THE SORPTION OF GAS BY CHARCOAL AS A DISSOLUTION PHENOMENON.

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It is generally considered that the sorption of gas by charcoal is caused by the condensation of gas on the surface of the charcoal. Since Saussure's extensive research on this subject⁽¹⁾ nobody raise a doubt on the hypothesis of adsorption.⁽²⁾ Recently, many suppositions have been proposed for the mechanism of sorption. Of them monomolecular film hypothesis of Langmuir⁽³⁾ and polymolecular film hypothesis of Polanyi⁽⁴⁾ are preeminent. None of them, however, do not sufficiently coinside with the results of experiments. McBain and others⁽⁵⁾ have the opinion that one part of the gas absorbed is kept on the surface of the carbon and the other part diffuse into the mass of it.

I have studied the sorption of gas by charcoal for last several years⁽⁶⁾ and recently was convinced that this phenomenon is caused by the dissolution of gas into the mass of charcoal. Of course the minimal quantity of gas may be adsorbed, positively or negatively, on the surface of the charcoal as is required by the Gibbs-Thomson's equation, but almost all quantity of gas absorbed is kept in the mass of charcoal as a solid solution. This has been proved by the facts described in this paper and by those which will be described in the later papers.

I have found no paper except Homfray's one⁽⁷⁾ which deals the sorption of gas by charcoal as a dissolution phenomenon. There is no follower of Miss Homfray since the publication of her paper sixteen years ago, and only the adsorption hypothesis prevails throughout the scientific world.

Velocity of Sorption of Carbon Dioxide by Charcoal under Constant Pressure. The velocity of sorption of gas by charcoal was already

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(1) Saussure, *Gilb. Ann.*, **70** (1814), 113.

(2) The term "adsorption" was firstly used by Kayser, *Wied. Ann.*, **14** (1881), 450. For earlier literatures see, Mülfarth, *Ann. Physik*, [4], **3** (1900), 328.

(3) Langmuir, *J. Am. Chem. Soc.*, **40** (1918), 1361.

(4) Polanyi, *Ber. deut. physik. Ges.*, **16** (1914), 1012; *Z. Elektrochem.*, **18** (1916), 55 & **26** (1920), 370.

(5) McBain, *Phil. Mag.*, **18** (1909), 916; *Z. physik. Chem.*, **68** (1909), 471; *Nature*, **117** (1926), 550. Gouy, *J. d. Phys.*, [4], **9** (1910), 457. Firth, *Z. physik. Chem.*, **86** (1914), 294. Sheldon, *Phys. Rev.*, **19** (1922), 253.

(6) Sameshima and Hayashi, *Science Reports of the Tohoku Imperial University*, **12** (1924), 289.

(7) Homfray, *Z. physik. Chem.*, **74** (1910), 129. See Coolidge, *J. Am. Chem. Soc.*, **48** (1926), 1795.

measured by numerous authors,⁽¹⁾ but their experiments were not suited for the present purpose. I have measured the velocity of sorption of carbon dioxide by the cane sugar charcoal.

The charcoal was made by heating the pure saccharose from Merck in a porcellain crucible to red heat and then transfered into a quartz tube and again heated in vacuo to 1,000° for 30 minutes. The carbon dioxide was made by the action of the hydrochloric acid on the marble and passed through the sodium bicarbonate solution, concentrated sulphuric acid and phosphorus pentoxide successively. The gas was, then, frozen by liquid air, exhausted, and finally sublimed in vacuo.

The weight of charcoal was determined in the following manner. The sample is introduced into a small tube, which is then connected to an evacuating system. Heat to 300' and evacuate to a pressure less than 0.001 mm., and then hermetically sealed and weighed. The tube is then cut open and the charcoal is transfered into the measuring apparatus (A in Fig. 1). The emptied glass tube and the pieses of glass are weighed and subtracted from the former value. Of course the correction for the bouyancy of the air must be applied.

The measuring apparatus is shown in Fig. 1. A is a vessel containing the known quantity of charcoal. This is heated to 300° by an electric furnace and evacuated by using a mercury diffusion pump for 30 minutes after the pressure diminishes less than 0.001 mm. The stopcock B and C are then closed, and the carbon dioxide gas is introduced through the cock D into the graduated burette E. The burette E consists of three parts, the upper part is made of a capillary tube of 2.3 mm. diameter, and the middle part an ordinary gas burette, and the lower part a ten c.c. burette of 7 mm. diameter.

