435. Studies in Chemisorption on Charcoal. Part V. The Influence of Ultraporosity on Adsorption.

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THE term ultraporosity (Ultraporosität) was first introduced by Herbst (*Biochem. Z.*, 1921, **115**, 204) to explain why carbon dioxide was adsorbed to a larger extent on a certain charcoal than sulphur dioxide, it being assumed that the sulphur dioxide molecule was considerably larger than that of carbon dioxide and therefore unable to enter the ultrapores. Actually, there is little difference between the two molecular diameters, and under comparable conditions sulphur dioxide is adsorbed to a markedly greater extent than carbon dioxide; nevertheless, this concept of the inaccessibility of small pores to large molecules is useful and has been retained.

An example of an almost perfect molecular sieve is afforded by the zeolite, chabesite, whose structure is extremely regular, the pores being, according to Schmidt (*Z. physikal. Chem.*, 1928, **133**, 280), approximately 3·5 Å. in diameter. The mineral is thus able to adsorb small molecules such as those of water and methyl and ethyl alcohols, but ether, benzene, and larger molecules are almost completely excluded. Charcoal does not exhibit such a definite effect, for its pores are not so uniform; the deviation from a constant pore size is not, however, sufficiently great to exclude the effect, but merely obscures its influence.

Bell and Philip (this vol., p. 1164), in measuring the areas of charcoals by the adsorption of various materials from solution, noticed that while the adsorption of benzoic acid increased regularly with time of activation in air at 800°, naphthalenesulphonic acid did not begin to be adsorbed until after 6 hours' and methylene-blue until after 10 hours' activation. This they explain as being due to the gradual opening up of pores by progressive oxidation, more highly activated charcoals having larger pores and therefore being capable of adsorbing larger molecules.

Further evidence of the influence of the size of ultrapores on the magnitude of adsorption has been derived from the study of the adsorption of fatty acids from solution. It was found by Traube that the adsorption of monobasic aliphatic acids at the water–air interface increased with the number of carbon atoms in the molecule, thus agreeing with Gibbs's equation for the increasing capillary activity up the series of these acids, at the same interface. Although most charcoals obey this rule, yet some adsorb quantities of fatty acids in the reverse order to that required by it. Dubinin (*Z. physikal. Chem.*, 1930, **150**, 145) discovered that prolonged activation in air reversed the order of magnitude of adsorption of propionic, valeric, and heptoic acids on such charcoals, so that Traube's rule was finally obeyed, presumably owing to the increase in pore diameter on oxidation.

In the present research, the work of Bell and Philip and of Dubinin has been extended to cover a larger range of conditions and materials, other effects of progressive activation have been investigated, and the whole correlated from the viewpoint of the ultraporosity concept.

EXPERIMENTAL.

All the charcoal used in the present work was ash- and hydrogen-free; its preparation is described elsewhere (King and Lawson, *Kolloid-Z.*, 1934, **69**, 21). Activation was carried out in a silica tube furnace, wound so as to ensure as uniform heating as possible within an 8 in. region, in the middle of which the charcoal was supported in two-tier silica trays. The greatest difficulty in obtaining reproducible results with pure charcoal lies in the fact that the surface layers are more extensively oxidised than, and even different in appearance from, the substance underneath. In these activations an attempt was made to reduce this effect to a minimum by the use of shallow layers, and by thorough mixing before a sample was taken out of the furnace. The ends of the furnace tube were closed except for inlet and outlet tubes for the activating gas and a pyrometer tube. The oxygen for activation was in all cases passed from a cylinder through three bubblers, the first containing pure water and the other two saturated calcium chloride solution, Kolthoff (*J. Amer. Chem. Soc.*, 1932, **54**, 4473) having shown that moist oxygen is more effective than the dry gas. The rate of flow was reasonably uniform after the initial

10 minutes, being about 5 c.c./min. Divergences from this rate caused marked differences in the activity of the charcoal.

