

SORPTION OF GAS BY MINERAL. V.

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In this paper the experimental results obtained with the following minerals are described: mordenite, thomsonite, scolecite, epistilbite and phillipsite. The sorptions of ammonia and carbon dioxide by these minerals have been measured. The procedure of measurements have already been described in the preceding reports.⁽¹⁾ In the present report the results of the measurements with zeolite minerals from foreign countries are given, while in the former reports the Japanese minerals have only been tested.

Mordenite. The locality of mordenite described in this report is Custer County, Idaho, U.S.A. It is a white soft matter of fibrous structure. The results of measurements are given in Tables 1, 2 and 3. The mineral was dehydrated by heating at 350°C. (Table 1) or 200°C. (Table 2 and Table 3) under evacuation. The pressures of the gases were kept at 760 mm. throughout the experiments.

The amounts of ammonia and carbon dioxide sorbed by this sample of mordenite is thus inferior to that which has been described in the former report.⁽²⁾ The present sample sorbs ammonia with extreme rapidity, about 90 per cent. of the total amount being sorbed during the

(1) Sameshima, this Bulletin, **2** (1927), 2; **4** (1929), 96. Sameshima and Hemmi, *ibid.*, **9** (1934), 27.

(2) Sameshima and Hemmi, this Bulletin, **9** (1934), 32.

Table 1.

Sorption of Ammonia
by Mordenite.

Mode of dehydration:
Heating at 350°C. for 30
minutes under evacuation.

Loss of weight by de-
hydration: 4.89%.

Time (min.)	Vol. (c.c.) of NH ₃ (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of mordenite
0.5	39.47
1	41.94
5	44.13
60	45.27
1440	45.94
1800	46.32

Table 2.

Sorption of Ammonia
by Mordenite.

Mode of dehydration:
Heating at 200°C. for 2.5
hours under evacuation.

Loss of weight by de-
hydration: 4.75%.

Time (min.)	Vol. (c.c.) of NH ₃ (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of mordenite
0.5	33.62
1	35.81
5	38.20
60	40.20
1620	41.15

Table 3.

Sorption of Carbon Di-
oxide by Mordenite.

Mode of dehydration:
Heating at 200°C. for 2.5
hours under evacuation.

Loss of weight by de-
hydration: 4.41%.

Time (min.)	Vol. (c.c.) of CO ₂ (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of mordenite
1	1.68
5	3.97
30	9.27
60	11.82
120	14.09
480	17.52
1440	18.18
3000	18.37

first few minutes. The behaviour is quite the same with that of chabazite,⁽³⁾ silica gel,⁽⁴⁾ and charcoal,⁽⁵⁾ and differs from other zeolite minerals.⁽⁶⁾ This fact shows that the dewatered mordenite does not form a compound with ammonia but only sorbs it into the cavities among the molecular gratings of the crystal. The dewatered mordenite forms a molecular sieve, and the sorption by such a matter may be classified as "the sorption of chabazite type."

Thomsonite. The composition of thomsonite is said to be $2[(\text{Na}_2\text{Ca})\text{Al}_2\text{Si}_2\text{O}_8] \cdot 5\text{H}_2\text{O}$. The mineral from Table Mountains, Golden, Colorado, U.S.A., has been used. It is an aggregate of radial groups of white fibrous crystals. The experimental results are given in Tables 4 and 5.

(3) Sameshima, *ibid.*, **4** (1929), 100.

(4) Sameshima, *ibid.*, **7** (1932), 133.

(5) Sameshima, *ibid.*, **5** (1930), 173.

(6) Sameshima, *ibid.*, **4** (1929), 97; **5** (1930), 304. Sameshima and Hemmi, *ibid.*, **9** (1934), 27.

Table 4.

Sorption of Ammonia by Thomsonite.

Mode of dehydration: Heating at 350°C. for 1 hour under evacuation.

Loss of weight by dehydration: 11.68%.

Time (min.)	Vol. (c.c.) of NH ₃ (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of thomsonite
0.5	0.60
1	0.80
120	0.92
1440	1.32
1800	1.46

Table 5.

Sorption of Ammonia by Thomsonite.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.

Loss of weight by dehydration: 4.27%.

Time (min.)	Vol. (c.c.) of NH ₃ (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of thomsonite
0.5	1.07
10	2.06
60	3.54
180	5.10
480	7.27
1440	10.66
2880	13.44
15 days	23.84

These tables show that the thomsonite dehydrated at 200°C. sorbs ammonia in a considerable amount, while that dehydrated at 350°C. sorbs but a small amount.

One gram of thomsonite, after dehydrated by heating to 200°C. for 2.5 hours under evacuation, sorbs 0.27 c.c. of carbon dioxide (N.T.P.) at 25°C. and 1 atmospheric pressure of gas during 4260 minutes. Thus the carbon dioxide is not practically sorbed by the dehydrated thomsonite.

