# 254. *Active Charcoal. Part I. The Adsorption Isotherms of Organic Acids on Ash-free Charcoals.*

By CHARLES OCKRENT.

IT is well known that, although the adsorptions of the members of an homologous series of organic substances in aqueous solution, at the air–solution interface, increase regularly as the series is ascended, yet at solid surfaces, such as charcoal, divergences from this rule of Traube are frequently observed. Much attention has recently been devoted to this problem, and a number of different theories have been developed to account for the mechanism of adsorption at irregular solid surfaces, and, in particular, charcoal. Sabalitschka and Finger (Diss., Berlin, 1927/28) found that with a sugar charcoal Traube's rule for the adsorption of the monobasic aliphatic acids was reversed. This observation has been confirmed by Nekrassov (*Z. physikal. Chem.*, 1928, **136**, 18, 379) and also by Dubinin (*ibid.*, 1929, **140**, 81; 1930, *A*, **150**, 145) and Bruns (*Kolloid-Z.*, 1931, **54**, 33). Dubinin showed that a sugar charcoal, activated by air at 550°, gave a series of adsorption values with aliphatic acids which obeyed Traube's rule, but that an 800°-activated sugar charcoal gave a reversed series, and he suggested that the difference between the two charcoals lay in the possibility that the surface of the former was composed of an amorphous modification while that of the latter consisted of a fine crystalline modification. Sabalitschka (*Pharm. Z.*, 1929, **74**, 1) suggested that the reversal of Traube's rule could be explained on the ultraporosity theory advanced by Herbst (*Biochem. Z.*, 1921, **115**, 204), *i.e.*, the fine capillary structure decreases the available adsorption area of the charcoal for the increasing molecular size of the ascending members of an homologous series; this view was not held by Nekrassov, who suggested that the difference between ash-free sugar charcoal (reversal of Traube's rule) and the impure charcoals lay in their different structures, the former charcoal presenting a highly polar phase, greater than water, and so naturally led to a reversal of the Traube rule. More recently, Dubinin and Bruns (*locc. cit.*) have accepted the theory of ultraporosity, and with slight modifications this is substantially the view of Krczil (*Kolloid-Z.*, 1932, **58**, 68).

In a previous investigation (this vol., p. 613) on the adsorption of a number of organic acids by activated charcoal, it was found that the surface areas occupied per molecule of the various acids were different. The differences could be ascribed to (1) the available area of the charcoal being different for the different acids, or (2) the available area being the same, but the areas of the acid molecules different. It is also possible, however, that, while the areas of the various acid molecules are different, these differences might limit the available area of the non-uniform surface of a solid, such as charcoal, since molecules of different sizes may occupy different parts of the surface, smaller molecules being accommodated in parts of the surface which may be too small for larger molecules. If the available area is independent of the size of the adsorbed molecules, then for any two given ash-free charcoals, the ratios of the amounts adsorbed should be the same for all adsorbed molecules. This can be tested by working with different charcoals prepared in various ways. With a view to investigate these problems, and also to elucidate the nature of active charcoal, the following investigation was carried out.

## EXPERIMENTAL.

*Preparation of Charcoals.*—The ash-free sugar charcoal, activated by atmospheric oxygen, prepared in a previous investigation (*loc. cit.*), was used as the starting material for the preparation of other charcoals. This original charcoal is hereafter referred to as charcoal A.

The agate mortar and pestle of an electrically driven grinding machine were subjected to steam, and some charcoal A was ground in it for several hours. This was then rejected in case it contained impurities from the agate, and the cavities in the mortar and pestle were thus filled with charcoal. More charcoal A was then ground for 120 hours continuously, the machine being enclosed in a box to keep out dust, and 6 g. of very finely divided charcoal were obtained (charcoal B).

More of charcoal A was later ground for 72 hours continuously, the mortar and pestle being treated in the same preliminary fashion as before (charcoal $C_1$). It should be emphasised that the periods of grinding are not to be taken as criteria for the relative fineness of charcoals B and $C_1$, as certain improvements were made in the machine after the grinding of charcoal B.

11·1 G. of charcoal $C_1$ were re-activated in porcelain boats, the apparatus employed being as described in the previous investigation. After the apparatus had been filled with the activating gas (purified atmospheric oxygen), the charcoal was degassed for 3 hours at 500°, and the activating gas (3 litres) was then admitted into the apparatus until the pressure was atmospheric. The gas was then allowed to flow over the charcoal, the temperature being maintained at 500°, at the rate of 119 c.c./min. for 20 mins., so that 2·38 litres were used; the charcoal was now allowed to cool in the closed vessel in an atmosphere of the activating gas. 9·7 G. of activated charcoal ($C_2$) were obtained. Complete combustion of 0·7430 g. of this charcoal gave less than 0·0002 g. of ash.

