SORPTION OF GAS BY MINERAL. III. SILICIC ACID MINERALS.

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In the first report of this series the results of experiments were described on heulandite and chabazite,(1) and in the second report on laumontite.(2) The present paper deals with the experiments on some silicic acid minerals.

(1) Sameshima, this Bulletin, **4**·(1929), 96
(2) Sameshima, this Bulletin, **5** (1930), 303.

The minerals tested are two kinds of chalcedonies, common opal, diatomaceous earth, natural silica gels and siliceous sinter. The gas used is ammonia, which has been prepared from ammonium chloride and lime, and dehydrated by potassium hydroxide, frozen and fractionated twice with liquid air.

The apparatus and the method of measurements are quite the same with those which were described already.(1) The experiments have been done at 25°C. and under about one atmospheric pressure of gas.

Chalcedony A. The mineral from Morofuno, Ibaraki Prefecture has been used. It is a translucent hard matter. The mineral lost 0.26% by weight on evacuating and heating to 300°C. The loss probably due to the evaporation of water which is contained in the mineral. The mineral which was dehydrated at 300°C. has been tested for the sorption of ammonia. The results are shown in Table 1.

Table 1. Chalcedony A.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of chalcedony, in c.c. (x)	
		Observed	Calculated
0.5	763.3	0.19	—
3.	763.3	0.28	0.21
10.	763.3	0.42	0.43
60	762.9	0.70	0.76
155	762.4	0.93	0.94
1335	759.3	1.39	1.34
4285	758.5	1.56	1.56
$x = 0.43 \log t$.			

In this table, the first column shows the time in minutes after the contact of mineral to ammonia, the second column the pressure of ammonia gas, the third column the volume of ammonia sorbed at 25°C. by the dehydrated material which has been obtained by treating one gram of air-dry mineral at 300°C. and evacuating, the figures being the volumes in c.c. reduced at normal temperature and pressure, and the fourth column the values calculated by the equation given at the bottom of the table, x being the volume of ammonia sorbed and t the time.

(1) Sameshima, this Bulletin, **2** (1927), 2; **4** (1929), 97.

Chalcedony B. Another sample of calcedony was tested, the locality of which being Akadani, Niigata Prefecture. The mineral is found as gravel of spherical shape the diameter of which being about 2-4 cm. and is called "sorobandama-ishi." It is a hard, translucent matter. The loss of weight by heating to 300°C. and evacuation amounts to 0.65%. The volumes of ammonia sorbed by one gram of air-dry mineral after dehydrating at 300°C. are given in Table 2.

Table 2. Chalcedony B.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T P.) sorbed at 25°C. by 1 gr. of chalcedony, in c.c. (x)	
		Observed	Calculated
0.67	758.3	0.44	—
3	758.3	0.71	0.70
6.5	758.3	0.89	0.89
14	758.2	1.08	1.08
23	758.2	1.19	1.20
29	758.1	1.26	1.26
55	757.9	1.44	1.42
90	757.9	1.56	1.54
313	757.8	1.83	1.85
$x = 0.57 \log t + 0.43$			

Thus chalcedony B absorbs more ammonia than chalcedony A, being parallel to the water contents of them.

Opal. The mineral from Hoosaka, Fukushima Prefecture has been used. It has a milky colour and a glassy lustre, and is like the boiled white-of-egg in appearance. The mineral contains much water than chalcedony. By heating to 300°C. and subjecting to evacuation its weight decreased to the amount of 5.01%. The substance thus dehydrated has been used for the experiment. It is, therefore, expected that more ammonia will be sorbed by this mineral than chalcedonies. The results are shown in Table 3.

The values in Tables 1 to 3 have been depicted in Fig. 1, taking the logarithm of time against the volume of ammonia sorbed. The straight lines are drown by the equations given under each table. The observed values are, quite satisfactorily, on the straight lines, excepting first one or two values in each series.

Table 3. Opal.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of opal, in c.c. (x)	
		Observed	Calculated
0.5	745.9	2.52	—
2	745.9	3.07	2.93
10	745.8	3.71	3.68
30	745.6	4.20	4.20
60	745.2	4.52	4.52
120	744.6	4.84	4.84
240	743.9	5.17	5.17
1460	755.6	5.99	6.02
4320	764.9	6.55	6.52

$x = 1.08 \log t + 2.60.$

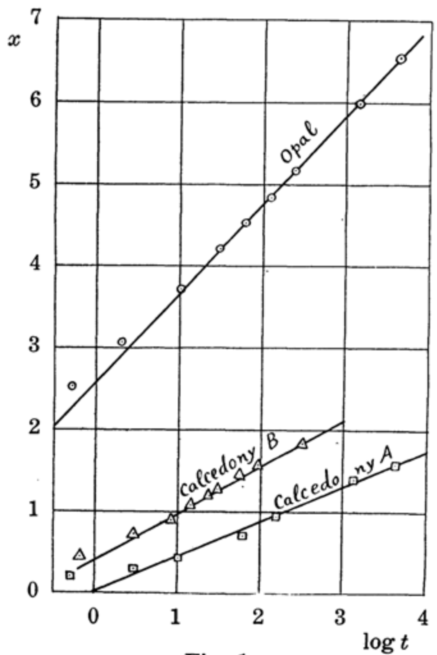

Fig. 1.

