SORPTION VELOCITY OF GAS BY POROUS SOLID.

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A great number of papers are published on the sorption of gas by such porous solids as charcoal and silica gel, etc.(1) The author have also contributed papers on this subject.(2) There are, however, comparatively small number of investigations concerning the kinetics of sorption. The velocity of sorption is usually measured by the decrease of gas pressure existing in contact with solid matter. Thus the pressure of gas varies according to the sorption amount. Such mode of experiment is good for the determination of the vacuum producing power or the gas collecting power of charcoal, etc. It is better, however, to measure the sorption velocity under constant pressure for the study of mechanism of sorption.

Few papers are published which describe sorption velocity under constant pressure by porous solid. Giesen(3) measured the sorption of air, carbon dioxide and ammonia by box-wood charcoal, and Bergter(4) of air, nitrogen and oxygen by coconut charcoal.

Many data on the sorption velocity have already been published by the present author and his collaborators.(5) Above all, the sorption of ammonia by sugar charcoal was measured extending over six months.(6) From this experiment, the author obtained the following equation,

$$x-a\log t=k\ ,$$

where x denotes the quantity of gas sorbed at time t, a and k being constants. This equation was derived as follows.

By the author's opinion, the sorption of gas by porous solid is a process of entering gas molecules into the molecular cavities of solid

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(1) Most of the important literatures on this subject are cited in the book: McBain, "The Sorption of Gases and Vapours by Solids" (1932).

(2) Sameshima and Hayashi, *Science Reports of the Tohoku Imperial University*, **12** (1924), 289; Sameshima and Watanabe, *J. Chem. Soc. Japan*, **47** (1926), 715; Sameshima, this Bulletin, **2** (1927), 1 and 246; **4** (1929), 96 and 125; *Chemical News*, **139** (1929), 61; this Bulletin, **5** (1930), 173 and 303; **6** (1931), 165; **7** (1932), 133.

(3) Giesen, *Ann. Physik*, **10** (1903), 838.

(4) Bergter, *Ann. Physik*, **37** (1912), 472.

(5) Sameshima, loc. cit.; Baba, this Bulletin, **5** (1930), 190.

(6) Sameshima, this Bulletin, **5** (1930), 173.

and forms a homogeneous solid solution.(1) The entering of gas molecules into comparatively large openings in solid is accomplished quickly. Then the gas molecules begin to enter into more narrow cavities among solid molecules overcoming a great resistance. Let us assume that the resistance encounters in entering into a narrow molecular cavity is proportional to the time required for it. Thus,

$$R = At$$

where R denotes the resistance, t the time and A a constant. Moreover, we obtain the following relation assuming the velocity of sorption is inversely proportional to the resistance,

$$\frac{dx}{dt} = \frac{B}{R},$$

where x is the quantity of gas sorbed, and B another constant. We have, therefore,

$$\frac{dx}{dt} = \frac{B}{At}.$$

Integrating this equation it becomes,

$$x = \frac{B}{A} \ln t + k$$

where k is the integration constant. Substituting another constant a we obtain,

$$x = a \log t + k \quad \dots\dots\dots\dots\dots\dots\dots\dots \text{(I)}$$

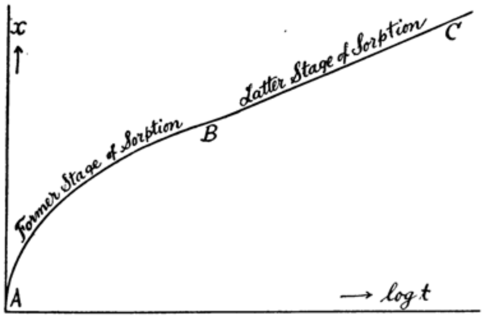

Fig. 1.

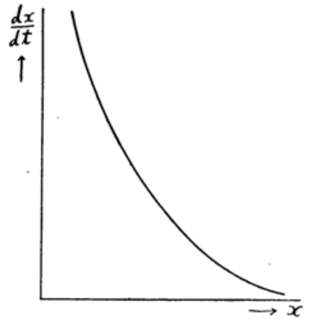

Fig. 2.

