ON DR. TARLÉ'S PAPER ENTITLED "THE SURFACE AREA AND SORPTION."

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I am glad to know that my paper under the title "The sorption of gas by charcoal as a dissolution phenomenon," which was published in the January number of this journal, has been read and criticised by Dr. Tarlé.[1] I can reply at once to the kind criticism of Dr. Tarlé.

1. In the first place, the method of measurement of the amount of absorbed gas was described in my paper (pages 2, 3 and Fig. 1). But I will explain it here again :—

Exactly weighed charcoal (evacuated, sealed in a tube and weighed) was put in the bulb A (cf. Fig. 1 in the paper cited above), and then evacuate the bulb A and the burette E. Close the cock B, introduce the carbon dioxide gas into the burette E and then close the cock D. Read the volume of the gas in the burette E after adjusting the pressure by the mercury reservoir G. Now open the cock B. Then the gas enters into the bulb A and is absorbed by the charcoal. The absorbed amount of gas can be traced time to time by reading the burette E. The final amount of absorption is known also by reading the burette E after sufficiently long time.

Now the absorbed amount of gas can be calculated as follows :—

$$V=v-v'-v'',$$

where V denotes the volume of gas absorbed by the charcoal taken,

v, the volume of gas introduced into the burette E,

v', the volume of gas remaining unabsorbed in the burette E,

v'', the volume of gas remaining unabsorbed in the bulb A.

The temperature and the pressure of the gas in various parts of the apparatus must, of course, be reduced to the same conditions, say 0°C. and 760 mm. The value of v'' can be obtained by the formula,

$$v''=(a-c)\frac{273.1P}{760T},$$

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(1) Former article in this journal.

where a denotes the capacity of the bulb A,
c, the volume of the charcoal,
P, the pressure of the gas,
T, the temperature of the gas in the bulb A.

Thus $(a-c)$ is the free space in the bulb A. A few of the actual data of observations are given in the following table (cf. Table 1 and Table 2 of the paper cited above).

	Time		v c.c.	v' c.c.	a c.c.	Wt. of charcoal gr.	c c.c.	v'' c.c.	V c.c.	Absorb. vol. for 1 gr. c.c.
	min.	sec.								
Granular charcoal. (third series)	—	15	53.200	19.071	6.046	0.8604	0.4097	5.220	28.909	34.382
	—	61	„	9.756	„	„	„	5.266	38.178	44.372
	4	25	„	6.041	„	„	„	5.165	41.994	48.808
	40	0	„	3.489	„	„	„	5.164	44.547	51.775
	79	0	„	2.930	„	„	„	5.164	45.106	52.424
	365	0	„	2.150	„	„	„	5.164	45.886	53.331
	3205	0	„	1.550	„	„	„	5.164	46.486	54.028
Powder charcoal.	—	22	53.837	9.697	6.046	0.8752	0.4168	5.158	38.982	44.540
	—	57	„	6.031	„	„	„	5.158	42.648	48.729
	5	8	„	3.398	„	„	„	5.158	45.281	51.738
	41	0	„	2.197	„	„	„	5.157	46.483	53.111
	100	0	„	2.006	„	„	„	5.158	46.673	53.329
	295	0	„	1.814	„	„	„	5.158	46.865	53.548
	3110	0	„	1.443	„	„	„	5.157	47.237	53.972

In this table the values of c (0.4097 and 0.4168) have been computed by the assumption that the density of charcoal is 2.10. Dr. Tarlé does not mention on the paper of Howard and Hulett.(1) It seems that their results are more trustworthy than any other density determinations ever published. They obtained the value 2.05–2.28 for the densities of various kinds of activated charcoals.

If we assume, however, the density to be 1.7 as Dr. Tarlé's opinion, then the values of c increase to 0.506 and 0.515 c.c. respectively. Accordingly V take lower values by 0.096 and 0.098 c.c. respectively than the values given in the table, which are 0.2% of the values of V. Then the absorbed volume of carbon dioxide by 1 gram of sugar charcoal at 25°C. and under 760 m.m. becomes 53.9 c.c. instead of 54.0 c.c. This is but small difference.

