252. *The Heat of Wetting of Charcoals of Graded Activity, in Relation to Adsorptive Capacity and Retentivity.*

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EARLIER studies in this laboratory of the effects of controlled air-oxidation of wood and sugar charcoals (Philip, Dunhill, Workman, J., 1920, **117**, 362; Philip and Jarman, *J. Physical Chem.*, 1924, **28**, 346; Page, J., 1927, 1484) have demonstrated the extent to which the progress of oxidation of a stock material is accompanied by decrease of bulk density and increase of adsorptive capacity. In the present investigation the heat of wetting of such charcoals of graded activity has been correlated with their adsorptive capacity and retentivity for vapour.

Various workers have already studied the heat of wetting of charcoal (*e.g.*, Herbst, *Kolloid-Z.*, 1926, **38**, 314; Andress and Berl, *Z. physikal. Chem.*, 1926, **122**, 81; Burstin and Winkler, *Brennstoff-Chem.*, 1929, **10**, 121) and Macy (*J. Physical Chem.*, 1931, **35**, 1397) finds that the heat of wetting of a charcoal by benzene is a measure, not so much of the adsorptive power of the charcoal for benzene vapour, as of its capacity for firmly-held vapour—the so-called " retentivity." The latter term is admittedly not capable of exact definition, but expresses the fact that when a charcoal has taken up a vapour to capacity according to the pressure conditions, a certain proportion of this adsorbed vapour can then be removed with extreme ease in a current of air, while the remainder is retained very firmly. In the present work, for practical purposes, the passage of air at room temperature over the fully charged charcoal was continued until there was no appreciable loss of weight in a half-hour period. A minimum of 4 hours' treatment was usually necessary to reach this condition. The retentivity—taken as the weight of vapour so retained by 1 g. of vapour-free charcoal—was usually 80—90% of the corresponding adsorbed vapour.

EXPERIMENTAL.

Preparation and Activation of Charcoals.—Three stock charcoals were used in the work, one birch-wood and two sugar charcoals, referred to as A and B. The stock birch-wood charcoal was prepared from ½" cubes, and thorough mixing of the product was effected in the manner described by Page (*loc. cit.*).

Sugar charcoal A was prepared by carbonising about 6 lbs. of pure cane-sugar in small quantities in a platinum basin at a dull red heat until the evolution of fumes ceased. The product was ground and sieved to give particles below 100 to the inch. Sugar charcoal B was obtained by carbonising in all about 10 lbs. of pure cane-sugar in an electrically heated 3" silica tube at 800° until fumes were no longer evolved. The product was ground, mixed, and sieved to give three grades of stock material, *viz.*, (*a*) 20—100, (*b*) 100—200, (*c*) >200 to the inch.

The activation was in all cases carried out by Page's method (*loc. cit.*), air from a cylinder of the compressed gas being passed, generally at the rate of 0·7 l. per hour, over the charcoal (about 10 g. in each batch) kept at a definite temperature, 700°, 800°, or 900°. The maximum times of activation were 9 hours for the birch-wood charcoal, 8 hours for sugar charcoal A, and 24 hours for B. A charcoal described below as " blank " refers, not to the stock material, but to a portion of this which had been heated, under activating conditions, to the activation temperature and then cooled at once. The extent to which the stock material is activated by this initial heat treatment varies notably with the time taken (see p. 1167), and the procedure normally adopted in all the activations was to start with the maximum current through the furnace and so secure rapid heating to the desired temperature.