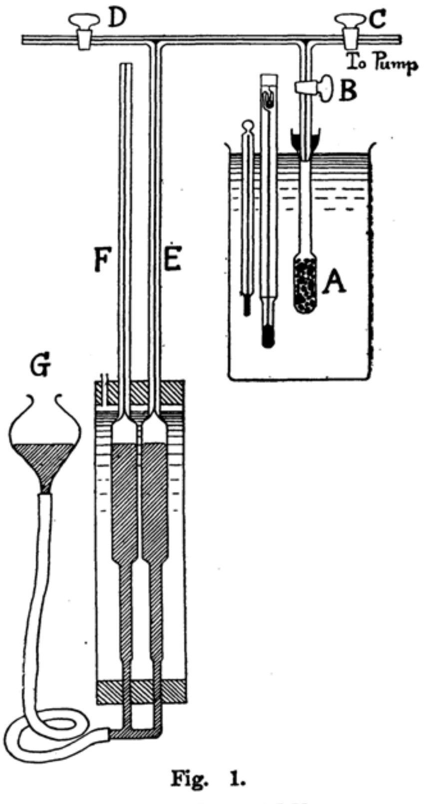

Fig. 1.

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(1) Giesen, *Ann. Physik*, 10 (1903), 833. Bergter, *Ann. Physik*, 37 (1912), 472. Harned, *J. Am. Chem. Soc.*, 42 (1920), 372. Driver and Firth, *J. Chem. Soc.*, 121 (1922), 2409. Gustaver, *Kolloidchem. Beihefte*, 15 (1922), 185. Iliin, *Z. physik. Chem.*, 107 (1923), 145. Rowe, *Phil. Mag.*, [7], 1 (1926), 659.

The latter two parts are kept in a water mantle as shown in the figure to prevent the change of temperature of the gas. A thermostat is brought to A by which it is kept to 25.00°, the constancy of temperature is indicated by a Beckmann thermometer. Now the cock B is opened and the carbon dioxide gas enters into the vessel A and is absorbed by the charcoal. The mercury reservoir G is raised to keep the gas pressure as constant as possible. The pressure of gas is read by the open manometer F and a barometer. The manometer F is made of three glass tubes of the same diameters to E as shown in the figure. The whole apparatus was calibrated with mercury before being assembled. This enabled the volume of gas in the different sections of the apparatus to be reduced separately to 0°C. from their observed temperatures.

The volume of the charcoal itself has been calculated assuming the density of charcoal to be 2.10⑴. Some investigators⑵ gave lower values for the density of charcoal, but the above given value is considered to be most reasonable from the fact that the charcoal has essentially identical nature to graphite.⑶ The results are shown in Table 1. After the first series of observations had finished, the tube A was heated to 300° and evacuated for 30 minutes and then the second series of observations has been undertaken. Quite reproducible results were obtained as shown in the table.

TABLE 1.

Quantity of charcoal used in the experiments = 0.8604 gr.

	Time. Min.	Time. Sec.	Volume of CO_2 absorbed by 1 gr. of charcoal at 25.00° (N.T.P.), in c.c.	Pressure of gas in mm. Hg.
First series.		26	36.88	763.3
		59	43.48	763.3
	2	40	47.67	763.3
	3	10	48.11	763.3
	4	45	48.99	763.3
	95		52.58	762.3
	180		52.98	761.3
	1630		53.87	760.2
	3120		53.90	755.5

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(1) Howard and Hulett, *J. Phys. Chem.* 28 (1924), 1082.

(2) Cude and Hulett, *J. Am. Chem. Soc.*, 42 (1920), 391. Harkins and Ewing, *J. Am. Chem. Soc.*, 43 (1921), 1787.

(3) Debye and Scherrer, *Physik. Z.*, 18 (1917), 300. Asahara, *Japanese Journal of Chemistry*, 1 (1922), 35.

