SORPTION OF GAS BY MINERAL. IV. ZEOLITES AND BENTONITE.

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In the first report of this series the results of experiments were described on heulandite and chabazite,[1] in the second report on laumontite,[2] and in the third report on silicic acid minerals.[3]

The present paper describes the experiments on the following minerals: laumontite, stilbite, mordenite, natrolite, apophyllite, analcite, inesite and bentonite. The gases tested were ammonia, carbon dioxide, sulphur dioxide, acetylene, oxygen and hydrogen.

Ammonia has been prepared from aqueous ammonia, carbon dioxide from calcium carbonate and hydrochloric acid, sulphur dioxide from sodium sulphite and sulphuric acid, acetylene from calcium carbide and water, oxygen from potassium permanganate, and hydrogen from zinc and sulphuric acid. These gases have been properly purified by the ordinary procedures.

The apparatus and the method of measurements are quite the same as those which were described in former reports.[4] The sorptions have been measured at 25°C. and 0°C. under about one atmospheric pressure.

Laumontite. The locality of the mineral is Takashima, Hokkaido, being the same sample which was used in the experiment described in the second report of this series. In the former experiment the sorptions of ammonia and carbon dioxide were measured, while in the present paper those of sulphur dioxide, acetylene and oxygen beside ammonia and carbon dioxide are described.

The mineral has been subjected to evacuation and heated to 200°C. for two and half hours. By this treatment the decrease in weight of laumontite amounts to 10.2%. Then the dehydrated mineral has been kept at 25°C. and the sorption velocity and amount of gases have been measured. The results are given in Table 1.

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(1) Sameshima, this Bulletin, **4** (1929), 96.
(2) Sameshima, this Bulletin, **5** (1930), 303.
(3) Sameshima, this Bulletin, **6** (1931), 165.
(4) Sameshima, this Bulletin, **2** (1927), 2; **4** (1929), 97; **5** (1930), 173.

Table 1.

Sorption of Gases by Laumontite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of laumontite in c.c.
NH_3	0.5	762.6	5.91
	3	762.6	7.65
	13	762.6	9.18
	52	761.8	11.14
	167	750.8	12.89
	396	754.0	14.13
	1380	756.9	15.21
CO_2	0.5	759.6	0.39
	9	759.6	0.69
	362	758.0	0.78
	1408	759.3	0.98
SO_2	0.5	764.2	1.33
	25	764.2	1.41
	702	763.4	1.82
	1356	768.7	1.96
C_2H_2	0.5	751.2	1.36
	3	751.2	1.96
	27	750.8	2.29
	420	750.4	2.82
	1200	755.8	3.65
O_2	0.5	754.0	0.20
	240	754.8	0.70
	1524	760.1	1.02

Stilbite. The chemical composition of stilbite is $(CaNa_2)\,Al_2Si_6O_{16}\cdot 6H_2O$. The mineral from Kurokura in Shizuoka Prefecture was used in the present experiments. Sorptions of ammonia at 25°C. by stilbite which was dewatered by various treatments have been measured. The results are given in Tables 2, 3 and 4.

Table 2.

Sorption of Ammonia by Stilbite.

Mode of dehydration : Evacuation for 2.5 hours in ordinary temperature.
Loss of weight by dehydration : 2.21%.

Time in min.	Pressure of NH_3 in mm.	Vol. of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of stilbite in c.c.
0.5	749.9	22.54
3	749.9	39.69
5	749.9	46.55
10	749.9	57.87
25	749.9	72.08
62	749.9	88.54
155	749.9	103.84
346	749.6	116.22
594	749.3	123.13
1410	754.7	128.21

Table 3.

Sorption of Ammonia by Stilbite.

Mode of dehydration : Heating at 100°C. for 2.5 hours under evacuation.
Loss of weight by dehydration : 9.19%.

Time in min.	Pressure of NH_3 in mm.	Vol. of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of stilbite in c.c.
0.5	751.7	20.11
3	751.7	30.98
12	751.7	42.37
30	751.7	51.77
90	751.7	66.88
180	751.5	80.43
360	751.8	93.45
482	751.9	98.18
1540	756.5	112.08

Table 4.

Sorption of Ammonia by Stilbite.

Mode of dehydration : Heating at 200°C. for 2.5 hours under evacuation.
Loss of weight by dehydration : 16.18%.

Time in min.	Pressure of NH_3 in mm.	Vol. of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of stilbite in c.c.
0.5	757.1	11.66
3	757.1	17.97
10	757.1	25.21
30	757.1	38.32
60	757.1	49.24
100	756.8	58.82
190	756.8	71.79
362	756.6	85.00
653	755.7	94.98
1620	754.1	108.42

Thus the mineral sorbs ammonia in considerable amounts, being greater than silica gel and laumontite, though less than chabazite. We see, moreover, that the sample dehydrated at the lower temperature sorbs the more ammonia. A sample was dehydrated at red-heat under evacuation, the weight loss of which being 17.09%. The sorption of this sample was tested but it sorbed almost no ammonia. One gram of this sample sorbed only 0.26 c. c. of ammonia after 1440 minutes. So it is probable that the constitution of the mineral is destroyed by red-heating.