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

Generally, the sorption velocity is expressed by a curve shown in Fig. 1, which has been drawn taking x against $\log t$. The curve converts into a straight line in the region of large t. Such a region, therefore, is expressed by Equation (I). The values of α and k can be evaluated by the slope and the height of intersection to x axis at $\log t = 0$. In the tables below, these values are given in the actual examples.

The former part of sorption, A to B in Fig. 1, cannot be expressed by Equation (I). This part corresponds to the entering of gas molecules into comparatively large openings in solid. The author proposes the following equation for this part,

$$\frac{dx}{dt} = K\frac{s-x}{x^n}$$

where s denotes the saturation amount, and K and n are constants. The value of s corresponds to the saturation value of the former part of sorption which amounts roughly to the height of B in Fig. 1. The exact value, however, cannot be obtained from the curve.

We assume, as usual, the velocity of sorption is proportional to the unoccupied space in solid, $(s-x)$. Moreover, the sorption proceeds by and by beginning with the place of greatest affinity between gas and solid. The places of great affinity will be occupied at first with great velocity, and the places of small affinity will be occupied slowly. In the later period, only the places of small affinity remains unoccupied by the gas molecule, so the sorption velocity becomes slower and slower in course of sorption. This behavior may be expressed by assuming that the velocity is inversely proportional to nth power of the occupied space x, thus $\frac{dx}{dt} \infty \frac{1}{x^n}$. The value of n is the measure of distribution of affinity between gas and solid.

We obtain, therefore, the following equation as already described.

$$\frac{dx}{dt} = K\frac{s-x}{x^n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(II)}$$

By integrating we have

$$-s^n \ln(s-x) + n s^{n-1}(s-x) - \frac{n(n-1)}{2} s^{n-2}\frac{(s-x)^2}{2} + \ldots\ldots$$
$$+ \frac{(-1)^{k-1} n!\, s^{n-k}}{(n-k)!\; k!}\frac{(s-x)^k}{k} + \ldots\ldots = Kt + \text{const.}$$

This is the general velocity equation for the former stage of sorption. The relation is expressed graphically as Fig. 2 plotting $\frac{dx}{dt}$ against x.

Now, taking the simplest case, we will assume $n=1$ in Equation (II), thus,

$$\frac{dx}{dt} = K\frac{s-x}{x} \quad \text{(III)}$$

By integration it becomes,

$$s-x-s\ln(s-x) = Kt+c\,,$$

where c denotes the integration constant. At $t=0$ the value of x is zero, so the integration constant is

$$c = s-s\ln s$$

Therefore, we have

$$s\ln\frac{s}{s-x}-x = Kt \quad \text{(IV)}$$

The former part of the curve in Fig. 1, from A to B, may be expressed by this equation.

Equation (IV) has been verified by experimental data. Good coincidence has been attained between calculated and observed data. Table 1 contains the data on the velocity of sorption of ammonia by sugar charcoal, the pressure of gas being 1 atmosphere and the temperature 25°C.(1) The first column indicates the time in minutes after the contact of ammonia to charcoal and the second the volume of gas sorbed by 0.3550 gr. recalculated to that at normal temperature and pressure. The third column of the table shows the value of K calculated by the equation

$$\frac{2.303\times 36.17}{t}\log\frac{36.17}{36.17-x}-\frac{x}{t} = K\,,$$

the fourth the value of k calculated by the equation,

$$x-1.032\log t = k\,,$$

the fifth the value of x calculated inversely from these equations taking $K=37.98$ and $k=35.10$ respectively, and the sixth the difference between observed (2nd column) and calculated (5th column) values of x.

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(1) Sameshima, this Bulletin, **5** (1930), 173.

Table 1.

Sorption of Ammonia by Sugar Charcoal (25°C., 1 Atm.)

[Sameshima, this Bulletin, **5** (1930), 175.]