Measurement of the Heat of Wetting.—Two calorimeters were used for this purpose, one being very similar to that described by Andress and Berl (*loc. cit.*), and depending on the expansion of the calorimeter liquid (alcohol) produced by the addition of a small quantity of heat. The calorimeter was a cylindrical Dewar vessel, immersed in a thermostat at 20°. The expansions were measured on a fine capillary tube, and in order to convert these readings into heat quantities, a calibration based on the known heat of neutralisation of hydrochloric acid by sodium hydroxide was carried out. The dimensions of the apparatus were such that a rise of 1 cm. in the capillary tube was the equivalent of 4·32—4·33 cals. liberated in the reaction vessel. The actual rise observed in any particular experiment on the heat of wetting varied from 1 cm. to 9 cms., according to the liquid used and the degree of activation of the charcoal, and the magnitude of the rise recorded in a given case was as a rule reproducible to within 0·3 cm. In measuring the heat of wetting, about 1 g. of charcoal was weighed into the reaction tube, which was fitted with a small stirrer, and at an appropriate moment 10 c.c. of the wetting liquid, previously kept in the thermostat for some time, were poured down the stem of the stirrer. In order to diminish any uncertainties involved in this manipulation, blank experiments without charcoal were made, and all precautions usual in calorimetric work were observed.

The second calorimeter was also a Dewar vessel, but the wetting was carried out in the vessel itself, the heat effect being derived from the rise of temperature observed on a Beckmann thermometer. The calorimeter was set up in a thermostat at 20°, and the heat of neutralisation was taken as the basis for the calibration of the apparatus. In experiments on the heat of wetting, 20 c.c. of the liquid were put in the calorimeter and, after steady temperature conditions had been attained, about 1 g. of charcoal, previously brought to the bath temperature, was added through a wide funnel tube. Readings of the thermometer were taken every half minute with occasional gentle stirring, and the corrected rise of temperature was obtained in the usual way from a temperature–time curve. The heat content of the calorimeter system was such that with 20 c.c. of benzene as the wetting liquid, 1° rise was the equivalent of 12·66 cals. liberated.

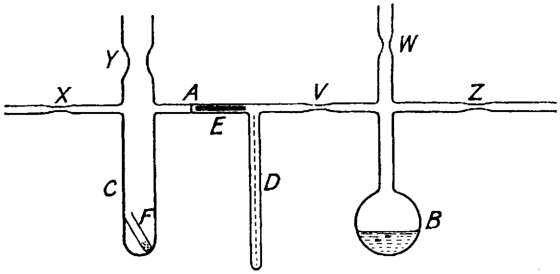
The results obtained with this second calorimeter were somewhat less accurate than those given by the first apparatus, but they were fully adequate for the purposes of the work. Moreover, they were obtained much more rapidly.

Measurement of Adsorptive Capacity and Retentivity.—For studying the power of the different charcoals to adsorb vapour, it was proposed to use desiccators, with the volatile liquid below and the charcoal samples in the upper part. It was thought desirable to ascertain whether the maximum amount of vapour adsorbed under these conditions (air present) was the same as that taken up by the same charcoal in the absence of air. Accordingly, two experiments were carried out with the apparatus shown in Fig. 1.

The system was divided into two parts by the glass septum *A*. About 1 g. of charcoal, contained in *F*, was introduced into the tube *C*, which was then sealed off at *Y*. After evacuation, the left half of the system was sealed off at *X*.

The graduated capillary tube *D* was of such a bore as to hold slightly more than sufficient benzene for adsorption on the charcoal. After introduction of benzene into the reservoir *B*, of about 10 c.c. capacity, the upper tube was sealed off at *W*. The part of the system to the right of *A* was then evacuated, and under the evacuation the benzene solidified. Alternate heating and cooling of this part of the system, while connexion with the pump was maintained, secured the removal of traces of air. After the benzene had been cooled in liquid air, the tube to the pump was sealed at *Z*. On warming *B* and cooling *D*, benzene was distilled into the capillary up to the zero mark on the scale, and the connecting tube was then sealed off at *V*.

Fig. 1.



When the septum *A* was now broken by the glass-rod plunger *E*, there was a very rapid adsorption by the charcoal used in the experiments—a 16-hour air-activated (800°) sugar charcoal. Frequent readings were taken on the capillary *D*, and it was observed that the adsorption was practically complete in 2—3 hours. The weight of benzene adsorbed per g. of charcoal was found in this way to be 0·211 g. When the experiment was repeated without first removing the air from the left part of the system, the amount of benzene finally held per g. of charcoal was substantially the same as before, but the equilibrium was not attained until after the lapse of 4—5 weeks. With the desiccator method and with the same charcoal, an adsorption value of 0·199 g. per g. of charcoal was obtained in about 30 hours, and in view of these results it was decided to adopt a 48-hour desiccator treatment of the charcoals as giving a satisfactory measure of their adsorption capacity.