*Adsorption Procedure.*—25 C.c. of the aqueous solutions of the substances investigated were used throughout, and were placed in glass tubes with good fitting ground-glass stoppers. As in the previous investigation, the solutions were shaken in the tubes for 1 hour by means of a slowly rotating series of discs to which the tubes were fastened. The tubes were then placed in a thermostat at $25° \pm 0·02°$ and kept for about 21 hours, and the solution was then separated by centrifuging and decantation.

The substances investigated were organic acids, purified in the course of the previous investigation. Carbon dioxide-free distilled water was used to make up all the solutions, and the concentrations of the acids were estimated by carbon dioxide-free sodium hydroxide solutions (0·01$N$). All glass vessels used were first cleaned with strong alcoholic caustic potash, and then rinsed three or four times with tap water, three or four times with good distilled water, and dried in an electric oven.

*Experimental Data.*—Adsorption isotherms of the following acids were obtained for the different charcoals.

| Acid. | Charcoal. | Acid. | Charcoal. |
|---|---|---|---|
| Formic ..................... | B, $C_1$, $C_2$ | Trichloroacetic ......... | $C_1$, $C_2$ |
| Acetic ..................... | B, $C_1$, $C_2$ | Salicylic .................. | B, $C_1$, $C_2$ |
| Monochloroacetic ...... | $C_1$, $C_2$ | Benzoic .................. | $C_1$, $C_2$ |

The results obtained in the previous investigation for the adsorption isotherms of these acids with charcoal A are referred to in the discussion.

The charcoals showed markedly different behaviour on centrifuging; in every case the solutions containing the finely ground but subsequently re-activated charcoal $C_2$ were clear and colourless after a short period of moderate centrifuging (5 mins. at 5000 r.p.m.), and similar results were obtained previously with charcoal A, but all the solutions containing the finely-ground charcoals B and $C_1$, with the exception of the trichloroacetic acid solutions with $C_1$, gave brown solutions, due to the presence of colloidal or semi-colloidal charcoal particles, and these could not be made to settle by vigorous and lengthy centrifuging (45 mins. at 9000 r.p.m.). It is probable that, since trichloroacetic acid is the strongest of those used, the colloidal particles were coagulated by its presence, since the particles of charcoal $C_1$ settled quite as readily as those of charcoals A and $C_2$ after a similarly short period of moderate centrifuging.

## *Discussion.*

In the previous investigation, it was shown that the results obtained with 7 different organic acids with charcoal A gave excellent agreement with the requirements of the adsorption theory of Langmuir (*J. Amer. Chem. Soc.*, 1918, **40**, 1360). According to his kinetic treatment, if the rate of adsorption is proportional to the concentration of solute in the solution and to the fraction of surface unoccupied by the solute molecules, and the rate of desorption is proportional to the surface concentration (*i.e.*, the amount adsorbed), then for equilibrium,

$$k\Gamma = C(1 - \Gamma/\Gamma_{\text{max.}}) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

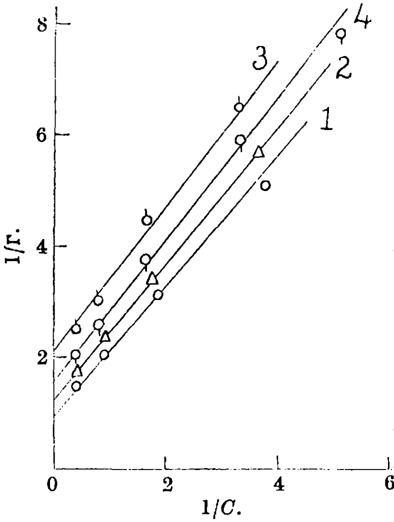
where $C$ is the concentration of solute in the solution, $\Gamma$ the number of adsorbed solute molecules per unit area, $\Gamma_{\text{max.}}$ the number of adsorbed molecules in a saturated layer of the surface, and $k$ the equilibrium constant. Equation (1) can be written in the form

$$1/\Gamma = k/C + 1/\Gamma_{\text{max.}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The experimental values of $1/\Gamma$ plotted against $1/C$ should give a straight line, the slope of which is $k$, and the intercept on the axis at $1/\Gamma_{\text{max.}}$, *i.e.*, where $\Gamma$ is a maximum and all the available surface is covered by a unimolecular layer of adsorbed molecules; $1/\Gamma_{\text{max.}}$ is therefore the surface area occupied by an adsorbed molecule. It has already been shown (*loc. cit.*) that straight lines were obtained for all the acids investigated with charcoal A. In Figs. 1, 2, 3, and 4, the $1/\Gamma$–$1/C$ curves for formic, acetic, monochloroacetic, and trichloroacetic acids are compared for the different charcoals. The results obtained with salicylic acid are similar.