Diatomaceous Earth. The diatomaceous earth from Saigo, Oki Islands has been used. The mineral was dehydrated by heating to 300°C. and subjecting to evacuation, the decrease in weight being 10.12%. Thus a considerable amount of water is contained in this mineral. Accordingly, as seen from Table 4, the amount of ammonia sorbed is also relatively high. The values are shown in Table 4 and Fig. 2.

Table 4. Diatomaceous Earth.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of air-dry earth after being dehydrated, in c.c. (x)	
		Observed	Calculated
0.5	752.4	11.69	—
2	752.4	14.20	14.87
5	752.3	15.46	15.43
10	752.2	15.92	15.86
30	751.8	16.61	16.54
60	751.2	16.97	16.97
120	750.9	17.33	17.39
240	749.4	17.67	17.82
1560	753.6	18.86	18.97
4330	763.5	19.57	19.60
7370	769.1	19.93	19.93
11635	766.3	20.21	20.21
18850	747.3	20.47	20.51
$x = 1.42 \log t + 14.44$			

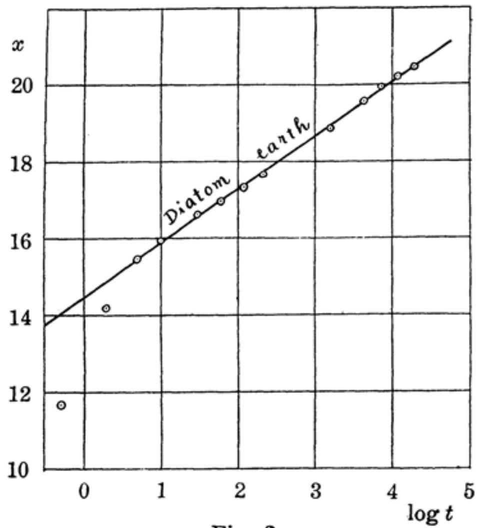

Fig. 2.

Siliceous Sinter and Natural Silica Gels. The three minerals which are described in the following lines were obtained from Nakabusa Hot Spring, Nagano Prefecture, The spring from which these minerals have been deposited, is erupting in boiling state, the temperature of which being 95°C. The altitude is about 1500 metres from sea level. Total solid matter in 100,000 parts of spring is 68 in which 24 parts are SiO_2. The value of P_H of the spring is 8.9.

In the course of flowing down the mountain side the temperature of spring descends and the deposition of silica takes place. The silica deposits in gel form of soft, gelatinous appearance of various colours. It is not a pure silica gel, but contains a considerable amount of organic matters like fungi, which may accelerate the deposition of silica from spring. The gel was dried in open air and the air-dry substance was analysed giving the following results.

Weight loss by heating at 150°C. and subjecting to evacuation:	5.03%
Ignition loss (mainly organic matter):	12.50%
SiO_2:	77.35%
Al_2O_3 and Fe_2O_3:	2.66%
CaO:	0.54%
Total	97.98%

The remainder (about 2%) is probably NaCl etc.

The silica which is found underneath of the layer of gelatinous deposit is like a soft cheese in appearance. It is probable that this cheese-like silica was produced as the result of the loss of elasticity by the death of fungi in the gelatinous silica. At the bottom of the spring flow or the dry places near the spring there is much quantity of siliceous sinter which is generally a hard white, bone-like matter.

Measurements were done on these three kinds of silicas. They were dehydrated by heating at 150°C. and evacuating and then measured the sorption of ammonia. The loss of weight by dehydration for gelatinous gel, cheese-like gel and hard sinter amount to 5.03, 4.01 and 3.44% respectively. The results of measurements are shown in Tables 5, 6, 7 and Fig. 3.

Theoretical. The mechanism of sorption of gas by porous matter has already been discussed.[1] The following equation for the velocity of sorption has been proposed in case of the sorption of ammonia by charcoal.[2]

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

(1) Sameshima, this Bulletin, **4** (1929), 125; *Chem. News*, **139** (1929), 61.
(2) Sameshima, this Bulletin, **5** (1930), 173.

Table 5. Gelatinous Silica Gel.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of air-dry gel after being dehydrated, in c.c. (x)	
		Observed	Calculated
1	757.6	18.95	—
5	757.6	23.73	—
10	757.6	25.66	—
25	757.5	28.14	28.69
71	757.9	31.01	31.14
200	759.0	33.68	33.58
1470	762.0	38.31	38.27
2850	769.7	39.76	39.84
4520	770.0	41.08	40.92
5790	761.2	41.59	41.50
8840	766.2	42.39	42.50
10130	759.1	42.66	42.82
$x = 5.42 \log t + 21.11$			

Table 6. Cheese-like Silica Gel.

