical Architecture ", Interscience, New York, 1948.

essentially similar to graphite in two dimensions but lacking the complete orientation shown by graphite in the third ; it is usually found in the purer carbons. The second type may possess a disordered cross-linked structure, possibly stabilised by the presence of other elements ; it is found in charcoals made from selected compounds rich in oxygen (*e.g.*, mellitic acid), the charcoals themselves containing not less than 4% of oxygen. The behaviour on carbonisation is in marked contrast to that of materials low in oxygen (*e.g.*, benzanthrone and bituminous coal).[153] Many types of charcoal and coke contain both structures. Crystallite dimensions of 20—60 Å suggest the probable existence of micro-pores of the sizes discussed above. In some cases, closed pores may exist,[154] or pores may be too small to be penetrated even by the small water [83] or nitrogen [12] molecules. These may be formed either by disordered stacking of crystallites or by inter-crystallite linking through non-graphitic carbon. Such blocks may be removed by slight oxidation.

Franklin claims that small graphitic layers are present to some extent in all carbons. For carbons prepared at temperatures up to 1000° there is a linear relationship between the layer diameter (up to about 25 Å) of this organised carbon and the percentage of non-organised carbon present.[155, 156] She divides carbons into three groups : (*a*) graphitic carbons, showing to a considerable extent the *three*-dimensional graphite structure, (*b*) graphitising carbons, which develop such a structure on being heated to a temperature between 1700° and 3000°, and (*c*) non-graphitising carbons which show no such growth even at 3000°. She claims that when samples from groups (*b*) and (*c*) are heated from 1000° to 1700°, they give two distinct plots of layer diameter against number of layers per group or crystallite, the former producing far more layers per crystallite than the latter. The claim, however, is not substantiated by a more recent investigation of a large range of chars and carbon blacks.[157]

The non-graphitising carbons contain linkages between the crystallites which bind them into a non-oriented state, thus incidentally maintaining a micro-pore structure between the crystallites. Even in fine-particle carbon blacks, having only negligible binding material, the lack of a suitable degree of orientation of the crystallites may be enough to prevent graphitisation.

During graphitisation the interlayer spacing in the disordered material is greater than in graphite, becoming equal to that in graphite in groups of oriented layers,[158] though in some cases a complete graphite (*X*-ray) pattern is not obtained, even after heating [33] to 3300°. The *c*-dimension of the graphite unit cell varies with the crystallite thickness, reaching a limiting value [159] at a thickness of 400—500 Å. The ordering of the layers

---

[153] T. D. Smith, *J.*, 1952, 923.

[154] Dresel and Roberts, *Nature*, 1953, **171**, 170.

[155] Franklin, *Proc. Roy. Soc.*, 1951, *A*, **209**, 196.

[156] *Idem*, *Acta Cryst.*, 1950, **3**, 107.

[157] Austin and Hedder, *Ind. Eng. Chem.*, 1954, **46**, 1520.

[158] Franklin, *Acta Cryst.*, 1951, **4**, 253.

[159] Bacon, *ibid.*, p. 137.

begins with pairs of adjacent layers. The probability of a pair of nearest neighbours having a graphite orientation has been suggested as a quantitative measure of the " degree of graphitisation ",[160] but the process may also involve the edgewise joining of layers.[157]

Steam activation of coconut-shell charcoal is reported not to alter the mean size of the graphitic crystallites, which have [161] a diameter of 10—12 Å, and a height of 40—50 Å. The adsorbing surface (available to nitrogen) is originally less than half the area presented by these crystallites, but becomes equal to the " *X*-ray " area as the activation proceeds. This suggests that the activation process consists mainly of removing amorphous material from regions between the crystallites. On the other hand, it has been claimed that the radius of the crystallites is reduced by steam activation ; [162] possibly this refers to the later stages of the process. Mechanical grinding reduces both the height and diameter of the crystallites in graphite.[163]

For a comparison of the structures of different carbon blacks, see Clark, Eckert, and Burton's paper.[164]