It is probable that ammonia combines chemically with the partially dehydrated thomsonite. The chemical analysis of the thomsonite from Table Mountains, Golden, Colorado, U.S.A., being the same locality with our sample, shows that the water content is 12.7% in average.⁽⁷⁾ The weight loss of our sample on heating at 350°C. amounts to 11.68%, so the dehydrated sample at this temperature is almost anhydrous and this sample has no combining power to ammonia. The mineral dehydrated at 200°C. lost water of only 4.2%, and this partially dehydrated sample has the ability of combining with ammonia. The dehydration of thomsonite at various temperatures was studied by Zambonini, whose observation agrees well with our present results.⁽⁸⁾

(7) Doelter, "Handbuch der Mineralchemie", Vol. II, 3rd Part (1921), 19.

(8) Doelter, *ibid.*, p. 24.

Scolecite. The mineral from Taigherhorn, Iceland, has been used. It is a big transparent colourless prismatic crystal. The composition of this mineral is said to be $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$. The result of measurement is given in Table 6.

Table 6.

Sorption of Ammonia by Scolecite.

Mode of dehydration: Heating at 200°C . for 2.5 hours under evacuation.

Loss of weight by dehydration: 4.99%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C . and 1 atm. press. by 1 g. of scolecite
1	2.00
5	3.90
30	8.31
60	11.50
120	16.87
180	21.91
300	30.23
1440	55.26
2880	58.51
3060	58.64

The sample dehydrated by heating at 200°C . for 2.5 hours under evacuation has been tested for the sorption of carbon dioxide. One gram of the mineral sorbed only 0.13 c.c. of carbon dioxide at 25°C . and 1 atmospheric pressure during 1680 minutes. Thus the mineral sorbs ammonia but no carbon dioxide.

It is probable that ammonia combines with the partially dehydrated sample of scolecite. The loss of water in the process of dehydration of the present sample amounts to 4.99%. On the other hand, the loss should be 4.59% or 57.1 c.c. of water vapour at normal conditions from one gram of the mineral by the calculation under the assumption that one mol of water evaporates from one mol of mineral. The present sample

of the ammoniacal scolecite, therefore, corresponds to the composition $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}\cdot \text{NH}_3$.

Epistilbite. The locality of the mineral used is Giebelbach near Fiesch, Valais, Switzerland. It is colourless transparent crystals of a few millimeter size. The composition is said to be $\text{H}_4\text{CaAl}_2(\text{SiO}_3)_6\cdot 3\text{H}_2\text{O}$.⁽⁹⁾ The result of the sorption experiment of ammonia is given in Table 7.

The sorption of ammonia does not yet arrive at saturation point and proceeds slowly. Sorption of 37 c.c. (N.T.P.) of ammonia by one gram of epistilbite corresponds to one mol of ammonia for one mol of

(9) Doelter, *ibid.*, p. 201.

the mineral, assuming the formula described above. Thus the ammoniacal epistilbite has the composition $H_4CaAl_2(SiO_3)_6 \cdot NH_3$.

The mineral sorbs carbon dioxide only in a small amount. One gram of the mineral, after being dehydrated by heating at $200^\circ C.$ for 2.5 hours, sorbs 0.55 c.c. of CO_2 gas (N.T.P.) at $25^\circ C.$ during 2820 minutes. So the sorption of ammonia by epistilbite may be considered as the chemical combination between these two substances.

Table 7.

Sorption of Ammonia by Epistilbite.

Mode of dehydration: Heating at $200^\circ C.$ for 2.5 hours under evacuation.

Loss of weight by dehydration: 9.26%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at $25^\circ C.$ and 1 atm. press. by 1 g. of epistilbite
1	0.59
5	1.36
60	3.72
300	7.56
1440	16.49
2880	20.83
5760	29.08
9 60	36.12

Table 8.

Sorption of Ammonia by Phillipsite.

Mode of dehydration: Heating at $200^\circ C.$ for 2.5 hours under evacuation.

Loss of weight by dehydration: 13.14%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at $25^\circ C.$ and 1 atm. press. by 1 g. of phillipsite
5	2.81
30	10.67
60	19.96
120	27.61
240	32.89
1440	44.67
7200	54.47
14460	58.82

Phillipsite. The locality of the mineral is Capo di Bove, Rome, Italy. It is a cluster of spherites of small translucent crystals. The composition may be $(K_2Ca)Al_2Si_6O_{16} \cdot 6H_2O$. The sorption of ammonia by this mineral has been measured and the result is given in Table 8.

From the result given in this table, the composition of the ammoniacal phillipsite may be $(K_2Ca)Al_2Si_6O_{16} \cdot 2NH_3$.

The sorption of carbon dioxide was measured. One gram of phillipsite, after being dehydrated by heating at $200^\circ C.$ for 2.5 hours under evacuation, sorbed 0.59 c.c. of CO_2 (N.T.P.) at $25^\circ C.$ and 1 atmospheric pressure of the gas during 1440 minutes. Thus the mineral sorbs a considerable amount of ammonia but not carbon dioxide, so the sorption of ammonia may be considered as a chemical combination.

Summary.

(1) The sorptions of ammonia and carbon dioxide under one atmospheric pressure at 25°C. by the dehydrated samples of mordenite, thomsonite, scolecite, epistilbite, and phillipsite have been measured.

(2) Mordenite sorbs either ammonia or carbon dioxide in a considerable amount. This is a sorbent of the chabazite type.

(3) Thomsonite, scolecite, epistilbite, and phillipsite sorb ammonia in a large amount but not carbon dioxide. These minerals combine chemically with ammonia and form definite compounds.

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