The trays of charcoal were introduced into the furnace when it had attained the temperature at which the activation was to be carried out; after various times, they were pulled out by means of a hooked glass rod, samples taken, and the charcoal returned to the furnace for further activation. The total time of activation varied from 30 to 48 hours. The samples were then weighed, and immediately shaken with the solutions of the required adsorbents, so that the slow formation of the surface oxide of carbon, which is characteristic of lower temperatures and has a marked effect on the adsorption of acids, should be minimised. In the present work the adsorption of acids was studied wherever possible, as they alone are freely adsorbed on every type of oxide surface.

In every experiment, 50 c.c. of the solution (*N*/50 in all cases except H-acid, eosin, and Congo-red, which were more dilute) were measured into a tube containing about 0·5 g. of charcoal, well shaken during 24 hrs., filtered, the first runnings rejected, and a 25 c.c. portion titrated with *N*/50-baryta solution. The eosin and Congo-red were estimated colorimetrically. Results are expressed throughout as equivs. × 10^{-5} adsorbed by 1 g. of charcoal, except for eosin and Congo-red, where mg. are used to show better the relative adsorption.

Results.

(1) *The Effect of Progressive Oxidation on the Adsorption of Molecules of Different Size.*—The adsorption of a series of compounds of increasing molecular size [benzoic, phenylacetic, phenylpropionic, and aminonaphtholdisulphonic (H) acids, eosin, and Congo-red] were measured on charcoal which had been activated for different times and at different temperatures. The results are shown in Table I.

TABLE I.

Time of actvn., hrs.	$CH_3{\cdot}CO_2H$.	$C_6H_5{\cdot}CO_2H$.	$C_6H_5{\cdot}CH_2{\cdot}CO_2H$.	$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.	H-Acid.	Eosin.	Congo-red.
Activation in oxygen at 450°.							
0	24·6	51·8	45·4	6·7	0	0	0
2	26·0	64·2	63·6	49·8	0	0	0
4	31·2	71·4	67·0	73·4	2·1	0	0
7	33·2	86·2	82·5	88·4	5·9	0	0
11	34·4	88·7	90·8	100·2	10·0	0·7	0
30	34·6	95·0	106·2	116·4	15·4	3·5	0
Activation in oxygen at 710°.							
0	24·6	51·8	45·4	6·7	0	0	0
1	40·4	83·6	68·2	64·2	11·4	0	0
2	48·8	93·2	84·0	81·4	17·1	0	0
3·5	51·4	102·0	91·5	88·8	18·8	0	0
5	54·5	114·0	103·2	97·2	23·0	0	0
7	61·8	135·4	138·0	138·0	36·4	1·0	0
11	77·8	159·6	154·6	176·4	43·2	2·8	0
21	91·6	168·2	209·2	212·4	53·0	4·3	0
30	—	189·2	—	—	72·8	6·4	0
Activation in oxygen at 950°.							
0	24·6	51·8	45·4	6·7	0	0	0
2	46·0	69·4	61·5	51·4	11·8	0	0
4	53·7	88·3	87·1	77·0	18·3	2·0	0
7	60·4	104·8	115·0	97·4	28·0	3·7	0
11	63·7	141·3	128·9	125·4	35·6	5·9	1·2
21	73·4	180·4	185	194	44·6	8·1	15·0
30	78·2	226	228	230	64·4	19	17·5
48	79·0	226	228	234	55·8	13	16·9
Activation by carbon dioxide at 950°.							
0	24·6	51·8	45·4	6·7	0	0	0
2	38·4	68·5	59·8	60·1	0	0	0
4	48·0	81·6	86·6	83·7	13·3	1·5	0
7	57·6	103·0	101·2	108·4	25·0	2·7	0
11	64·6	119·9	129·0	134·4	35·2	4·4	3·1

The smallest molecules (acetic, benzoic, and phenylacetic acids) are all adsorbed to a considerable extent on the unactivated charcoal, and activation produces a regular increase in the amount of adsorption with time, corresponding to a gradual increase in the surface area by oxidation. The pores of unactivated charcoal thus seem to be sufficiently large for the complete penetration by those molecules.