FIG. 1.

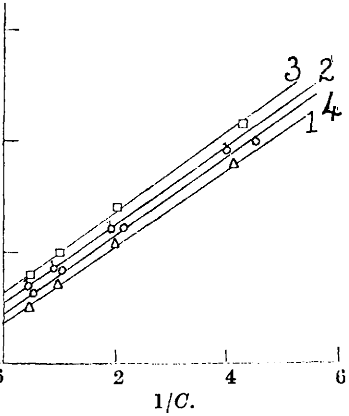
*Formic acid.*



1. *Charcoal A.* 3. *Charcoal $C_1$.*
2. ,, *B.* 4. ,, *$C_2$.*

FIG. 2.

*Acetic acid.*



1. *Charcoal A.* 3. *Charcoal $C_1$.*
2. ,, *B.* 4. ,, *$C_2$.*

In the table are given the values of $\Gamma_{max.}$ extrapolated from the curves, and also the values of *k*, for all the acids with the different charcoals.

| Charcoal. | $\Gamma_{max.}$ | *k*. | *A/M*.* |
|---|---|---|---|
| | *Formic acid.* | | |
| A | 1·0 | 1·15 | 82 |
| B | 0·77 | 1·17 | 106 |
| $C_1$ | 0·47 | 1·30 | 174 |
| $C_2$ | 0·61 | 1·23 | 134 |
| | *Acetic acid.* | | |
| A | 1·33 | 0·70 | 62 |
| B | 1·00 | 0·70 | 82 |
| $C_1$ | 0·80 | 0·71 | 102 |
| $C_2$ | 1·11 | 0·70 | 74 |
| | *Monochloroacetic acid.* | | |
| A | 1·33 | 0·25 | 62 |
| $C_1$ | 1·05 | 0·25 | 78 |
| $C_2$ | 1·39 | 0·20 | 59 |

| Charcoal. | $\Gamma_{max.}$ | *k*. | *A/M*.* |
|---|---|---|---|
| | *Trichloroacetic acid.* | | |
| A | 0·168 | 1·8 | 487 |
| ($C_1$ | 0·132 | 2·0 | 620) |
| $C_2$ | 0·294 | 1·9 | 279 |
| | *Salicylic acid.* | | |
| A | 0·476 | 0·031 | 172 |
| B | 0·521 | 0·030 | 157 |
| $C_1$ | 0·602 | 0·033 | 136 |
| $C_2$ | 0·893 | 0·027 | 92 |
| | *Benzoic acid.* | | |
| A | 0·541 | 0·023 | 152 |
| $C_1$ | 0·667 | (0·023) | 123 |
| $C_2$ | 0·953 | (0·023) | 86 |

* See p. 1870.

The manner in which $\Gamma_{max.}$ varies for the different acids with the charcoals, *viz.*, activated A, finely ground B and $C_1$, and finely ground and re-activated $C_2$, can be summarised thus :

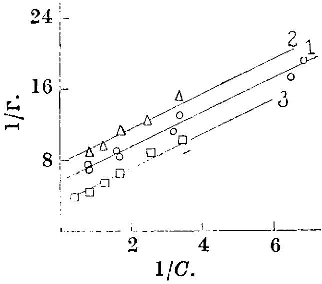
| Small molecules. | $\Gamma_{max.}$ for different charcoals. |
|---|---|
| Formic, acetic, monochloroacetic | $A > B$ or $C_1$<br>$C_2 > C_1$<br>$A > C_2$ (monochloroacetic $A \bumpeq C_2$) |
| Larger molecules. | |
| Salicylic, benzoic * | $A < B$ or $C_1 < C_2$ |
| Trichloroacetic | $A < C_2$ |
| All the acids | $C_2 > C_1$ |

* On account of shortage of charcoals $C_1$ and $C_2$, with benzoic acid sufficient measurements have not been made to ascertain the slope *k*. It is assumed that this will have the same value for these charcoals as for charcoal A. $\Gamma_{max.}$ is extrapolated from the points available on this assumption.

