SORPTION OF AMMONIA BY CHARCOAL.

By Jitsusaburo SAMESHIMA.

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The author studied the sorption phenomena by charcoal⁽¹⁾ and chabazite⁽²⁾ of carbon dioxide, etc., and concluded that the gas molecules enter into the molecular cavities in the solid body and form a homogeneous solid solution.⁽³⁾

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(1) Sameshima, this Bulletin, **2** (1927), 1 and 246; Sameshima and Hayashi, *Science Reports of the Tohoku Imperial University*, **12** (1924), 289.

(2) Sameshima, this Bulletin, **4** (1929), 96.

(3) Sameshima, this Bulletin, **4** (1929), 125; *Chem. News*, **139** (1929), 61.

In the present paper, the result of investigation of the sorption of ammonia by charcoal is reported. The sorption amount by charcoal of ammonia was already measured by numerous authors.(1) A few reports are found on the velocity of sorption of ammonia by charcoal,(2) which, however, are not so exact and the observations did not continued sufficiently long period of time.

The present experiment was undertaken, at first, for the purpose to compare the sorption amounts and velocities of ammonia by granular and by powder charcoals, just as reported in the case of carbon dioxide.(3) But by the experiment, it has been known that the sorption amount by charcoal of ammonia cannot be measured exactly for the equilibrium state cannot be attained even after several months. The measurement has been continued for six months, but the charcoal was still absorbing the gas in considerable velocity. This is a very remarkable fact. So it is almost impracticable to measure the sorption amount of ammonia by charcoal exactly.

Experimental. The apparatus and the method of measurement are quite the same with those which were described already.(4) The charcoal has been made by heating the pure saccharose from Merck in a porcelain crucible to red heat and then transferred into a quartz tube and again heated in vacuo to ca. 1000°C. for 30 minutes. The ammonia was prepared from ammonium chloride and lime, and dehydrated by potassium hydroxide, frozen and fractionated twice with liquid air.

In the experiment, 0.3550 gram of charcoal has been used. The volume of ammonia in the apparatus has always been read after the temperature of charcoal was adjusted to 25.00°C., and the pressure of gas to 760 mm. The volume of gas absorbed can be calculated and then reduced to that at normal temperature and pressure. The results are shown in Table 1.

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(1) Hunter, *Phil. Mag.*, **29** (1865), 116; *J. Chem. Soc.*, **24** (1871), 76; Joulin, *Ann. chim. phys.*, **22** (1881), 398; Kayser, *Wied. Ann.*, **12** (1881), 526; **14** (1881), 450; Chappuis, *Wied. Ann.*, **19** (1883), 21; Vaubel, *J. prakt. Chem.*, **74** (1906), 232; Titoff, *Z. physik. Chem.*, **74** (1910), 668; Hempel, *Z. Elektrochem.*, **18** (1912), 724; Richardson, *J. Am. Chem. Soc.*, **39** (1917), 1828; Firth, *J. Chem. Soc.*, **119** (1921), 926; Ruff, *Z. angew, Chem.*, **38** (1925), 1164; Henglein and Grzenkowski, *Z. angew. Chem.*, **38** (1925). 1186; Magnus and Cahn, *Z. anorg. allg. Chem.*, **155** (1926), 205; Ruff and Hohlfeld, *Kolloid-Z.*, **36** (1925), 23; Ruff and Roesner, *Ber.*, **60** (1927), 411.

(2) Giesen, *Ann. Physik*, **10** (1903), 842; Pickles, *Chem. News*, **121** (1920), 25.

(3) Sameshima, this Bulletin, **2** (1927), 1.

(4) Sameshima, this Bulletin, **2** (1927), 1 and 246.

Table 1.