Surface Complexes

The analyses quoted in Table 1 show that most of the carbons contain appreciable amounts of hydrogen and oxygen. These amounts appear more significant if expressed on an atomic basis. The sugar charcoal prepared at 550° has roughly 30 atoms of hydrogen and 9 of oxygen for every 100 atoms of carbon ; the charcoal prepared at 800° has about 20 atoms of hydrogen and 6 of oxygen for every 100 atoms of carbon. From the structure revealed by *X*-ray analysis,[4, 165] it is clear that these elements must be present mainly at the edges of the giant molecules forming the layer planes, and must therefore cover a large fraction of the carbon atoms at the adsorbing surfaces. In accordance with this, the heat of immersion of carbon blacks in polar liquids (capable of hydrogen-bonding with oxide groups) is proportional to the oxygen content per unit surface area.[45] The " extraneous " elements appear to be essential constituents of at least the highly adsorbent carbons, inasmuch as these have only been prepared in forms containing substantial amounts of hydrogen and usually of oxygen ; furthermore the forms of amorphous carbon which resist graphitisation always contain extraneous elements.

Removal of both hydrogen and oxygen is only possible by heat treatment sufficiently drastic to alter the structure of the material in the direction of making it less adsorbent. Alternatively, the removal may not be permanent ; charcoals outgassed at 1200° chemisorb almost as much oxygen as they originally held when they are again exposed to air at room temperature.[30] Nor is it possible to prepare a material of high surface area from carbon of high purity except by reducing it to very fine particles,

[160] Houske and Warren, *J. Appl. Phys.*, 1954, **25**, 1503.

[161] Arnell and Barss, *Canad. J. Res.*, 1948, **26**, *A*, 236.

[162] Turkevitch, Hubbell, and Hillier, *Discuss. Faraday Soc.*, 1950, **8**, 348.

[163] Bacon, *Acta Cryst.*, 1952, **5**, 392.

[164] Clark, Eckert, and Burton, *Ind. Eng. Chem.*, 1949, **41**, 201.

[165] H. L. Riley, *Chem. and Ind.*, 1939, **17**, 391.

and when graphite is frictionally reduced to powder over 1% of the surface can at once chemisorb hydrogen,[166] an observation in harmony with the view that some fracture of the layer planes themselves takes place.[167] Diamond normally carries adsorbed gases which are only removed completely by outgassing at 1000° ; [168] and " Graphon ", a partially graphitised carbon black, though essentially hydrophobic, has hydrophilic sites amounting to 1/1500 part of the surface ; this may account for the effect of water vapour on the lubricating surface of graphite.[169]

Nature of Surface Complexes.—The combined hydrogen and oxygen are said to form " surface complexes ", the extent of which is indicated by outgassing at temperatures up to 1200°. The oxygen complexes of charcoals usually cover less than half the surface. An elementary indication of their nature is obtained by analysing the gases given off in such heating for hydrogen, carbon monoxide, carbon dioxide, methane, and water. Hydrogen is driven off at considerably higher temperatures than are the oxides of carbon.[33, 170]

This method of analysis also shows how far it is possible to alter the nature of the surface complexes. Steam activation, for example, particularly at temperatures between 800° and 1200°, increases the amount of hydrogen chemisorbed, but adds only small amounts of oxygen,[53, 171] and may even reduce it for some carbon blacks.[146] Washing charcoals with hydrochloric acid to remove ash may also modify the surface complexes.[27] Physical adsorption of vapours is no longer thought to displace complexes.[30] Water vapour, however, may react slowly with the surface even at room temperature.[12, 50, 172]

Acid–Base Properties of Carbons.—Further evidence as to the nature of surface complexes has come from a study of the adsorption of strong electrolytes, which has been critically reviewed by Steenberg.[5] Early work on charcoals of high ash content is of doubtful value, but the importance of working with ash-free charcoals was recognised many years ago by Bartell and Miller.[57] The important distinction must be made here between adsorption of strong and of weak electrolytes, as the latter may be adsorbed as undissociated molecules, and thus be subject to quite different influences.[77, 173] Results obtained in adsorption of synthetic dyestuffs (usually strong electrolytes) have often proved very disappointing when applied (inappropriately) to some of the natural dyestuffs (often weak electrolytes) encountered industrially.