For the determination of retentivity, the charcoals which had been exposed to benzene vapour for 48 hours in desiccators, as already described, were placed in U-tubes. Through these a slow stream of air was drawn at room temperature, and this was continued, as stated above, until constancy of weight over half-hour periods was obtained.

Results.

Heat of Wetting and Duration of the Activation.—Reference has been made to the decrease of bulk density and the increase of adsorptive capacity which, as shown in previous investigations, go *pari passu* with increasing duration of the air-oxidation treatment. Measurements of the heat of wetting of charcoals activated for different periods show quite definitely that the progressive change in the charcoals brought about by this treatment is marked also by a steady rise in the heat of wetting. This may be illustrated by the following figures (Table I) for methyl and ethyl alcohols and benzene as wetting liquids, the adsorbent in each case being birch-wood charcoal activated at 800° for different periods.

Although the increase of the heat of wetting is very definite in the cases of methyl and ethyl alcohols, the rise is still more rapid with benzene. The heat of wetting of birch-wood charcoals

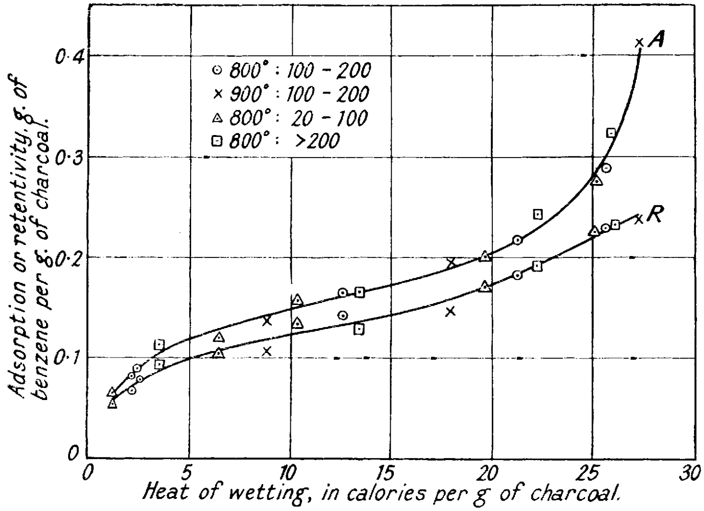
TABLE I.

Activation, hrs.	Heat of wetting (cals./g.).			Activation, hrs.	Heat of wetting (cals./g.).		
	MeOH.	EtOH.	C_6H_6.		MeOH.	EtOH.	C_6H_6.
" Blank "	11·3	14·75	6·9	5	—	18·3	22·0
1	—	—	10·9	6	16·8	—	22·4
2	—	17·3	16·1	7	—	19·9	—
4	16·2	—	19·4	9	17·5	21·3	—

activated at 900° exhibits a similar steep rise; indeed, one specimen activated for 6 hours at 900° gave a heat of wetting with benzene of no less than 38 cals. per g.

In the case also of both sugar charcoals a general increase of the heat of wetting with the time of activation was observed, and the increase is more regular than with the birch-wood charcoal. The values of the heat of wetting were found to be greater for sugar charcoal A than for B, but in both cases they were lower than the values obtained with the birch-wood charcoal for a given time of activation. Some of the figures obtained for the heat of wetting of sugar charcoal B with benzene are given in Table II.

FIG. 2.



A = *Adsorption-heat of wetting curve.* R = *Retentivity-heat of wetting curve.*

Heat of Wetting in Relation to Adsorption and Retentivity.—According to Macy (*loc. cit.*), the heat of wetting is a measure, not so much of the adsorption, as of the retentivity. The measurements made in the present investigation, so far as they concerned the birch-wood charcoal and sugar charcoal A, were not decisive in favour of that view, for the relationship between heat of wetting and adsorption on the one hand and retentivity on the other was parallel and roughly linear in both cases. It was realised, however, that the maximum time of activation for both these charcoals was 8—9 hours, and it was in order to cover a wider range of activated material that sugar charcoal B was prepared.