Date D. H. M. S.	Time duration from the beginning in minutes	Apparent volume of NH_3 absorbed by 0.3550 gr. of charcoal in c.c. (N.T.P.)	Leak estimated by blank experiment in c.c.	Corrected volume of HN_3 absorbed by 0.3550 gr. of charcoal in c.c. (N.T.P.)
1928, July 18, 10–30–0 A.M.	0	0	0	0
10–30–20 A.M.	0.33	22.317	0	22.317
10–30–46 A.M.	0.77	24.345	0	24.345
10–31–16 A.M.	1.27	32.305	0.01	32.29
10–31–50 A.M.	1.83	34.120	0.01	34.11
10–32–20 A.M.	2.33	35.040	0.01	35.03
10–33–54 A.M.	3.90	35.937	0.02	35.92
10–40–50 A.M.	10.83	36.528	0.045	36.483
10–51 A.M.	21	36.846	0.070	36.776
11–37 A.M.	67	37.326	0.143	37.183
12–50 P.M.	140	37.578	0.196	37.382
3–36 P.M.	306	37.927	0.235	37.692
July 19, 10–10 A.M.	1420	38.681	0.325	38.356
19, 2–10 P.M.	1660	38.733	0.332	38.401
20, 1–35 P.M.	3065	39.032	0.357	38.675
21, 12–15 P.M.	4425	39.197	0.360	38.837
23, 11–50 A.M.	7280	39.416	0.367	39.049
24, 12–10 P.M.	8740	39.508	0.370	39.138
25, 11–50 A.M.	10160	39.591	0.373	39.218
27, 1–30 P.M.	13140	39.685	0.380	39.305
30, 11–0 A.M.	17310	39.813	0.390	39.423
Aug. 1, 10–10 A.M.	20140	39.912	0.397	39.515
3, 2–20 P.M.	23270	39.993	0.404	39.589
6, 12–0 M.	27450	40.082	0.414	39.668
8, 10–15 A.M.	30225	40.147	0.421	39.726
13, 11–15 A.M.	37485	40.249	0.438	39.811
16, 11–15 A.M.	41805	40.313	0.448	39.865
22, 1–0 P.M.	50550	40.419	0.468	39.951
27, 1–30 P.M.	57780	40.518	0.485	40.033
31, 10–30 A.M.	63360	40.575	0.498	40.077
Sept. 7, 12–20 P.M.	73550	40.666	0.522	40.144
17, 11–15 A.M.	87885	40.790	0.556	40.234
28, 2–20 P.M.	103910	40.960	0.594	40.366
Oct. 13, 10–40 A.M.	125290	41.084	0.644	40.440
30, 1–40 P.M.	149950	41.233	0.702	40.531
Nov. 19, 1–50 P.M.	178760	41.347	0.770	40.577
Dec. 10, 1–30 P.M.	208980	41.427	0.841	40.586
24, 2–30 P.M.	229200	41.491	0.888	40.603
1929, Jan. 28, 12–10 P.M.	279460	41.618	1.006	40.612

The charcoal in the apparatus was heated to 300°C. evacuating by a mercury diffusion pump for 30 minutes. Then keeping the temperature of charcoal to 25.00°C., the gas was introduced into it and the sorption began to take place. The contaction of charcoal and gas took place at half past ten before noon on July 18th, 1928. The observation continued, then, to the end of January 1929, extending more than six months. The first column of Table 1 shows the date and time, the second column the time duration in minutes of contact of charcoal and gas, the third column the volume of ammonia absorbed by 0.3550 gram of charcoal calculated by the manner described already,(1) the fourth column the amount of leak of the apparatus estimated by a blank experiment which is described below, the fifth column the corrected volume of ammonia absorbed by 0.3550 gram of charcoal.

After the sorption experiment by charcoal had been finished, the blank experiment has been done without the charcoal, other conditions remaining unchanged. The blank experiment was continued three and half months as shown in Table 2.

Table 2.

Date D. H. M.	Time duration from the beginning in minutes	Volume of NH_3 decreased in c.c. (N.T.P.)
Feb. 1, 11–40 A.M.	0	0
11–46 A.M.	6	0.029
11–58 A.M.	18	0.067
1– 4 P.M.	84	0.163
2–21 P.M.	161	0.204
3, 3–40 P.M.	3120	0.348
5, 2–30 P.M.	5930	0.352
7, 3–40 P.M,	8880	0.359
10, 1–10 P.M.	13050	0.405
15, 12– 0 M.	20180	0.419
19, 1–10 P.M.	26010	0.414
25, 2–20 P.M.	34720	0.423
Mar. 4, 2–40 P.M.	44820	0.456
14, 4–50 P.M.	59350	0.488
28, 2–50 P.M.	79390	0.532
Apr. 12, 1–30 P.M.	100910	0.582

The decrease of volume of ammonia in the apparatus was read and is shown in the third column of Table 2. There was a considerable decrease of volume at the first day of observation, which is probably due to the sorption of ammonia by the glass wall and the grease on the stop-cocks. From the third day forward (reading was not taken on the second day) the

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(1) Sameshima, this Bulletin, **2** (1927), 246.

amount of decrease was nearly in linear relation with time, being about 0.1 c.c. per month. This may be the leakage through the grease of stopcocks.