It has long been known that different charcoals can adsorb strong acids or bases ; they may even change the pH of distilled water when shaken

---

[166] Savage and Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 2362.

[167] Savage, *J. Appl. Phys.*, 1949, **20**, 747.

[168] Bowden and Young, *Proc. Roy. Soc.*, 1951, *A*, **208**, 444 ; Bowden, Young, and Rowe, *ibid.*, 1952, *A*, **212**, 485.

[169] Young, Chessick, Healey, and Zettlemoyer, *J. Phys. Chem.*, 1954, **58**, 313.

[170] Loebenstein and Deitz, *ibid.*, 1955, **59**, 481.

[171] Long and Sykes, *Proc. Roy. Soc.*, 1948, *A*, **193**, 377.

[172] McBain and Sessions, *J. Colloid Sci.*, 1948, **3**, 213.

[173] Kipling, *J.*, 1948, 1483.

with it alone,[8] a property which, for carbon blacks, is directly related to the volatile content.[174] The pH produced with standard quantities of carbon black and water ranges from 2·6 to 5·7 for various grades of impingement black and from 8·2 to 9·3 for non-impingement blacks. If the blacks are heated in the absence of air, the pH to which they give rise increases from 3·6 after treatment at 400° to 10·8 at 1100° ; [175] in moist oxygen sugar charcoals give figures of 4·0 for 200° to 9·1 for 920°.[176]

The work of many laboratories has shown that acids are adsorbed if the carbons are activated in air or oxygen at temperatures of 50° or over, and bases are adsorbed if the temperature remains below 600°. Steenberg proposes to refer to the former, which do not adsorb alkali-metal hydroxides, as H charcoals, and to the latter as L charcoals. Both types can be made from the same material. Indeed, if a charcoal activated at a high temperature is cooled *slowly* in air or oxygen, it becomes an L charcoal. A very careful quantitative study of the effect of temperature on the relative capacities of activated sugar charcoals for strong acids and bases has been made by Wilson and Bolam ; [177] measurement of the adsorption of iodine at each stage showed that changes in adsorption of acids and bases were not due solely to alteration in surface area, and must have been due to alteration in the nature of the surface (cf. Weller and Young [178]).

Steenberg has reviewed the several early theories of adsorption of acids and bases, some of which postulated the existence of quite specific surface oxides. For example, it was suggested [179] that charcoal could have two basic oxides, *A* and *B*, and one acidic oxide, *C* (Fig. 6). A rather different matter is the oxidising properties shown by some charcoals (*e.g.*, liberation of iodine from acidified potassium iodide) which has been attributed to the existence of peroxide groups on the surface.[180]

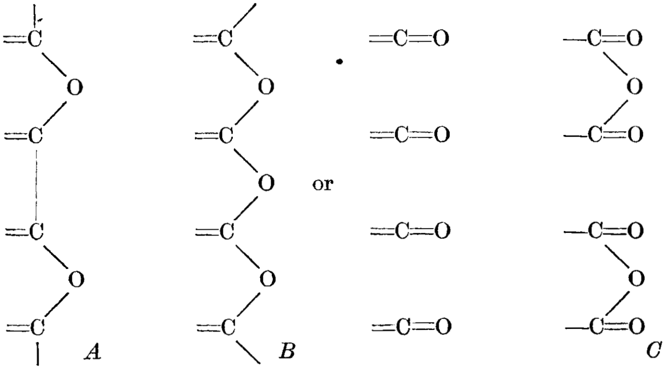


FIG. 6

---

[174] Cines, *Rubber Age* (*New York*), 1951, **69,** 183.

[175] Wiegand, *Ind. Eng. Chem.*, 1937, **29,** 953.

[176] King, *J.*, 1935, 889.

[177] Wilson and Bolam, *J. Colloid Sci.*, 1950, **5,** 550.