At any way, the question on the density of charcoal gives no serious effect on my result. My result are always referring to 1 gram of charcoal,

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(1) Howard and Hulett, *J. Phys. Chem.*, **28** (1924), 1088.

not 1 cubic centimeter of it. So the error which might come from the uncertainty of the density of charcoal is less than 0.2% in the final results. And in the comparison of the absorption velocities by granular and by powder charcoals, this uncertainty gives entirely no effect on the results, because the amounts of charcoals used are always nearly equal in granular and in powder ones.

The "activation," in my opinion, is nothing more than the purification process of the impure charcoal. This is analogous to the fact that the purified water dissolves much hydrochloric acid gas than the impure water. The ordinary charcoal contains much organic matters as well as inorganic "ash." These impurities can be removed by heating in the steam or in the air, or treating with chemicals etc. The amounts of impurities, however, can by no means be estimated by the elementary analysis. The surface area may somewhat increase by the partial oxidation of the charcoal, and this may result the increasing of the absorption velocity of gas in the "break point" experiment.(1)

Dr. Tarlé measured the volume of pores of charcoals. I do not know how these volumes were computed, but if he obtained these volumes from the differences of true densities and block densities (i.e. apparent densities), then it is almost meaningless to compare them with the absorption capacities. There is no relation between the surface area and the volume of pores which have been computed in such a manner. The surface area may depends upon the average volume of individual pore, but not the total volume of pores.

The charcoal probably changes its structure from amorphous to crystallinic by prolonged heating to the temperature higher than 1000°C., and this results the diminution of the absorption capacity of gas as was already described in the former paper (page 9).

2. It is true that the charcoal has a great numbers of small pores. But the surface area of it must, certainly, increase by grinding. In Dr. Tarlé's calculation, he considered that one cubic centimeter of charcoal produce 10000 particles by grinding. Then assuming the particles are cubic in form, the length of one side of these particles becomes, in average, 0.46 mm. This is evidently far from the truth. I have examined my powdered charcoal microscopically, and known that the particles range from 0.01 mm. down to those smaller than the lower limit of microscopical observation. Let us assume that the average length be 0.001 mm., then the number of particles derived from one cubic centimeter of charcoal is 10^{12}. Accordingly, the sum of the surface areas of these particles is, $6 \times 0.001^2 \times 10^{12} = 6 \times 10^6$ sq.

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(1) Chaney, Ray and John, *Ind. Eng. Chem.*, 15 (1923), 1244.

mm. = 6 sq. meter. If we assume that the total area of one gram of charcoal be 100 square meters,(1) and the block density of it be 0.5, then the increase of area by grinding amounts to 12% of the total area. The increase of area by grinding of the porous substance is less than that by grinding of the compact substance. So the above figure must be lowered to 6% or so. This is far above the experimental error of the determination of absorption capacity. In the present study, the experimental error is 0.2%. Even if the length of the particles be 0.01 mm. in average, the increase in area becomes to 0.6%, which still beyond the experimental error. Therefore the adsorption amount must increase by grinding if the adsorption theory be true.

The idea that the gas molecules condense on the surface of charcoal is merely a hypothesis. It is more natural, I think, to consider the absorption of gas by charcoal is caused by the dissolution than by the adsorption. There are numerous examples of absorption of gases by solid substances which can be explained by dissolution or compound forming theory, that is one phase theory, namely, the absorption of hydrogen by palladium, oxygen by silver, and hydrogen, carbon dioxide or water vapour by rubber etc.

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(1) Lamb and Coolidge, *J. Am. Chem. Soc.*, **42** (1920), 1168.
Garner, McKie and Knight, *J. Phys. Chem.*, **31** (1927), 641.