The results obtained with benzene in this series of charcoals (particle size 100—200 to the inch) are set out in Table II; the corresponding graphical representation is found in Fig. 2,

TABLE II.

Sugar charcoal B. Temperature of activation 800°.

Activation, hrs.	" Blank "	3	7	8	14	24
Heat of wetting	2·3	2·5	10·1	12·6	21·3	25·6
Adsorption, g. per g. charcoal	0·081	0·088	0·152	0·164	0·218	0·289
Retentivity, g. per g. charcoal	0·071	0·080	—	0·142	0·183	0·227

which, however, also includes data obtained with different particle sizes at 800°, and some for material activated at 900°.

An inspection of Fig. 2 shows that for the middle range of activation the heat of wetting is approximately proportional both to the adsorption and to the retentivity. The highly activated charcoals, however, exhibit a different behaviour in that for them the heat of wetting is much more a measure of the retentivity than of the adsorption. This result is to some extent a confirmation of Macy's view.

Peculiarities of the Early Stages of Activation.—Previous work by Thrasher (unpublished) and the observations made in the course of the present work revealed some peculiar features of incipient activation. These are indicated, for example, by comparing the adsorption values (benzene) obtained with " blank " and " 13-hour " sugar charcoals. The " blanks " were prepared by heating samples of the stock material as quickly as possible up to the chosen temperature and then cooling them rapidly. The charcoal particles were in each case between 20 and 100 to the inch. The results were as follows :

Temp. of activation		600°	700°	800°	900°	1000°
Adsorption value	" Blank "	0·075	0·067	0·046	0·030	0·020
	3-Hours	0·097	0·097	0·115	0·133	0·134

The decrease of the " blank " value is very striking.

It was further observed that in a series of " blanks " prepared at a given temperature (800°) from the stock sugar charcoal B the benzene-adsorption value fell off as the rate of raising the temperature diminished ; *i.e.*, a slow heating does not have the effect of a long activation : on the contrary, the highest " blank " value is obtained with a maximum temperature–time gradient.

In view of these observations, attention was concentrated on the short-period activation of sugar charcoal B, the stock of which, as already stated, had been obtained by carbonisation in a wide silica tube at 800°. The size of the particles used in these short-period activations was between 100 and 200 to the inch. The results are shown below :

Activation period, hrs.	" Blank "	0·5	1·5	2·0	2·5	3·0
Benzene-adsorption value	0·081	0·041	0·047	0·047	0·050	0·088

The figures show that there is a definite decrease in activity as a result of the first half-hour's treatment and that the " blank " value is regained only after about 3 hours' activation. Reference to the figures in Table II will show that little difference in activity was found between the " blank " and the 3-hour charcoal, whether the activity was measured by the heat of wetting, the adsorption, or the retentivity. Another sample of sugar charcoal B treated at 900° showed a slight decrease of activity in the first half-hour, but after 1 hour gave a value well above that of the corresponding " blank."

In the present investigation the decrease of activity during the early stages of treatment was observed only with sugar charcoal B. The previous experiments of Thrasher, however, already mentioned, showed that both with birch-wood and sugar charcoals the activity, as tested by the rate of reduction of potassium permanganate, decreased in a similar manner during the early stages of air treatment.

Heat of Wetting and Surface Area of Charcoal.—Various authors (see Bartell and Fu, *Colloid Sym. Ann.*, 1930, **7**, 135; Berl and Burkhardt, *Z. angew. Chem.*, 1930, **43**, 330) have correlated the heat of wetting of a charcoal with its power of adsorbing substances from solution, the latter being taken as a basis for estimating the surface area. Such estimates are, however, notoriously divergent, and vary with the molecular size of the adsorbed substance. The study, from this point of view, of the charcoals of graded activity used in the present investigation, has given significant results, as shown in Table III. Weighed portions, about 1 g. of sugar charcoal B, activated for different periods at 800°, were shaken, in each case for 2 days, with aqueous solutions of benzoic acid (2·86 g. per l.), naphthalenesulphonic acid (4·53 g. per l.), and methylene-blue (1·58 g. per l.), the amount adsorbed being determined by subsequent titration.

