

## THE SURFACE AREA AND SORPTION.

By Michael TARLÉ.

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In the "Bulletin of the Chemical Society of Japan"<sup>(1)</sup> appeared an interesting report by Prof. Jitsusaburo Sameshima under the title: "The Sorption of Gas by Charcoal as a Dissolution Phenomenon." Prof. Sameshima made measurements of amounts of carbon dioxide absorbed by various kinds of charcoal (activated in the same way), and found, that the amounts absorbed are independent of the area of the surface of the charcoal; therefore he considers the phenomenon of sorption not as a condensation of gas on the surface, but as a dissolution of the gas in the charcoal. In my opinion this deduction is based on misunderstanding: the interesting experiments of Prof. Sameshima do not prove the correctness of his point of view.

1. It is not quite clear in what way has been the amount of absorbed gas measured. The experimental part has been probably described in the former publications of Prof. Sameshima, which are unavailable for me at present. So far one can judge the volume absorbed has been measured indirectly and the measurements are partly based on the knowledge of the volume of the charcoal; this volume is calculated under assumption that the density of the charcoal is 2.1. This assumption might be correct for highly active charcoals only; in other words for charcoal, which has been heated for a rather long period of time (6 to 24 hours) at a temperature of 800–1000°C if, and as in experiments under discussion, has not been treated by chemical agents. Now, it is highly probable that being activated in this way, the raw charcoal changes its former structure and passes from the amorphous state to cristalline (graphite). During this transition period—possibly under the influence of unsaturated atoms<sup>(2)</sup>—the charcoal has a high absorbing capacity. After the transition is finished and the whole of the charcoal is changed to graphite, the high active properties disappear. The process of transition can be followed by measurements of the true density of the charcoal, as has been shown by me in a paper submitted to the Anti-Gas Branch of the Chemical Warfare Department in London in 1918. I repeated now some of those measurements at the Research Laboratory of the Moukden Arsenal (in connection with an investigation of the velocity of sorption problem, soon to be

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(1) This journal 2 (1927), 1.

(2) O. Ruff, *Z. angew. Chem.*, 38 (1925), 1164.

published) and again found that the true density is a function of the duration and temperature of the activation process and is closely connected with the absorbing capacity. Different kinds of charcoal (of different origin and of different kind of activation) showed following results :

No.	Absorbing capacity for chlorine (%) $A$	True density <sup>(1)</sup> $D$	Volume of the pores per 1 gr. $C$	$\frac{A}{C}$
1	11.1	1.44	—	—
2	23.0	1.52	1.18	19.3
3	32.2	1.94	0.96	33.5
4	36.6	1.43	1.30	27.1
5	38.5	1.91	1.15	33.5
6	40.1	2.10	1.32	30.6
7	52.0	1.84	1.79	29.1

We see from this table that in only one case has been the density 2.1. As Prof. Sameshima activates his charcoal only *one* hour at 800°C. we may assume that its density has been lower than 2.1 (probably 1.7–1.9) and therefore the amounts of the absorbed gas (the absorbing capacities) are not represented quite correctly by the figures of Prof. Sameshima. The correction will vary with the kind of charcoal used and, although not a large one, may change the opinion “that the amounts of absorbed carbon dioxide . . . by various kinds of charcoals are nearly equal in each other.” Furthermore we see from the above table that the rate “ $A : C$ ” is nearly constant and from this we may assume, that—at least in some cases—the absorbing capacity is nearly proportional to the volume of the pores and therefore cannot be explained by the dissolution theory of Prof. Sameshima. His statement, that “ . . . It is not conceivable that different materials give the charcoals of nearly same surface area . . .” is also contradicted by facts. The activation process changes the original wood structure, the original difference of the structure with the progressing process disappears, the final density becomes about 2.1, the charcoal assumes the structure of the graphite. So the surface area (after activation) will depend not so much on the original structure, as on the method of activation. As the charcoals in the experiments of Prof. Sameshima has been activated in the same way the total absorbing capacity will not differ much from each other:

2. The second important point of the investigation of Prof. Sameshima is “that the absorbed amounts by the granular and by the powder charcoal are the same. . . . The dissolved (absorbed ? M.T.) quantity of gas depends

(1) These density figures are not absolutely correct, as we do not know the density of the liquid which filled the micropores and is compressed; but the volume of the micropores is evidently small comparing with the volume of the macropores. The mistake is also of a small order. See the investigation by Harkins and Ewing, *J. Am. Chem. Soc.*, 43 (1921), 1790.

only upon the amount of charcoal, and does not depend upon the surface area of it." This point is surely based on a misunderstood conception of the surface area of an absorber. The experimental method of Prof. Sameshima has been as follows. The amount of the gas absorbed by granulated charcoal has been measured, then the charcoal powdered (in a mortar, by hand), the charcoal heated, the gas removed, and the charcoal again brought in contact with gas. The first measurement of the absorbed amount gives practically the same result as the second one, and from this Prof. Sameshima concludes that the absorbing capacity is independent of the surface area, because the surface area of a powder is, in his opinion, much larger than that of the granules. This conclusion is incorrect, because for a very porous body both areas will be practically equal.<sup>(1)</sup> The surface area of a porous body consists of two areas: area of the external surface and that of the internal surface (interface), i.e. the surface of the macro- and micropores.<sup>(2)</sup> The second area is of another order of magnitude and incomparably larger than the first one; therefore the changing of the first area will have no practical influence upon the second one, which is not changed by grinding.

Let us make the following calculation. We take one piece of charcoal, a cube of 1 c.c., with an outside surface of 6 sq. cm. We do not know accurately the internal surface area; Lamb<sup>(3)</sup> assumes that it is equal to 100 sq. meters for 1 gr. of charcoal; Cude and Hulett<sup>(4)</sup> found it to be about 200 sq. meters; from the study of microphotograms taken at the Central Scientific Laboratory of the Russian War Office during the European war<sup>(5)</sup> I found the area of the macropores only to be about 10 sq. meters for 1 gr. of activated charcoal. If we take even this low figure as a base of our calculation and assuming that the apparent density is 0.5 we get for the total area—both external and internal—of our cube  $6 + 50000 = 50006$  sq. cm. Now let us grind the charcoal. If we break it to 10000 small particles, each particle having a volume of 0.0001 c.c., the external surface of each particle will be  $0.002116 \times 6 = 0.0127$  sq. cm. As we have 10000 such particles the external area will be equal to 127 sq. cm., and the total area will be  $50000 + 127 = 50127$ . So the change of the area produced by grinding equals to 0.2% of the area only. In other words the powdering produces a negligible effect upon the surface area and therefore the experiments of Prof. Sameshima do not prove the correctness of the dissolution theory.

Manchurian Arsenal, Moukden, China.

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(1) Cude and Hulett, *J. Am. Chem. Soc.*, 42 (1920), 398.

(2) Harkins and Ewing, *J. Am. Chem. Soc.*, 43 (1921), 1798.

(3) *J. Am. Chem. Soc.*, 42 (1920), 1146.

(4) Loc. cit.

(5) Prof. Chlopine, "The Foundations of the Anti-Gas Defence." Petrograd (Leningrad), 1926.