[178] Weller and Young, *J. Amer. Chem. Soc.*, 1948, **70,** 4155.

[179] Schilow, Schatunowskaja, and Tschmutow, *Z. phys. Chem.*, 1930, *A*, **149,** 211.

[180] Lamb and Elder, *J. Amer. Chem. Soc.*, 1931, **53,** 137 ; King, *J.*, 1933, 842.

Recently authors have been more cautious of formulating specific groupings, and especially of postulating the existence of a basic surface oxide—a concept out of harmony with the properties of any of the oxides existing in bulk. The work of Steenberg and of Wilson and Bolam suggests that adsorption of bases is due to the existence of an acidic oxide (or, as the latter authors suggest, to two types of oxide, cf. Long and Sykes [171]), whereas the adsorption of hydrochloric acid is due to the primary adsorption of hydroxonium ions by the carbon surface, the chloride ions being secondarily adsorbed by electrostatic attraction. Wilson and Bolam's fully oxygenated charcoal contained 80·5% of carbon, 16·5 of oxygen, and 0·5 of hydrogen, the remainder being water, *i.e.*, 15 atoms of oxygen for every 100 of carbon, which must represent a high percentage of oxygen atoms if referred to the number of carbon atoms present in the surface.

Acids can be displaced from H charcoals by organic solvents, suggesting that the primarily adsorbed ions are not held by specific forces.[5] Alkalis adsorbed on L charcoals cannot be so displaced, and appear to be attached to specific groups. They can, however, be removed completely by washing with strong acids; this process is not merely neutralisation at the surface because such adsorption–desorption cycles can be repeated, showing that the surface of the charcoal is not irreversibly altered.[178]

A more direct analysis of the surface oxides uses the Grignard reagent, methylmagnesium iodide, to determine the types of grouping present in the oxygen complexes.[181] In carbon blacks an average of only 26% reacted, of which rather more was present as carbonyl than as hydroxyl oxygen. The remainder is assumed to be present as ether oxygen, possibly binding graphitic layers together. Another technique is to record the emission spectra obtained from the impact of fast electrons used to remove the surface groups.[182] Among the groups desorbed from carbon blacks were OH, CH, CO, CO_2^+, and CHO. The last two are taken to indicate the presence of carboxyl and aldehyde groups respectively. The suggestion that oxygen complexes may be involved in the bonding of carbon blacks to rubber,[183] a process presumed to involve the double bonds in the polymer,[184] will no doubt stimulate further work of this kind.

From these analyses and other experimental evidence of their own, Garten and Weiss have suggested that the surface oxide groups, together with the condensed-ring structures of the graphitic crystallites, may form a quinone–quinol system.[39] Electrolytic reduction of H charcoals rendered them markedly acidic. This would not be achieved by reduction of carbonyl oxygen (to alcohol), and ether oxygen would not suffer reduction, but quinonoid groups could be reduced to phenolic groups of a quinol character. The titration curves of L charcoals suggest that they also contain phenolic groups (cf. ref. 185), but not carboxylic groups unless there has

[181] Villars, *J. Amer. Chem. Soc.*, 1948, **70**, 3655.

[182] W. R. Smith and Schaeffer, Proc. 2nd Rubber Technology Conference, London, 1948.

[183] Schaeffer, Polley, and W. R. Smith, *J. Phys. Colloid Chem.*, 1950, **54**, 227.

[184] Polley, Schaeffer, and W. R. Smith, *Canad. J. Chem.*, 1955, **33**, 314.

[185] Villars, *J. Amer. Chem. Soc.*, 1947, **69**, 214

been extensive autoxidation. Sugar charcoal prepared at temperatures between 600° and 700° can adsorb both acids and bases. This might well contain both quinone and quinol groups; indeed a semiquinone system could be stabilised by resonance involving many structures, as is well illustrated in the original paper.