TABLE 1. (*Continued.*)

	Time.		Volume of CO_2 absorbed by 1 gr. of charcoal at 25.00° (N. T. P.), in c.c.	Pressure of gas in mm. Hg.
	Min.	Sec.		
Second series.		33	39.32	760.0
	2	50	47.86	760.0
	10	27	50.26	760.0
	12	25	50.44	760.0
	13	45	50.57	760.0
	15	20	50.75	760.0
	22	12	51.18	760.0
	25	55	51.36	760.0
	35	0	51.65	760.0
	40	30	51.77	760.0
	49	30	51.95	760.0
	65		52.24	760.0
	91		52.52	760.0
	146		52.85	760.0
	199		53.06	760.0
	220		53.11	760.0
	257		53.16	760.0
	281		53.22	760.0
	353		53.32	760.0
	387		53.37	760.0
Third series.		15	34.38	768.2
		25	37.91	768.2
		44	42.22	768.2
		61	44.37	768.2
	4	25	48.81	760.0
	26	10	51.25	757.7
	32	20	51.59	760.0
	35		51.71	760.0
	40		51.78	760.0
	42		51.89	760.0
	55		52.13	760.0
	79		52.42	760.0
	196		53.12	760.0
	294		53.23	760.0
	315		53.28	760.0
	365		53.33	760.0
	1470		53.95	761.4
	1610		53.95	760.0
	3090		54.04	760.0
	3205		54.03	760.0

After the sorption had been measured, the charcoal was powdered in an agate mortar as fine as possible. The powdered charcoal was put into a glass tube and was connected to an evacuating system, heat to 300° and evacuated for 30 minutes, then hermetically sealed and weighed, in the same manner as in the case of granular charcoal. The powder was transfered into the vessel A in Fig. 1 and then measured the quantity of absorption of carbon dioxide gas. The results are shown in Table 2.

TABLE 2.

Quantity of powder charcoal used in the experiments = 0.8752 gr.

Time. Min.	Time. Sec.	Volume of CO_2 absorbed by 1 gr. of powder charcoal at 25.00° (N.T.P.) in c.c.	Pressure of gas in mm. Hg.
	22	44.54	760.0
	33	46.63	760.0
	43	47.68	760.0
	57	48.73	760.0
2	48	51.01	760.0
3	54	51.38	760.0
5	8	51.74	760.0
7	0	52.09	760.0
10	50	52.43	760.0
18	20	52.72	759.7
29	30	52.94	760.0
41		53.11	760.0
100		53.33	760.0
140		53.44	760.0
235		53.52	760.0
295		53.55	760.0
1440		53.85	760.0
1785		53.91	760.0
2880		54.01	760.0
2910		54.00	760.0
2975		53.97	760.0
3110		53.97	760.0

Graphically it becomes as Fig. 2. In this figure the logarithm of the time in seconds is taken in abscissa and the absorbed volume of carbon dioxide in ordinate.

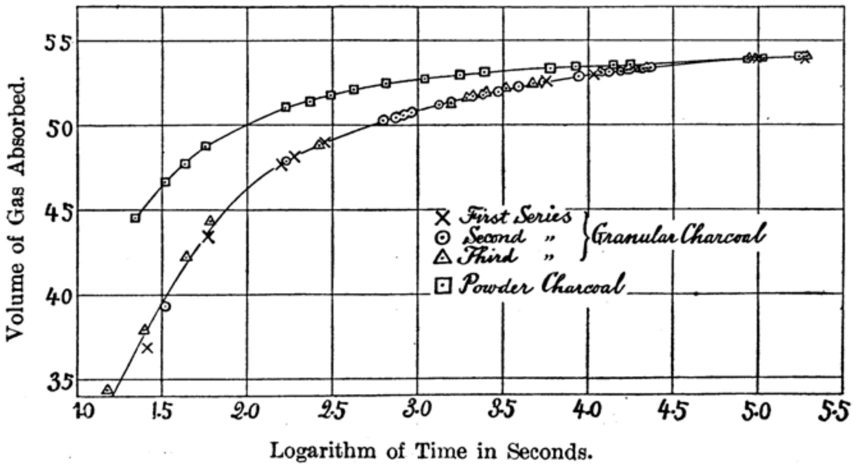

Fig. 2.

We see, from the above results, that the absorbed quantity of carbon dioxide by granular charcoal and by powder charcoal are quite the same. Moreover, the powder charcoal absorbs the gas more rapidly than the granular one. If we assume that the gas dissolves into the charcoal, then the above phenomena can be explained very smoothly. The dissolved quantity of gas depends only upon the amount of charcoal, and does not depend upon the surface area of it. So the same amount of charcoal absorbs the same quantity of gas, so long as the purity and the chemical nature of the carbon are the same, no matter what the surface area may be. By powdering the charcoal, the surface area must increases, so the velocity of dissolution must, of course, increases. From the adsorption hypothesis, the adsorbed quantity of gas must increases or decreases(1) by powdering the substance, but in my experiment it is not so. Quantitative discussions may appear in a later paper.