TABLE III.

Activation period, hrs.	Grams adsorbed.		
	Benzoic acid.	Naphthalene-sulphonic acid.	Methylene-blue.
" Blank "	0·046	0·018	0·002
3	0·057	0·018	0·003
6½	0·119	0·018	0·003
10	0·245	0·085	0·005
15	0·334	0·250	0·036
23	0·417	0·323	0·146

The significant feature of Table III is not so much the absolute adsorption values for the different substances as the fact that in the case of naphthalenesulphonic acid, and still more in that of methylene-blue, the occurrence of any appreciable adsorption is delayed until a late stage in the activation of the charcoal. When it once sets in, the rise in the adsorption value with increase in the period of activation is comparatively rapid. With benzoic acid, on the other hand, there is a rise even between the " blank " and the 3-hour charcoal which, though small, is quite definite. It was also found that the later benzoic acid adsorption values are proportional to the heats of wetting with benzene of the four charcoals concerned.

DISCUSSION.

The present study of charcoals of graded activity indicates that the increase of available surface previously revealed by the progressive decrease of bulk density on air-activation is accompanied by a steady rise in the heat of wetting. It should be emphasised that with the most highly activated sugar charcoals the heat of wetting, like the retentivity, showed no steep rise such as was found for the adsorption values. In the last case, some of the vapour (benzene) held by the very active charcoal may be in the liquid form, and on that account its quantity cannot be regarded as so reliable a measure of the available surface as the retentivity. It certainly looks as if both the heat of wetting and the retentivity are determined mainly by the area of the available surface.

The early stages of activation as described above (p. 1168) present certain peculiar features, not hitherto recorded. There is little doubt that the primary result of high-temperature treatment on a stock charcoal is to decrease its adsorptive power, and that a continuation of the treatment for some time is necessary before a positive activation effect is obtained. This result appears difficult to reconcile with the progressive oxidation which is mainly responsible for increasing activation. It may be, however, that another factor which has frequently been regarded as important in charcoal activation, *viz.*, hydrocarbon distillation, may play a significant part in the early stages. The result of the first carbonisation may be to give a carbon surface fairly free from hydrocarbons, but to leave appreciable quantities of such substances in the interior of the charcoal granules. The first effect of the subsequent high-temperature air treatment would be to bring the hydrocarbons to the surface, where their clogging action would involve a reduced adsorptive power. Gradually, however, by distillation and oxidation the hydrocarbons would be removed, and the available surface would then be steadily increased by progressive oxidation.

Lastly, attention should be directed to Table III. From earlier observations (Paneth, Garner, Rideal, and others; cf. Philip, *Trans. Inst. Chem. Eng.*, 1929, **7**, 77), it is highly probable that the widely different estimates of the specific surface of charcoal are connected with the dimensions of the adsorbed molecules. The results given in Table III emphasise the significance of this factor, for they appear to show that, until the charcoal capillaries have been opened out sufficiently by the progressive oxidation, no appreciable adsorption of large molecules can occur. The larger the molecule, the further must the progressive oxidation go before appreciable adsorption occurs. When, however, this stage is reached, further oxidation is accompanied by a rapid increase of adsorptive power.

SUMMARY.

1. Charcoals of graded activity—both wood and sugar charcoals—have been prepared by air treatment at 700—900°.
2. The heats of wetting with benzene (mainly) and the adsorption and retentivity (for benzene vapour) have been determined.
3. The heat of wetting is found, in general, to be more definitely related to the retentivity than to the adsorption.
4. The air-treatment in its initial stages has been found to reduce the adsorptive power of sugar charcoal.
5. No appreciable adsorption of dissolved substances of large molecular dimensions (such as naphthalenesulphonic acid and methylene-blue) occurs with sugar charcoal until a certain stage in the air-oxidation has been reached.

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