Now by the method of least square applying to the values below 3120 minutes in the table, we obtain the following linear equation.

$$l = 0.00000235\,t + 0.350$$

where l denotes the volume of leakage in c.c. and t the time in minutes.

The values below 0.357 (corresponds to 3065 minutes) in the fourth column of Table 1 have been calculated by this equation, while those above 0.332 (corresponds to 1660 minutes) in the same column have been obtained by interporation from the leakage curve depicted by the values of Table 2.

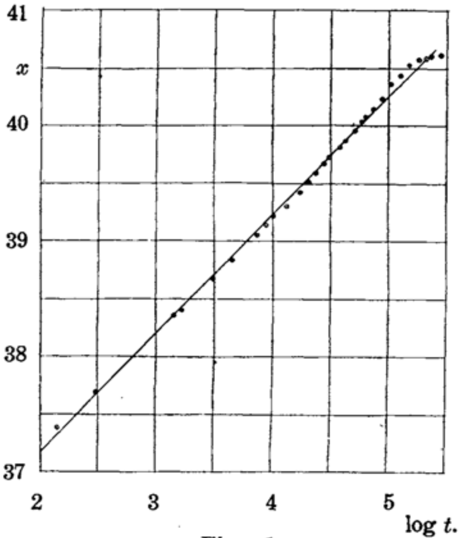

Fig. 1.

Now putting the volumes of gas sorped against the logarithms of time we obtain Fig. 1. This is nearly a straight line. The values above 67 minutes in Table 1 are not shown in the figure, for this part does not lie on the straight line.

It is very remarkable fact that the charcoal absorbs ammonia for such a long period. What is the cause of this phenomenon? Does a chemical reaction takes place between charcoal and ammonia? It is described in early literatures(1) that the carbon react with ammonia at the elevated temperature forming ammonium cyanide and hydrogen. Thus,

$$C + 2NH_3 = NH_4CN + H_2.$$

If this reaction proceeds at room temperature in a measurable velocity, however slow it may be, the volume of gas must decrease. To decide this point the following experiments have been undertaken.

After the sorption experiment had been finished, the gas remaining in the apparatus and that absorbed by charcoal was pumped out and collected into a gas burette using an apparatus shown in Fig. 2.

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(1) Kuhlmann, *Lieb. Ann.*, **38** (1841), 62; Langlois, ibid., **38** (1841), 64; Weltzien, ibid., **132** (1864), 224.

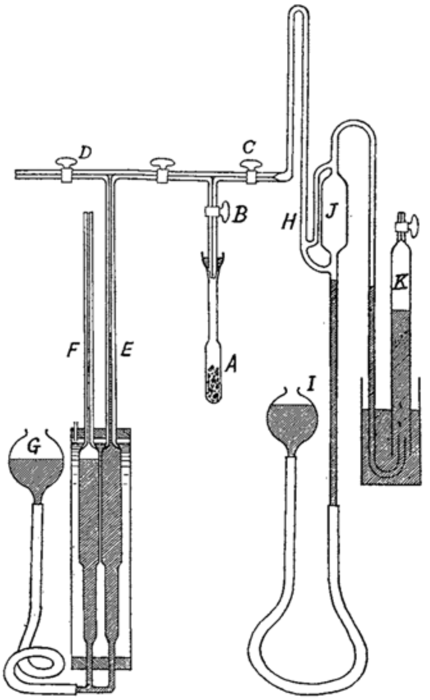

Fig 2.

A is the bulb containing charcoal, E the burette to measure the volume change of ammonia and F the niveau tube just as described already.(1) H is a Töpler pump and K a gas burette. At first the gas space, J, in the Töpler pump is well evacuated, and the burette K is filled with mercury. Then by opening the stop-cock C ammonia enters into J, which is then transferred into K by elevating I. This is repeated many a times until most of the gas, absorbed and unabsorbed, collects in K. During this process the bulb A is heated to 100°C. By this manner, the volume of gas collected in K was 46.3 c.c. at N.T.P., while the ammonia initially introduced was 50.50 c.c. at N.T.P.

This gas was almost completely absorbed by introducing 17 c.c. of dilute sulphuric acid (0.2 n.) into the tube K. The gas remained unabsorbed by sulphuric acid was only 0.3 c.c. It was known, therefore, that there was no hydrogen in the gas.