It is seen then that, for small molecules, the adsorption *decreases* after charcoal A has been ground and increases again when it is reactivated. For larger molecules, the adsorption *increases* after the grinding and increases still further after the reactivation. For molecules of all sizes, the adsorptions increase with the finely ground reactivated charcoal as compared with the finely ground non-reactivated charcoal, but only for larger molecules are the adsorptions with the finely ground reactivated charcoal greater than those with the original activated charcoal A; for smaller molecules they are, in general, less. The variations of $\Gamma_{max.}$ for the acids with the different charcoals are shown in Fig. 5.

FIG. 4.

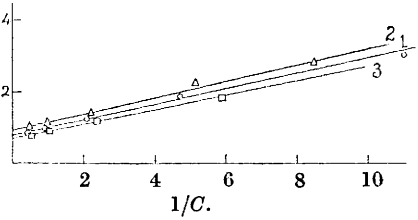
*Trichloroacetic acid.*



1. *Charcoal A.*
2. ,, $C_1$.
3. ,, $C_2$.

FIG. 3.

*Monochloroacetic acid.*

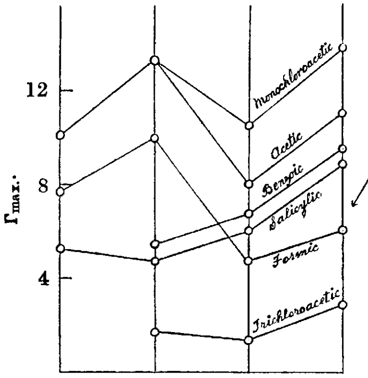


1. *Charcoal A.*
2. ,, $C_1$.
3. ,, $C_2$.

Although $\Gamma_{max.}$ is, in the main, markedly different for each acid with the different charcoals, yet the constant *k* is practically the same for each acid and is *independent* of the charcoal. This means that the rate of adsorption (or evaporation) is the same for the molecules of each acid with the different charcoals, and therefore the surface conditions of the various charcoals must be identical, despite their different modes of preparation. The charcoals have therefore fundamentally the same surface structure and differ only in their available surface areas.

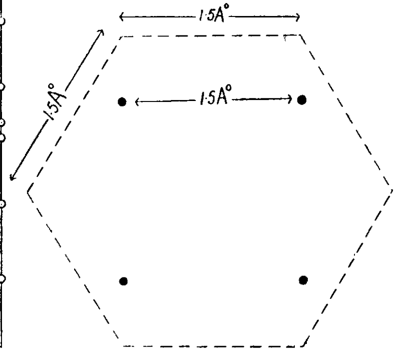
In the last column of the table are given values of $A/M$, the calculated number of carbon atoms of the charcoals for each adsorbed molecule of the acids. These numbers are surprisingly low and it is manifest that the available surface area of each charcoal is very large compared with its bulk. This becomes even more apparent when the areas of the adsorbed molecules are taken into consideration. For example, consider the adsorption of salicylic acid with charcoal $C_2$. The number of carbon atoms of this charcoal per adsorbed molecule is 92; it is probable that the adsorbed acid molecule is oriented so that the benzene plane lies on the surface of the charcoal, and the polar hydroxyl and carboxyl groups are oriented towards the aqueous phase. The area of the benzene ring is approximately 24 Å.U., and the distance between adjacent carbon atoms in the charcoal about 1·5 Å.U. It will be seen from Fig. 6, where the benzene ring is represented by the broken lines and the carbon atoms of the charcoal by dots, that the space covered by each acid molecule must be at least equivalent to 4 or 5 carbon atoms of the charcoal surface. To account for this surface, therefore, as a minimum requirement, the ratio of the number of carbon atoms at the surface to the total number in the bulk of the charcoal must be 4 : 92. This provides an enormous area which is available for adsorption. Clearly, then, the charcoal particles must possess a very large number of ultraporous cavities of molecular dimensions; in fact, the particles of charcoal are probably largely assemblies of such ultrapores.

FIG. 5.



*Charcoals.*

FIG. 6.