In H charcoals the quinone structure involves the fixation of some double bonds, so that the structure becomes olefinic instead of aromatic. This would explain the several addition reactions, including the chemisorption of halogens and the formation of peroxide groups (which, in conjunction with adjacent quinone groups, permit the adsorption of acids through formation of 'oxonium groups). The double bonds would also form sites for combination with rubber polymers, leading to cross-linking which results in mechanical reinforcement of the rubber. In vulcanised rubbers, carbon–sulphur–polymer links would be formed.[186]

Effect on Adsorption of Non-electrolytes.—The effect of activation temperature on adsorption from solutions of non-electrolytes or weak electrolytes is not so profound. Adsorption of fatty acids from aqueous solution depends only on the surface area available, and is otherwise independent of the temperature of preparation of the charcoal.[41, 173, 187, 188] On the other hand, the difference between H and L charcoals may be sufficient to affect the competition between the components of a binary organic mixture for the surface. Thus benzene is more strongly adsorbed on H charcoals than is ethyl alcohol, in which respect the charcoals show the opposite affinity from that of silica gel.[77] L charcoals, however, show much greater affinity than H charcoals for alcohols, and can be made to approach silica gels in their behaviour.[189] This may be due to the existence of polar groupings not dissimilar from those present in the oxide gels.

In the physical adsorption of vapours, the oxygen complexes have little effect except on the most polar substances such as water. It is, however, not sufficiently realised that " carbon " adsorbents do not present a surface of elementary carbon to the adsorbate, but one which can usually be regarded as a hydrocarbon surface, modified in places by combined oxygen. This point is particularly significant when carbons are compared with other adsorbents.

Heating in the absence of an activating agent may lead to a rapid decrease in surface area at temperatures above 800°;[187] the process involved has been described as sintering, but can also be interpreted more specifically as part of a gradual progress towards graphitisation. Furthermore, heating to a much higher temperature (say, up to 2000°) leads to a progressive loss of hydrogen. Adsorption may then take place on a true carbon surface instead of the " hydrocarbon " surface which is presented by most charcoals made at relatively lower temperatures; the change

[186] Stearns and Johnson, *Ind. Eng. Chem.*, 1951, **43,** 146.

[187] Linner and Williams, *J. Phys. Colloid Chem.*, 1950, **54,** 605.

[188] Hansen, Hansen, and Craig, *ibid.*, 1953, **57,** 215.

[189] Bartell and Lloyd, *J. Amer. Chem. Soc.*, 1938, **60,** 2120.

from a heterogeneous to a homogeneous surface results in the adsorption isotherm for argon changing from being smooth to being stepwise.[33, 190]

Summary

The main conclusions of the foregoing survey are : (*a*) The adsorptive capacity of any type of charcoal can be varied, within limits, by controlling the activation process, the upper limit of activity being set by the nature of the raw material, and, in part, by its treatment during carbonisation.

(*b*) The adsorptive capacity for any given type of adsorbate depends on the distribution of pore sizes, different types of charcoal being suitable for different purposes ; the finest pores have diameters between 15 and 50 Å. The adsorptive capacity of carbon blacks depends primarily on the particle size.

(*c*) Most " carbons " contain chemically bonded hydrogen and oxygen, and may also contain appreciable quantities of ash ; both types of impurity may affect adsorption. Ash can usually be removed. The chemically bonded elements, however, result in there being presented to adsorbates, not a carbon surface, but something more nearly described as a hydrocarbon surface modified by some oxygen groups.

(*d*) Most " carbons ", because they are not pure carbon, cannot be regarded as a third allotropic form of the element, " amorphous carbon ". They represent incomplete conversion of organic compounds into carbon, and, if the process can be completed, graphite is formed.

(*e*) Highly porous charcoals cannot be formed from pure carbon. Combined hydrogen and oxygen are responsible for the forms in which charcoals can be made. These are so numerous that care should be taken in choosing a charcoal suitable both in physical and chemical properties for the purpose intended.

The author is grateful to the Chief Scientist, Ministry of Supply, for permission to refer to previously unpublished work.

[190] Amberg, Spencer, and Beebe, *Canad. J. Chem.*, 1955, **33**, 305.