Phenylpropionic acid, on the other hand, although appreciably adsorbed by the unactivated charcoal, is adsorbed nearly 8 times as much by charcoal which has been activated for 2 hours, a process which gives only a 6% increase for acetic acid under the same conditions. Subsequent increase in adsorption is much less, being only 19% in the final 19 hours of the activation. This behaviour is to be explained on the assumption that the average pore size is just a little larger than the effective diameter of the phenylpropionic acid molecule, and that a short oxidation, increasing the diameter of the ultrapores, makes a comparatively large surface available for the adsorption of these molecules. Still further oxidation opens a few of the smaller pores to this critical size, and also increases the adsorption, as in the case of the smaller molecules, by increasing the surface area generally. This effect is still more noticeable in the case of the larger molecules of H-acid and eosin, which are not adsorbed appreciably until the charcoal has been oxidised for 4 and 11 hours respectively. Congo-red, with still bigger molecules, cannot enter any of the pores even after 30 hours' oxidation of the charcoal.

The low activity of the 450°-activated charcoal for acids is not to be ascribed entirely to the restricted oxidation at that temperature, but to the fact that this is the optimum temperature for the formation of the acidic surface oxide of carbon which inhibits to some extent the adsorption of acids; *e.g.*, on the 450° charcoal the adsorption of acetic acid is 34·4 at the point where the pores are sufficiently open to allow the adsorption of eosin to become first measurable, but on the 710° charcoal which has a basic oxide film, the adsorption becomes 61·8 for the same pore size. At this temperature, the adsorption of even the smaller molecules which have access to all the ultrapores becomes much greater after an oxidation lasting only one hour, while afterwards it increases gradually, as on the 450° charcoal. This is due to the rapid displacement of the acidic surface oxide, characteristic of low temperatures, by the basic oxide formed at 710°. The first hour's oxidation is sufficient to allow the free access of the phenylpropionic acid molecules to the ultrapores, the adsorption of this substance rising from 6·7 to 64·2, while H-acid, whose adsorption could not be detected in the unactivated charcoal, has the value 11·4. Congo-red is still unadsorbed after 30 hours, but the eosin adsorption can be detected after 7 hours' activation. Again, the 950° oxidation has some different features from those already discussed. The increase in adsorption during the initial period is smaller, and in spite of a presumably more extensive oxidation, the adsorption in the case of the smaller molecules is always less than at the corresponding time at 710°. This is due to the appearance of still another factor, *viz.*, graphitisation, which sets in at high temperatures and partly counteracts the effect of oxidation. This is most noticeable after long times of heating, the adsorption of H-acid, eosin, and Congo-red actually decreasing between the 30-hour and the 48-hour charcoal. The effect of graphitisation on the smaller molecules is not so marked, but there is little increase in the adsorption of the first four members of our series during the final 18 hours' treatment.

In spite of the deactivating influence of graphitisation, the increase in pore size is more rapid at this temperature than in the other cases, the adsorption of eosin being noticed after 4 hours, and that of Congo-red, which had not been adsorbed by any of the lower-temperature activated charcoals, after 11 hours.

Carbon dioxide reacts readily with charcoal at high temperatures, forming the monoxide and removing some of the charcoal. In this way it has the same effect as oxygen and might be expected to produce the same type of surface. It was found that in each case the amount of material adsorbed by this charcoal was very much the same as in the oxygen activation at the same temperature. Adsorption of eosin was first noticed after 4 hours, and that of Congo-red after 11 hours, just as with the oxygen-activated charcoal. The carbon dioxide-activation has, however, one advantage over that with oxygen, in that the total loss of weight of charcoal is much less, oxidation being less drastic.

In all the sugar charcoals tested, the pore size was that of the sample used above, or even less; several wood charcoals were found which had pores large enough to enable them to adsorb Congo-red after much shorter periods at lower temperatures, but in order to eliminate the possibility of the results being influenced by impurities and to test the effect of progressive oxidation on the entrance of smaller molecules, the ash-free sugar charcoal was used throughout.