The Amounts of Carbon Dioxide Absorbed by Various Kinds of Charcoals.(2) The absorptive capacities were measured of carbon dioxide by the various kinds of charcoals and the results are shown in Table 3. In each case the capacities were measured after the charcoals had been heated to 300° in vacuo.

TABLE 3.

Material from which the charcoal was obtained	Treatment.	Temp. °C.	Press. mm.	Volume of CO_2 absorbed by 1 gr. of charcoal (N.T.P.) c.c.	Ash content %
Bamboo wood.	The material was carbonized at 400°–500°, and then heated to 800° for 1 hour.	20.1	759	44.8	3.0
Cherry wood.	do.	22.0	758	43.0	1.5
Ebony wood.	do.	25.0	758	36.7	14.0
Cork.	do.	24.0	756	49.0	7.2
Cocoanut shell.	do.	23.2	754	46.3	2.8
Rice.	do.	25.0	755	46.0	1.7
Soy-bean.	do.	16.2	765	3.6	20.5
Kahlbaum's "Kohle activ".	—	23.3	758	44.2	6.1
Bamboo wood.	The charcoal was boiled with aqua regia, washed with water and heated to 300°	25.0	758	43.4	0.8

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(1) See Freundlich, "Kapillarchemie" 3rd. ed. (1923), p. 177.

(2) More detailed descriptions are found in the *Journal of the Chemical Society of Japan* (in Japanese), 47 (1926), 715.

TABLE 3. (*Continued.*)

Material from which the charcoal was obtained	Treatment	Temp. °C.	Press. mm.	Volume of CO_2 absorbed by 1 gr. of charcoal (N.T.P.) c.c.	Ash content. %
Cane sugar.	The sugar was carbonized in a crucible and then heated to 1,000° in vacuo for 30 minutes.	25.0	760	54.0	0
Carbon* monoxide soot.	CO was decomposed by hot iron. The charcoal was treated with HCl.	25.5	759	7.1	5.9 (Fe_2O_3)
Naphthalene** soot	———	25.0	762	38.0	—
Anthracite.	Anthracite was treated with HNO_3 and heated to 1,000°	20.2	765	45.6	8.1

* By the courtesy of Dr. Asahara in the Institute of Physical and Chemical Research.

** Made in the Laboratory of Prof. Michaelis in Aichi Medical University, Nagoya.

We see from Table 3 that the amount of absorbed carbon dioxide at ordinary temperatures (20–25°) by various kinds of charcoals are nearly equal in each other, viz. 35–50 c.c., notwithstanding the materials from which the charcoals have been made are so divergent. In the case of the soy-bean charcoal, the ash content is so high as 20% and such an impure charcoal cannot be compared with other purer charcoals. The bamboo charcoal was made by the carbonization of the hard fibrous stem of that tree, the sugar charcoal was made by the carbonization of the fused mass of sugar, while naphthalene soot by the imcomplete oxidation of the combustible vapour. It is not conceivable that so different materials give the charcoals of nearly same surface area. The surface area must, of course, be different in each charcoals, while they show nearly equal absorptive capacities. This fact can only be explained by the dissolution theory and not by the adsorption theory. The content of ash and other impurities will change the absorptive capacities of the charcoals, just as the dissolved salts or alcohol diminishes the solubility of hydrochloric acid gas in the water. The "activation" process is probably a process of removing the impurities and enlarging the surface area by etching which will enable the ability of rapid absorption of the gas.

One gram of the pure cane sugar charcoal absorbs 54.0 c.c. of carbon dioxide (N.T.P.) at 25.0° and under the gas pressure of 760 mm. We may take this quantity as the solubility of carbon dioxide in pure charcoal. For impure charcoal the solubility of gas will change according to the amounts, the chemical nature and the state of existence (i.e. physical mixture, solid solution or compound) of the impurities. The soy-bean charcoal and the carbon monoxide soot are the examples of the great effect of impurities. The carbon dioxide is an unsuitable gas to test the effect of impurities, because CaO, MgO etc. in the ash will chemically absorb this gas. The experiments for other gases will be undertaken later.

Absorptions of Carbon Dioxide by Charcoal at Various Temperatures and Pressures.(1) The determinations were made of the absorption amounts of carbon dioxide by another sample of bamboo charcoal at different temperatures and pressures and the results are summarized in Table 4.

Table 4.

Volumes of CO_2 absorbed by 1 gr. of bamboo charcoal (N.T.P.) in c.c.