Time in min.	Sorption amount in c.c.	Velocity constants		Sorption calculated	Difference
t	$x_{\text{obs.}}$	K	k	$x_{\text{calc.}}$	$x_{\text{calc.}}-x_{\text{obs.}}$
0.33	22.317	37.57		22.41	+ 0.09
0.77	24.345	20.90 ?		28.94	+ 4.60
1.27	32.29	38.16		32.30 former	+ 0.01
1.83	34.11	38.00		34.11 stage	0
2.33	35.03	38.64		34.98	− 0.05
3.90	35.92	36.93		35.95	+ 0.03
10.83	36.483		—	—	—
21	36.776		35.412	36.465	− 0.311
67	37.183		35.299	36.985	− 0.198
140	37.382		35.167	37.315	− 0.067
306	37.692		35.127	37.665	− 0.027
1420	38.356		35.103	38.353	− 0.003
1660	38.401		35.078	38.423	+ 0.022
3065	38.675		35.077	38.698	+ 0.023
4425	38.837		35.074	38.863	+ 0.026
7280	39.049		35.063	39.086	+ 0.037
8740	39.138		35.070	39.168	+ 0.030
10160	39.218		35.083	39.235	+ 0.017
13140	39.305		35·054	39.351	+ 0.046
17310	39.423		35.049	39.474	+ 0.051
20140	39.515		35.073	39.542	+ 0.037
23270	39.589		35.083	39.606	+ 0.017
27450	39.668		35.087	39.681	+ 0.013
30225	39.726		35.102	39.724	− 0.002
37485	39.811		35.091	39.820	+ 0.009
41805	39.865		35.096	39.869	+ 0.004
50550	39.951		35.097	39.954	+ 0.003
57780	40.033		35.119	40.014	− 0.019
63360	40.077		35.122	40.055	− 0.022
73550	40.144		35.122	40.122	− 0.022
87885	40.234		35.132	40.202	− 0.032
103910	40.366		35.189	40.277	− 0.089
125290	40.440		35.179	40.361	− 0.079
149950	40.531		35.189	40.442	− 0.089
178760	40.577		35.157	40.520	− 0.057
208980	40.586		35.096	40.590	+ 0.004
229200	40.603		35.071	40.632	+ 0.029
279460	40.612		34.991	40.721	+ 0.109

Former stage: $$\frac{2.303\times 36.17}{37.98}\log\frac{36.17}{36.17-x}-\frac{x}{37.98}=t\,.$$

Latter stage: $$35.10+1.032\log t=x\,.$$

These results are depicted in Fig. 3 and Fig. 4. Fig. 3 shows the velocity of former stage of sorption and Fig. 4 that of latter stage of sorption. In Fig. 3 x is plotted against t while in Fig. 4 x against $\log t$. In these figures the observed data are shown by circlets and the calculated one by curves.

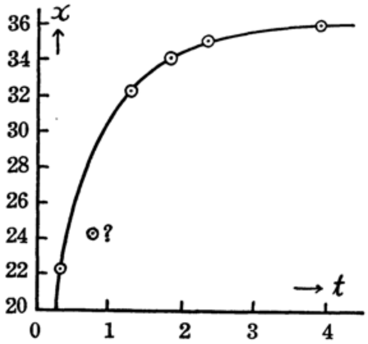

Fig. 3.

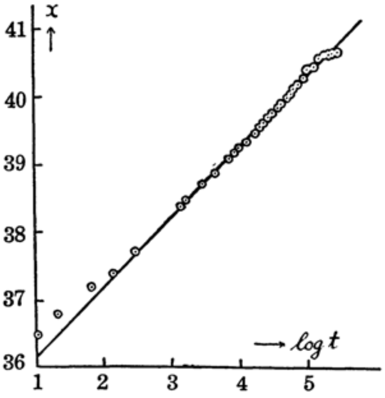

Fig. 4.

From Table 2 to Table 13 the results on various cases are given, in which, for the sake of brevity, only the values are given of time (t), the observed volume of gas sorbed (x_{obs}) and calculated value of x (x_{calc}). The calculations were done by the equations indicated under each table. The coincidence between observed and calculated values are generally good.

Table 2.

Sorption of Ammonia by Box-wood Charcoal (20°C., 488 mm.)

[Giesen, *Ann. Physik*, **10** (1903), 842.]

t	$x_{obs.}$	$x_{calc.}$	
1	28.	31.3	
2	39.7	39.7	
3	45.7	44.7	
4	48.7	48.2	former stage
5	50.7	50.5	
6	52.2	52.2	
7	52.9	53.5	
8	53.3	—	
9	53.6	—	
10	53.7	—	
15	54.3	54.4	
20	54.5	54.5	
30	54.7	54.6	
60	55.0	55.3	
120	55.1	55.1	
180	55.2	55.2	
240	55.2	55.2	

Former stage:

$$\frac{2.303\times 58}{13.7}\log\frac{58}{58-x}-\frac{x}{13.7}=t\,.$$

Latter stage:

$$53.6+0.7\log t=x\,.$$

Table 3.