(2) *Progressive Oxidation and Traube's Rule.*—In the above experiments the three acids, benzoic, phenylacetic, and phenylpropionic, form a series to which Traube's rule should apply: the amount of adsorption should increase with molecular weight. On the unactivated charcoal with small ultrapores, the reverse is found to be true, but at each temperature this was finally

reversed on prolonged oxidation either with oxygen or with carbon dioxide, showing that *all* the pores were finally accessible to all these molecules.

In order to extend this observation, the effect of progressive activation on the adsorption of the aliphatic fatty acids was studied with two charcoals, a purified sugar charcoal and an impure charcoal, produced by the combustion of molasses at 450°. The results are in Table II.

TABLE II.

The effect of progressive oxidation at 450° on the adsorption of fatty acids.

Time of actvn., hrs.	Pure sugar charcoal.					Molasses charcoal.				
	$H{\cdot}CO_2H$.	$CH_3{\cdot}CO_2H$.	$C_2H_5{\cdot}CO_2H$.	$C_3H_7{\cdot}CO_2H$.	$C_4H_9{\cdot}CO_2H$.	$H{\cdot}CO_2H$.	$CH_3{\cdot}CO_2H$.	$C_2H_5{\cdot}CO_2H$.	$C_3H_7{\cdot}CO_2H$.	$C_4H_9{\cdot}CO_2H$.
0	21·4	25·3	39·2	46·8	42·8	124	132	108	97·8	90·2
1	23·7	28·4	42·4	50·4	50·0	217	247	231	182	164
3	25·0	29·6	50·8	64·4	82·8	—	—	—	—	—
4	—	—	—	—	—	251	272	269	255	251
6	—	—	—	—	—	274	280	291	289	287
12	—	—	—	—	—	289	297	309	315	308

The pores in the pure sugar charcoal, as might be expected from the foregoing experiments, are sufficiently large to allow the entrance of the molecules of all the acids employed, and Traube's rule is obeyed for the unactivated charcoal by the first four members of the series, the fifth and largest being adsorbed to a less extent. This is clearly due to the fact that there is a small proportion of pores not sufficiently large to allow the adsorption of valeric acid. Oxidation for one hour lessens the anomaly, and valeric and propionic acids are then adsorbed to approximately the same extent; after 3 hours' oxidation, all the pores are sufficiently large to allow all the acids to enter normally, and the rule is obeyed.

The impure molasses charcoal had pores of considerably smaller diameter, although its higher activity indicated that it had more of them; hence Traube's rule was reversed except for formic and acetic acids. Once again, oxidation gradually reversed this, and after 12 hours only the valeric acid molecules were too large to penetrate all the pores.

The activity of the molasses charcoal was very much greater than that of the pure sugar charcoal, due to a large extent to its lower temperature of formation. The activity of this impure charcoal almost doubled during the first hour's heating in oxygen, presumably owing to the removal of hydrocarbons by the gas stream. After this initial period, the activation took place in much the same way as with pure charcoal.

(3) *Evacuation of Charcoals.*—The large increase in activity of impure charcoal on initial treatment with oxygen seemed to be a direct proof of the removal of hydrocarbons and other volatile surface impurities as one of the mechanisms of activation. Evacuation of such a charcoal was therefore carried out to determine if that process had the same type of effect and if it altered the size of the pores appreciably; a "Hyvac" pump was used, the charcoal being heated in a silica test-tube in an electric furnace. The unevacuated charcoal had a rich black colour and a faint amine-like odour. Evacuation at 450° did not remove this entirely, but the product of evacuation at 1000° had no smell and was steel-grey in appearance. A considerable amount of tarry matter collected in the liquid-air traps. The results are in Table III.

TABLE III.

Effect of activation on the activity of impure charcoal.