Press. \ Temp.	0°	10°	20°	30°	40°
50 mm.	15.5	11.7	9.0	6.3	3.6
100 mm.	22.1	17.4	13.7	10.1	6.3
200 mm.	30.0	24.8	20.1	15.4	10.6
300 mm.	35.0	29.4	24.5	19.2	14.2
400 mm.	38.8	32.8	27.9	22.3	17.1
500 mm.	41.6	35.6	30.8	25.0	19.4
600 mm.	43.9	38.1	33.1	27.1	—

If we plot the logarithm of the volume against the logarithm of the pressure, Fig. 3 is obtained. Form Fig. 3 we see that the Freundlich's formula can hardly be applied in this case.

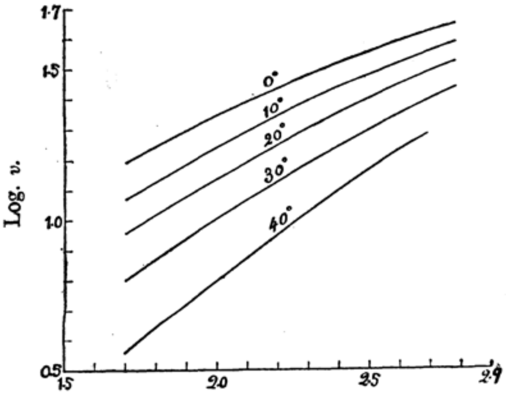

Fig. 3.

Numerous authors have tested whether the Henry's law can be applied for the absorption of gases by solids. In the case of hydrogen the law is applicable,(2) *but in other gases it is not* so. In Fig. 3 we see that the tangent of curves approach to unity at the high temperature and low pressure, for example at 40' it becomes,

$$\frac{d(\log v)}{d(\log p)} = \frac{4}{5}, \qquad \text{or} \qquad v = kp^{0.8}$$

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(1) This experiment was done in 1922 in the Chemical Laboratory of the Tohoku Imperial University, Sendai.

(2) Titoff, *Z. physik Chem.*, 74 (1910), 641.

where v denotes the absorbed volume of gas, p the pressure and k a constant. The charcoal absorbs too much carbon dioxide to be applied the Henry's law, just as the cases of the dissolutions of ammonia or hydrochloric acid gas in the water. The amount of absorbed gas increases by lowering the temperature, which is quite similar to the dissolution of gas in water. There are parallelisms between the temperature effect on the absorption of gas by charcoal and by water.

Change of Absorption Amount by the Change of Modification. It is generally known that a substance in amorphous modification absorbs much gas than its crystalline modification.(1) It is doubtful that there is really amorphous substance in solid modification from the standpoint of the phase rule, X-ray analysis or colloid chemistry. Some of them may be the supercooled liquids and others may be the imperfect crystals of somewhat irregular atomic arrangements. But in any case, the so-called amorphous substance is the modification which will be situated between the perfect crystalline phase and the liquid phase. So it is expected that the solubility of gas by the amorphous modification is greater than that by the crystalline one, and probably less than that by the liquid if a comparison at the same temperature could be done. The absorptions of gases by silica gel, alumina or some of the fine powder of metals may ascribe to this cause.

The author wishes to express his thanks to Dr. G. Asahara and Dr. T. Totsuka for furnishing some of the charcoals. The author's thanks are also due to Mr. M. Kishino and Mr. T. Watanabe for their assistances in the experiments.

Summary.

1. The velocities of absorptions of carbon dioxide by the granular and the powder charcoals have been measured.

2. The velocity of absorption by the granular charcoal is smaller than that by the powder one.

3. It was confirmed that the absorption amounts by the granular and by the powder charcoal are the same.

4. The solubility of carbon dioxide in one gram of pure cane sugar charcoal at 25.0° and under 760 mm. has been determined to be 54.0 c.c. (N.T.P.).

5. The amounts of absorptions of carbon dioxide by various kinds of charcoals have been measured. Most of them absorb nearly equal amount of the gas, notwithstanding the divergence of the materials from which the charcoals were made.

6. The amounts of absorptions of carbon dioxide by bamboo charcoal at various temperatures and pressures have been measured.

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(1) See Freundlich "Kapillarchemie" 3rd. ed. (1923), p. 178.

7. The fact that the amorphous substance absorbs more gas than the crystalline one has been interpreted.

8. All of the facts mentioned above favoured the dissolution theory for the sorption of gas by charcoal.

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