Time in min. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of air-dry gel after being dehydrated, in c.c. (x)	
		Observed	Calculated
1	761.8	23.96	—
5	761.8	27.73	—
10	761.8	29.02	—
30	761.7	30.91	30.57
62	761.8	32.38	32.33
120	762.1	33.85	33.94
210	762.1	35.20	35.30
1370	762.5	39.55	39.87
2810	754.8	41.48	41.61
5700	761.4	43.44	43.33
12930	759.0	45.36	45.33
17200	761.4	46.04	46.02
22930	765.7	46.70	46.72
41680	759.6	48.00	48.17
$x = 5.60 \log t + 22.30$			

Table 7. Hard Siliceous Sinter.

Time in mm. (t)	Pressure of gas in mm.	Volume of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of air-dry mineral after being dehydrated, in c.c. (x)	
		Observed	Calculated
1	759.9	6.53	—
5	759.9	8.22	—
15	759.8	9.49	—
70	759.3	11.85	—
220	759.7	14.20	—
1665	760.1	19.05	19.14
2990	752.9	20.97	21.18
4555	754.5	22.44	22.63
8895	764.3	25.07	24.96
12900	771.3	26.40	26.26
15790	759.2	27.06	26.95
20275	763.1	27.91	27.83
29130	758.4	29.12	29.08
36210	752.4	29.80	29.84

$$x = 8.00 \log t - 6.63$$

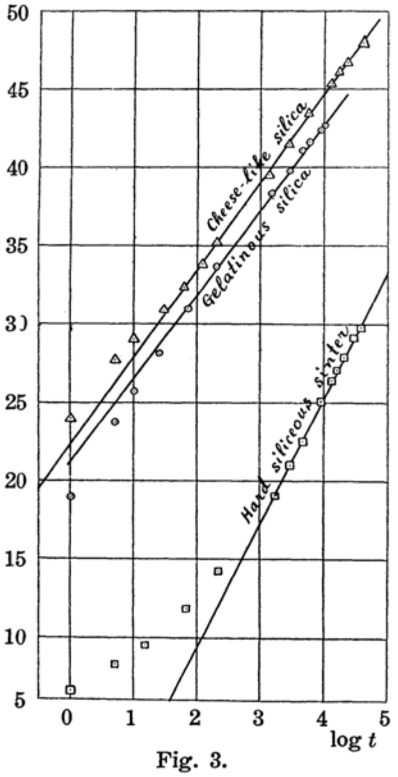

Fig. 3.

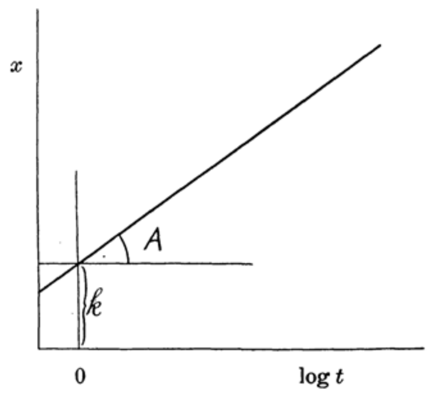

Fig. 4.

where x is the quantity of gas sorbed at time t, and K and k are the constants. This equation shows a straight line on a diagram drawn x against $\log t$ (Fig. 4). The trigonometrical tangent of the angle A between the straight line and the $\log t$ axis gives the value of K. The value of x cutting by the straight line at $\log t=0$ gives the value of k. As shown in Figs. 1, 2 and 3, this equation can be applied in the present experiments. And by the above manner we can easily evaluate the values of K and k from the observed line. The equations thus obtained were given under each table of observed data.

At the initial stage of sorption the velocity is not expressed by the equation as seen from the figures. In the case of sorption of ammonia by sugar charcoal such a non-linear part lasted about one hour.[1] In the present cases, it lasts shorter period, excepting siliceous sinter, thus 2-3 minutes for chalcedonies, 5 minutes for opal, 2 minutes for diatomaceous earth, and 10 minutes for silica gel, while 200 minutes for siliceous sinter.

The entering of gas molecules into relatively large openings among solid molecules are accomplished in relatively short time. This part of sorption cannot be expressed by the present equation and deviate from the straight line relation. But the latter part of sorption can thus well be expressed by our derived equation.

Summary.

1. Sorption of ammonia by dehydrated materials of chalcedonies, opal, diatomaceous earth, natural silica gels and siliceous sinter have been measured.

2. All these substances sorb considerable amounts of ammonia at ordinary temperature.

3. The sorption velocity can be expressed by the equation

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

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

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(1) Sameshima, this Bulletin, **5** (1930), 179.