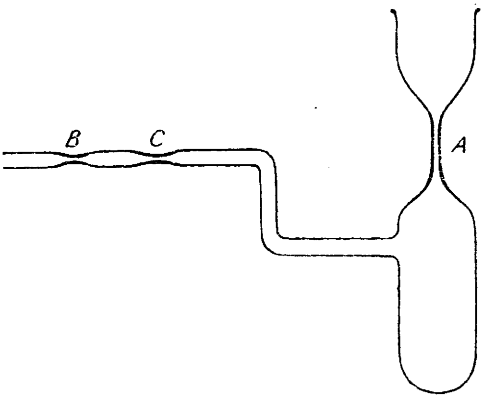
Temp. of evacn.	$H{\cdot}CO_2H$.	$CH_3{\cdot}CO_2H$.	$C_2H_5{\cdot}CO_2H$.	$C_3H_7{\cdot}CO_2H$.	$C_4H_9{\cdot}CO_2H$.
(unevacuated)	118	132	107	97·8	90·2
450°	122	171	176	188	178
1000	129	182	187	195	193

Evacuation at 450° caused a very large increase in activity for all the substances used, owing to the removal of organic impurities. That this was the real reason for the increase in activity was shown by a similar experiment with pure charcoal whose activity for benzoic acid increased only from 51·8 to 59·5 on evacuation at 1000°. With the impure charcoal also, the activity increases relatively little more on evacuation at 1000° than at 450°, most of the volatile impurities being removed at quite low temperatures. In the evacuation of the pure charcoal, the increase in activity must be ascribed to oxidation by means of the oxygen already chemically held on the surface, *i.e.*, to partial or complete removal of the surface oxide film, thus resulting in a slight increase in area and pore diameter.

The purification of the molasses charcoal by evacuation naturally empties the ultrapores and increases their diameter, so much so that Traube's rule becomes valid except for valeric acid even after the 450° evacuation, an effect which requires **12** hours' heating in oxygen at the same temperature to complete, although the activity, and hence the general surface area, is increased to a greater extent by oxidation than by evacuation. Evacuation is thus an excellent way of increasing the pore size of unactivated charcoals.

(4) *The Effect of Progressive Oxidation on the Density of Charcoal.*—It is obvious that the ratio of the volume of the pores to that of the solid in an adsorbent will determine its density, and as the same ratio expresses the area of surface available for adsorption, the density must be proportional to the adsorption capacity. This was found to be the case by Chaney, Ray, and St. John (*Ind. Eng. Chem.*, 1923, **15**, 1244) for gas-mask charcoals.

The determination of the density of charcoal is complicated by the fact that it varies with the immersion liquid, owing to the different wetting properties and powers of penetration which the latter may possess; for instance, Cude and Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 391) give 1·854 as the density of a charcoal measured in water and 1·797 in benzene. Differences in particle size and temperature of out-gassing also cause relatively large differences in the value of the density. Most experimenters recommend that the charcoal should be evacuated at 700—800° before its density is determined, but this causes displacement, not only of adsorbed gases, but also of the chemically held oxide film. Such a treatment therefore causes radical changes in the surface of the charcoal and, as we have seen, alters the size of the pores considerably. We conclude that the density of a charcoal evacuated at a high temperature is characteristic of its properties *after* that process but not before.



In the present determinations, a charcoal of particle size 100—200 mesh was chosen, and its density measured immediately, and after various times of activation in oxygen at 450°. The measurements were made in a special pyknometer of the type illustrated in the fig. The charcoal was introduced at the funnel at the top of the pyknometer which was sealed off at *A*. It was then placed in a boiling water-bath and evacuated with a "Hyvac" pump for **5** hours to remove nitrogen, moisture, and other physically held substances but not the oxide film, sealed at *B*, and weighed. The pyknometer was now completely filled by carefully breaking the constriction *C* under the surface of boiled-out distilled water. It was found, in agreement with the work of Cude and Hulett (*loc. cit.*), that penetration was not complete till after about one month, the specific gravity increasing gradually during that period. This was very much less with the charcoals activated for longer times, and is obviously another ultrapore effect. After equilibrium had finally been established, the pyknometer, with its contained charcoal and water, was weighed, the charcoal removed, the pyknometer weighed full of water, and then finally when empty and dry. The results were :

Temp. of actvn., hrs.	0	1	3	7	24
d	1·551	1·602	1·675	1·716	1·792

The density thus increases steadily with time of activation, indicating an increase in the pore volume of the charcoal, corresponding to that found from the adsorption experiments. It is interesting to note, in conjunction with the above facts, that the *bulk* density of the charcoal used *decreased* from 0·58 for the unactivated material to 0·38 after 48 hrs.' activation at 950°.