Sorption of Carbon Dioxide by Box-wood Charcoal (18.5°C., 621 mm.)

[Giesen, *Ann. Physik*, **10** (1903), 842.]

t	$x_{obs.}$	$x_{calc.}$	
1	18.8	18.5	
2	22.3	22.8	former stage
3	25.2	25.1	
4	26.4	26.5	
5	27.3	27.3	
6	27.6	27.5	
7	27.7	27.7	
8	27.8	27.8	
9	27.9	27.9	
10	27.9	28.0	
15	28.3	28.5	
20	28.7	28.7	
30	29.3	29.2	
60	30.4	29.9	
120	30.8	30.6	
180	31.1	31.0	
240	31.2	31.3	
300	31.2	31.5	

Former stage:

$$\frac{2.303\times 29.3}{10.56}\log\frac{29.3}{29.3-x}-\frac{x}{10.56}=t.$$

Latter stage:

$$25.7+2.35\log t=x\,.$$

Table 4.

Sorption of Carbon Dioxide by Boxwood Charcoal (18.2°C., 496 mm.)

[Giesen, *Ann. Physik*, **10** (1903), 842.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$	
1	16.0	16.2	former stage
2	20.4	20.2	
3	22.8	22.5	
4	23.9	24.0	
5	24.7	24.8	
6	25.2	25.2	
7	25.3	25.3	
8	25.4	25.4	
9	25.5	25.5	
10	25.6	25.6	
15	25.8	25.9	
20	26.0	26.0	
30	26.3	26.3	
60	26.8	26.8	
120	27.4	27.3	
180	27.6	27.6	
240	27.6	27.9	
300	27.6	27.9	

Former stage:

$$\frac{2.303\times 27.0}{8.64}\log\frac{27.0}{27.0-x}-\frac{x}{8.64}=t.$$

Latter stage:

$$24.0+1.58\log t=x.$$

Table 5.

Sorption of Air by Coconut Charcoal (18°C., 735.6 mm.)

[Bergter, *Ann. Physik*, **37** (1912), 482.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.75	16.31	—
1	17.15	—
2	18.45	18.47
3.67	19.27	19.14
5	19.56	19.48
7	19.87	19.85
9	20.09	20.06
10	20.23	20.25
13	20.49	20.54
15	20.62	20.70
20	20.93	21.02
25	21.17	21.27
30	21.47	21.47
40	21.78	21.78
50	22.01	22.03
60	22.28	22.23

Latter stage:

$$17.7+2.55\log t=x.$$

Table 6.

Sorption of Ammonia by Silica Gel (25°C., 1 Atm.)

[Sameshima, this Bulletin, **7** (1932), 134.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$	
0.5	29.00	28.84	former stage
1	35.14	35.23	
2	40.19	40.36	
5	43.29	43.19	
10	43.64	43.72	
20	43.96	43.94	
185	44.64	44.63	
1470	45.26	45.28	
7315	45.87	45.78	
17370	46.01	46.05	
33225	46.26	46.25	
77760	46.53	46.52	

Former stage:

$$\frac{2.303\times 43.5}{37.0}\log\frac{43.5}{43.5-x}-\frac{x}{37.0}=t.$$

Latter stage:

$$43.0+0.72\log t=x\,.$$

Table 7.

Sorption of Ammonia by Silica Gel (25°C., 1 Atm.)

[Sameshima, this Bulletin, **7** (1932), 134.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$	
0.5	29.93	29.66	former stage
1.17	37.30	37.25	
2	41.11	40.93	
4	42.94	43.11	
6	43.20	43.20	
10	43.39	43.38	
15	43.52	43.51	
30	43.76	43.75	
50	43.96	43.92	
135	44.27	44.25	
280	44.48	44.50	
1585	45.02	45.08	
11520	45.85	45.75	

Former stage:

$$\frac{2.303\times 43.5}{40.3}\log\frac{43.5}{43.5-x}-\frac{x}{40.3}=t.$$

Latter stage:

$$42.6+0.775\log t=x\,.$$

Table 8.