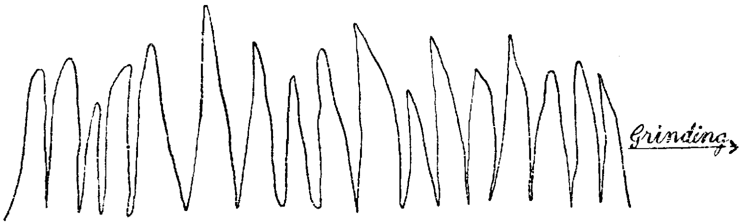


*The Processes of Grinding and Activation.*—It is now possible, on the basis of these conclusions, to make deductions as to the nature of the processes of grinding and activation. The charcoal A was obtained by rough grinding by hand for a few minutes, of the coarse masses of the inactive charcoal obtained from the complete combustion of A.R. saccharose and the subsequent degassing and activation of the inactive charcoal by atmospheric oxygen at 500°. B and $C_1$ were obtained by the vigorous grinding of A, and $C_2$ was prepared by reactivation of $C_1$. The solutions containing charcoals B and $C_1$ became colloidal solutions (except with trichloroacetic acid), but those containing $C_2$ were clear and colourless; nevertheless, all the acids with $C_2$ showed increased adsorption as compared with $C_1$, thus indicating a larger available surface for the former than for the latter. Since the cavities of the charcoals are of ultra-porous dimensions, the size of the adsorbed molecules will determine their capacity to penetrate the ultrapores, so that smaller molecules will be able to penetrate pores which may be too small for larger ones; further, if the pores taper towards the interior of the charcoal masses, or are irregular in diameter, the smaller molecules will be able to penetrate the pores more deeply than the larger ones. The effect of grinding on charcoal A will be to increase the number of particles, and, at first sight, it might appear that this will necessarily lead to an increase in the available surface area, especially so when grinding results in charcoals B and $C_1$ which give solutions containing colloidal charcoal particles. This is not necessarily true, however, for molecules of different sizes. Grinding will tend to make the particles spherical by knocking off the superficial protuberances; some of these pieces are apparently of colloidal or semi-colloidal dimensions and are completely separated; others, however, by the process of grinding, will be pressed into the cavities of the larger particles and will block up some of the ultrapores, leading finally to charcoals B and $C_1$, as shown diagrammatically in Fig. 7. The grinding will then have the following effects: it will (1) increase the surface area by increasing the number of particles, (2) decrease the surface area by blocking up some of the ultrapores, and (3) increase the surface area at the mouths of the ultrapores by the external area of the particles closing the ultrapores. The effect of (1) is to increase the available area for the adsorption of all molecules, no matter what their size may be; the effect of (2) will be mostly felt by the smaller molecules, since they will be unable to penetrate the ultrapores to the same extent as before, and much less by the larger molecules; and the effect of (3) will be to increase the surface for all molecules. The net effect of grinding may then be to *increase* the available surface area for large molecules, but to *decrease* it for smaller molecules; thus the smaller molecules of formic, acetic, and monochloroacetic acids are less adsorbed after grinding, whereas the larger molecules of salicylic and benzoic acids show increased adsorption; the adsorption of trichloroacetic acid is rather a special case, since this has the effect of coagulating the colloidal or semi-colloidal particles of charcoal $C_1$, thus leading to a decrease in the surface area and a consequent decrease in the adsorption.

After activation of charcoal $C_1$ to give $C_2$, all acids show increased adsorption on the latter, and therefore indicate a larger adsorption area, although solutions of the latter contain no colloidal particles; clearly, these must have been completely burned off by the oxygen. Now the effect of heating in oxygen must be such that *all* the charcoal particles are partially consumed at the surface, so that after activation, for a given weight of charcoal, there will be on the average more particles than previous to activation, so that the available surface area will be increased; further, the pieces of charcoal blocking up the ultrapores of the ground material will be partially, or in some cases completely, burned off, the net result of which will also be to increase the available area of the charcoal. These effects of activation will then all tend to increase the surface area for a given weight of charcoal, and so lead to the increased adsorption of all the acids as compared with the non-activated ground material. This is

FIG. 7.

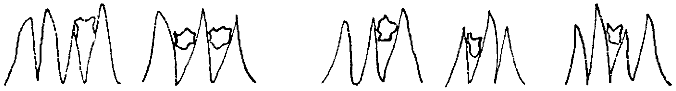
*Processes of grinding and activation.*



*Charcoal A.*

*Colloidal particles.*

*Charcoal B or $C_1$.*



*Charcoal $C_2$.*

found to be the case, as shown in the table by comparing $\Gamma_{max.}$ for charcoals $C_1$ and $C_2$. The adsorptive capacity of $C_2$ (as compared with A) will then, especially for the smaller molecules, be determined by the intensity of re-activation to which it has been subjected, a conclusion which is confirmed by the results obtained by Dubinin (*Z. physikal. Chem.*, 1930, *A*, **150**, 145), who found that the activity of a given charcoal was dependent, not only on the temperature of activation, but also on the rate of flow and the volume of the activating gas.