DISCUSSION.

Many determinations of the surface areas of charcoal have been carried out, and many theories based on the results calculated from them. It is interesting to regard some of these determinations from the point of view of ultraporosity. The results of Paneth and Radu (*Ber.*, 1924, **57**, 578, 1221) for the areas of different charcoals measured by the adsorption of different substances have become almost classical and are quoted below :

Adsorbed substance.	Mol. wt.	Carbo animalis (Merck).		Lime charcoal (Kahlbaum).		Bone charcoal (Kahlbaum).		Sugar charcoal, activated.	
		Mols. × 10^{20}.	m^2.	Mols. × 10^{20}.	m^2.	Mols. × 10^{20}.	m^2.	Mols. × 10^{20}.	m^2.
Methylene-blue	338	4·14	220	1·89	101	3·17	168	0·47	24·8
Ponceau-2R............	480	1·90	119	0·98	61	1·65	103	0	0
Acetone	58	18·5	452	11·0	268	14·7	359	2·29	55·9

It is at once obvious that the calculated surface, m^2, varies greatly with the substance used to measure it, the large dye molecules being adsorbed to a less extent than the small molecules of acetone, or, as we prefer to imagine it, being unable to enter the smaller pores. This is especially noticeable in the case of sugar charcoal, whose pores are smaller than those of animal and wood charcoals (see p. 1977), allowing the adsorption of acetone and, to a smaller extent, of methylene-blue, but not of Ponceau-2R. In each of the other charcoals investigated by Paneth and Radu, the area calculated from the adsorption of Ponceau-2R is less than that from methylene-blue and still less than that from acetone—there are fewer pores sufficiently large to allow the entrance of the large molecules. The area calculated in each case indicates, not the total area of the charcoal surface, but that available to the molecule in question.

The magnitude of adsorption on a given charcoal must depend on both the physical and the chemical nature of the adsorbate and adsorbent. In the former category are to be considered the available area of the adsorbent, and the relative sizes of its pores and of the molecules adsorbed; in the latter, the chemical condition of the surface, the properties of the specific surface oxide that may already be adsorbed (*e.g.*, in the case of the adsorption of water, see King and Lawson, *Trans. Faraday Soc.*, 1934, **30**, 1094), and the chemical nature of the adsorbed molecules. Not only does the actual group forming the linkage with the carbon or surface oxide influence the adsorption, but also the orientation of the adsorbed molecules to give strong or weak subsidiary valency forces on the surface, which will or will not tend to form a second adsorbed layer.

If the functions of ultraporosity and of the surface oxides of carbon in determining the adsorption are appreciated, it begins to be possible to understand the reasons for the existence of charcoals with specific properties. For instance, a charcoal activated for a short time at 450° and covered with the low-temperature oxide film would adsorb bases readily, acids of small molecular size to a less extent, and acids of larger molecular dimensions only inappreciably. A charcoal activated for a longer period at the same temperature would adsorb large-molecule acids as well. A 750°-activated charcoal would adsorb acids strongly, especially if heated for a considerable time, the larger organic acids being adsorbed but all bases excluded.

SUMMARY.

(1) The effect of progressive activation of ash-free charcoals on the adsorption of molecules of different size has been studied. It is found that the larger molecules are only appreciably adsorbed at a comparatively late stage in the oxidation, and this is ascribed to a gradual increase in the pore size.

(2) Traube's rule is invariably obeyed if the ultrapores are sufficiently enlarged by oxidation.

(3) The density of charcoal increases regularly with time of oxidation.

(4) The pore diameter of charcoals is increased by evacuation, the activity of impure charcoals increasing greatly and that of pure charcoals less.

(5) The concept of ultraporosity is applied to the results of other workers on the area of charcoals, and reasons are put forward for the specific nature of adsorptions by certain charcoals.

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