Sorption of Carbon Dioxide by Silica Gel (25°C., 1 Atm.)

[Sameshima, this Bulletin, **7** (1932), 135.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$	
0.5	4.66	4.65	former stage
1	5.03	5.17	
2	5.38	5.38	
5	5.56	5.60	
10	5.66	5.66	
60	5.82	5.81	
255	5.93	5.93	
1380	6.08	6.07	
2995	6.16	6.13	
11490	6.27	6.24	
34550	6.34	6.34	
82050	6.40	6.40	

Former stage:

$$\frac{2.303\times 5.4}{12.0}\log\frac{5.4}{5.4-x}-\frac{x}{12.0}=t.$$

Latter stage:

$$5.47+0.19\log t=x.$$

Table 9.

Sorption of Ammonia by Opal (25°C., 1 Atm.)

[Sameshima, this Bulletin, **6** (1931), 168.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.5	2.52	—
2	3.07	2.93
10	3.71	3.68
30	4.20	4.20
60	4.52	4.52
120	4.84	4.84
240	5.17	5.17
1460	5.99	6.02
4320	6.55	6.52

$$2.60+1.08\log t=x.$$

Table 10.

Sorption of Ammonia by Diatomaceous Earth (25°C., 1 Atm.)

[Sameshima, this Bulletin, **6** (1931), 165.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.5	11.69	—
2	14.20	14.87
5	15.46	15.43
10	15.92	15.86
30	16.61	16.54
60	16.97	16.97
120	17.33	17.39
240	17.67	17.82
1560	18.86	18.97
4330	19.57	19.60
7370	19,93	19.93
11635	20.21	20.21
18850	20.47	20.51

$$14.44+1.42\log t=x.$$

Table 11.

Sorption of Ammonia by Chabazite (25°C., 1 Atm.)

[Sameshima, this Bulletin, **4** (1929), 101.]

t	$x_{\text{obs.}}$	$n_{\text{calc.}}$	
0.3	115.6	119.0	former stage
1	149.1	148.5	
2.5	181.7	181.9	
5	194.9	194.9	
10	197.2	197.1	latter stage
30	198.4	198.0	
68	198.5	198.6	
270	199.9	199.6	
1430	200.4	200.8	

Former stage:

$$\frac{2.303\times198}{126}\log\frac{198}{198-x}-\frac{x}{126}=t.$$

Latter stage:

$$195.4+1.73\log t=x.$$

Table 12.

Sorption of Carbon Dioxide by Chabazite (25°C., 768.9 mm.)

[Baba, this Bulletin, **5** (1930), 194.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.42	23.3	—
1	36.8	—
1.5	41.6	42.0
2	44.1	43.5
3	45.9	45.5
5	47.8	48.0
10	51.0	51.5
20	54.3	55.0
42	59.1	58.7
60	60.9	60.5
120	64.2	63.9

$$40.0+11.5\log t=x.$$

Table 13.

Sorption of Carbon Dioxide by Chabazite (25°C., 772 mm.)

[Baba, this Bulletin, **5** (1930), 195.]

t	$x_{\text{obs.}}$	$x_{\text{calc.}}$
0.45	38.6	—
2	70.4	—
3	75.1	75.5
5	77.6	77.5
10	80.2	80.0
20	82.4	82.6
45	85.3	85.5
80	87.8	87.7
120	89.3	89.2
180	90.8	90.7
1200	96.2	97.7

$$71.5+8.5\log t=x.$$

Summary.

1. The sorption by porous solid of gas under constant pressure and temperature proceeds, generally, in two stages. The mechanisms of sorption of each stage are described.

2. The velocity of the former stage is expressed by the equation

$$\frac{dx}{dt} = K\frac{s-x}{x^n}$$

where x denotes the amount of gas sorbed at time t, and K, s and n are constants. In the simplest case where $n=1$, this equation is integrated in the following form,

$$\frac{s}{t}\ln\frac{s}{s-x} - \frac{x}{t} = K.$$

3. The velocity of the latter stage of sorption is expressed by

$$x-\alpha\log t = k$$

where α and k are constants.

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