The fact that the equilibrium constant $k$, for a given acid, is independent of the charcoal, proves conclusively that the charcoal surfaces are not distinguishable, since even slight modifications in the nature of the surface would certainly be expected to influence the rate of adsorption and evaporation. Hofmann, Groll, and Lemcke (*Z. angew. Chem.*, 1931, **44**, 841), in an *X*-ray examination of purified active charcoals, showed that the crystal structure was the same as that of graphite, and that increasing size of crystals is accompanied by increasing hardness, decreasing adsorptive capacity for phenol, and decreasing catalytic activity for the reaction $H_2 + Br_2 \longrightarrow 2HBr$. The identity of the *X*-ray diagrams of graphite and different active charcoals has also recently been confirmed by Berl, Andress, Reinhardt, and Herbert (*Z. physikal. Chem.*, 1932, *A*, **158**, 273), who have shown that there is no amorphous modification present on the charcoal surface, and have suggested that the properties which distinguish active charcoal from graphite are related to the breaking off of the three-dimensional crystal lattice of the graphite up to the separation of a metamorphous phase, resulting in an active charcoal.

Measurements of the densities of charcoal with different liquids provide additional evidence for the existence of ultrapores. For most liquids the results are abnormally low and inconsistent, but Howard and Hulett (*J. Physical Chem.*, 1924, **28**, 1082) have shown that for different charcoals and graphite, with helium gas, the densities are constant, their results being as follows :

| Charcoal ..................... | Coconut | Sugar | Kelp | Graphite |
|---|---|---|---|---|
| Density ..................... | 2·12 | 2·26 | 2·28 | 2·28 |

The low values and variations with different liquids can be ascribed to their different penetrabilities of the ultrapores. Krczil (*loc. cit.*, p. 183) has measured the heats of wetting of alcohol and benzene for particles of different sizes of various charcoals, the particles being separated by appropriate sieves, and has found that the heats of wetting are constant for a given charcoal and independent of the particle size. The inconsistent results of the attempt of Paneth and Radu (*Ber.*, 1924, **57**, 1221) to determine the surface areas of a number of charcoals by finding the maximum amount adsorbed of a number of different substances, and calculating the areas on the assumption of a unimolecular layer of adsorbed molecules of known dimensions, can also be ascribed to the different degrees of penetration of the adsorbed molecules, since in each case it was found that the smallest molecules adsorbed gave the largest calculated areas.

An $X$-ray examination and an analysis of the elements of the charcoals used in this investigation are now in progress and will be concluded soon.

## *Summary.*

(1) Adsorption isotherms at 25° have been obtained for aqueous solutions of formic, acetic, monochloroacetic, trichloroacetic, salicylic, and benzoic acids with three different ash-free sugar charcoals of different stages of activation (with oxygen) and grinding, and the results compared with the isotherms obtained with another ash-free oxygen-activated sugar charcoal in a previous investigation.

(2) All the acids, with every charcoal, are in satisfactory agreement with the adsorption equation of Langmuir, which can be written in the form $k\Gamma = C(1 - \Gamma/\Gamma_{\text{max.}})$, where $k$ is the equilibrium constant.

(3) Each acid has the same value of $k$ for all the charcoals, despite their different modes of preparation. The rate of adsorption (and evaporation) is therefore the same for a given acid and is independent of the charcoal, and it is concluded that the charcoals have identical surface structures and differ only in their available areas. The results obtained are in agreement with $X$-ray analysis of graphite and active charcoals.

(4) The maximum number of molecules adsorbed ($\Gamma_{\text{max.}}$) for each acid, which is equivalent to a unimolecular layer, requires a large number of carbon atoms at the charcoal surfaces, and these are an appreciable proportion of the total number of carbon atoms in the bulk of the charcoals.

(5) It is shown that active charcoal is an assembly of ultrapores of molecular dimensions, and that the available surface area is determined by the dimensions of the adsorbed molecules.

(6) The effects of grinding and activation of charcoal are explained on the basis of changes in the capacities of the ultrapores, and the variations of $\Gamma_{\text{max.}}$, for a given acid, with the different charcoals are thus accounted for.

(7) It is shown that the effect of grinding a charcoal may be such that the available surface area may be decreased for small molecules, leading to decreased adsorption, although at the same

time, it may be increased for larger molecules, resulting in increased adsorption.

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