Now, the bulb A was detached from the apparatus and the charcoal was transferred into a glass tube, which was subsequently heated, evacuated, sealed and weighed. By subtracting the weight of glass tube, the exact weight of the charcoal can be known. The weight of charcoal thus determined was 0.3541 gram. As the charcoal initially taken for the experiment was 0.3550 gram, the loss is only 0.0009 gram which can be attributed to the experimental error.

Thus it was ascertained that there was no perceptible chemical reaction between charcoal and ammonia at room temperature, and the slow decrease of the volume of ammonia must be attributed to some physical cause such as diffusion or sorption into the deep part of charcoal body.

Theoretical. The diffusion velocities of a substance, say gas, into solid bodies of simple shapes are calculated. Let x be the quantity of gas

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(1) Sameshima, this Bulletin, **2** (1927), 2.

absorbed by the solid body of definite surface area, t the time, and a, b, c, etc. the constants. Then the diffusion into a plate of finite thickness is given by an equation of the following form.(1)

$$x=a\left(\frac{1}{2}-\frac{4}{\pi^2}e^{-bt}-\frac{4}{9\pi^2}e^{-9bt}-\ldots\ldots\right)$$

By a similar calculation, using Fourier's theorem, we obtain a formula for the diffusion into a plate of infinite thickness, thus,

$$x=a\sqrt{t}\,.$$

Moreover, we can deduce the formula for the diffusion into a sphere,

$$x=a-b\left(e^{-ct}+\frac{1}{4}e^{-4ct}+\frac{1}{9}e^{-9ct}+\ldots\ldots\right)$$

All these formulas, however, are not applicable to the values of Table 1. A porous substance like charcoal has a very complicated surface, so the diffusion velocity may not be calculated exactly. But at any rate, in the present case, there is neither evidence nor numerical support of the diffusion theory.

Now the sorption theory will be examined. Here "sorption" means the entering of the gas molecules into the molecular cavities and forming a solid solution.(2) The entering of gas molecules into relatively large openings among solid molecules are accomplished easily. So the sorption process of the main part of gas is finished in relatively short time. In the present experiment it takes about one hour. About 37 c.c. of ammonia has been absorbed during this period as shown in Table 1. This part of the sorption curve cannot yet be treated quantitatively.

Then the gas molecules begin to enter into more narrow cavities among solid molecules. The narrower the cavity, the greater the resistance. Let us assume that the resistance encounters in entering into a narrow molecular cavity is proportional to the time required for it. Thus,

$$R=a\,t,$$

where R denotes the resistance, t the time and a a constant.

On the other hand, we may assume that the velocity of sorption is inversely proportional to the resistance, So

$$\frac{dx}{dt}=\frac{b}{R}$$

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(1) McBain, *Z. physik. Chem.*, **68** (1910), 477.

(2) Sameshima, this Bulletin, **4** (1929), 127.

where x is the quantity of gas sorped, and b another constant. Therefore we have,

$$\frac{dx}{dt}=\frac{b}{at}$$

More precise explanation may be necessary. Assume an ammonia molecule attacks on a narrow channel to enter itself, encountering a great resistance. When the attack has been continued for t minutes the molecule enters itself to a certain depth in the solid. Namely, it takes t minutes for the dissolution of the ammonia molecule in charcoal. Then a space has been cleared where another ammonia molecule can settles. This results the sorption of one molecule of ammonia. Thus the sorption velocity depends upon the dissolution velocity.

Now the above equation is integrated,

$$\int dx=\frac{b}{a}\int\frac{1}{t}dt+k$$

or

$$x=\frac{b}{a}\ln t+k,$$

where k is the integration constant. Using another constant K, we have

$$x=K\log t+k.$$

So the sorption amount, x, and the rogarithm of time, $\log t$, is in a linear relation, which has been observed in the present experiment as shown in Fig. 1.

Summary.

1. The sorption velocity of ammonia by sugar charcoal has been measured, extending over six months.
2. It was known that the charcoal absorbs ammonia for a very long time, taking more than several months to arrive at the equilibrium condition.
3. The sorption velocity from one hour forward can be expressed by an equation.

$$x=K\log t+k,$$

where x is the sorption amount, t the time, and K and k are the constants.

4. The mechanisms of sorption have been discussed.
5. The sorption velocity depends upon the dissolution velocity of ammonia molecules into the narrow molecular cavities of charcoal.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.