Sorption of ammonia by stilbite at 0°C. instead of 25°C. has been measured, the result of which being given in Table 5.

Table 5.

Sorption of Ammonia by Stilbite.

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

Time in min.	Pressure of NH_3 in mm.	Vol. of NH_3 (N.T.P.) sorbed at 0°C. by 1 gr. of stilbite in c.c.
0.5	762.3	5.69
3	762.3	11.20
12	762.3	17.98
60	762.3	29.78
240	761.9	47.36
1585	760.0	86.91
4435	759.3	111.75
8800	765.5	121.61
14365	758.1	126.04

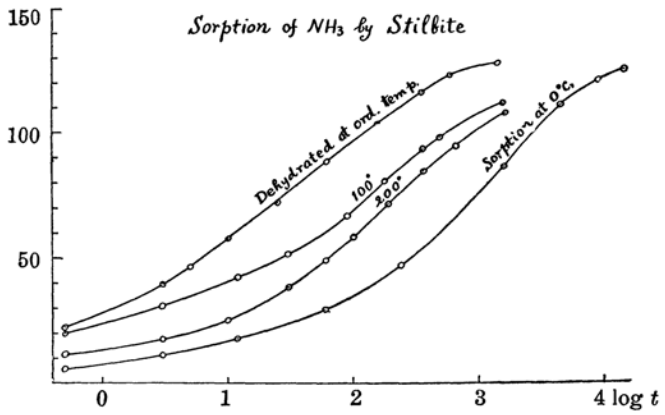

Fig. 1.

The data in Tables 2, 3, 4 and 5 are depicted in Fig. 1, where the volume of ammonia sorbed is taken in ordinate and the logarithm of time in abscissa. As seen from the figure, the sorption velocity at 0°C. is smaller than that at 25°C., and the amount of ammonia sorbed is nearly the same in two temperatures. From these facts it is probable that the ammonia combines chemically with stilbite. This conclusion is supported by the fact that this mineral sorbs almost no gases in considerable amount except ammonia as shown in Table 6.

Table 6.

Sorptions of Various Gases by Stilbite.

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

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of stilbite in c.c.
CO_2	1200	756.0	2.22
SO_2	285	764.1	3.08
C_2H_2	190	753.5	1.41
O_2	1285	754.8	1.48
H_2	1440	764.1	0.69

Mordenite. The composition of mordenite is said to be $3[(K_2, Ca)O \cdot Al_2O_3 \cdot (SiO_2)_{10}] \cdot 20H_2O$. Locality of the mineral used in the present ex-

periments is Arasawa-mura in Iwate Prefecture.[5] It has white fibrous structure of a few millimeters in length. Some parts have the appearance of glass-wool. Two samples from the same locality were tested.

Sample I. The mineral was dehydrated by heating to 300°C. for 2 hours under evacuation. The loss of weight by this treatment was 9.7%. Sorptions of ammonia and carbon dioxide at 25°C. have been measured on this dewatered sample. The results are shown in Tables 7 and 8, and Fig. 2.

Table 7.

Sorption of Ammonia by Mordenite.

Time in min.	Pressure of NH_3 in mm.	Vol. of NH_3 (N.T.P.) sorbed at 25°C. by 1 gr. of mordenite in c.c.
0.5	755.3	40.30
1	755.3	47.39
2	755.3	52.83
5	755.3	58.84
10	755.3	64.85
30	755.1	74.75
60	755.0	80.60
120	754.5	85.36
1270	754.2	91.86
3010	760.1	92.58
7060	757.3	93.23

Table 8.

Sorption of Carbon Dioxide by Mordenite.

Time in min.	Pressure of CO_2 in mm.	Vol. of CO_2 (N.T.P.) sorbed at 25°C. by 1 gr. of mordenite in c.c.
1	764.5	1.12
5	764.5	2.07
30	764.5	4.40
180	764.5	10.38
450	764.4	15.70
1520	766 8	25.95
4440	759.1	36.28
10200	761.3	43.65
23430	757.5	49.48
60780	751.5	54.15

(5) K. Kawai and K. Kinoshita, *Journal of Geography* (*Chigaku-Zasshi*), **41** (1929), 53. K. Kawai, ibid., **41** (1929), 74.

Sample II. The mineral was dehydrated by heating to 300°C. for 2.5 hours under evacuation, the loss of weight being 11.73%. Sorption of ammonia, carbon dioxide, sulphur dioxide, acetylene, oxygen and hydrogen have been measured. This mineral sorbed large amounts of these gases except hydrogen. No measurable quantity of hydrogen was sorbed by this mineral. The results of measurements are given in Table 9 and Fig. 3.

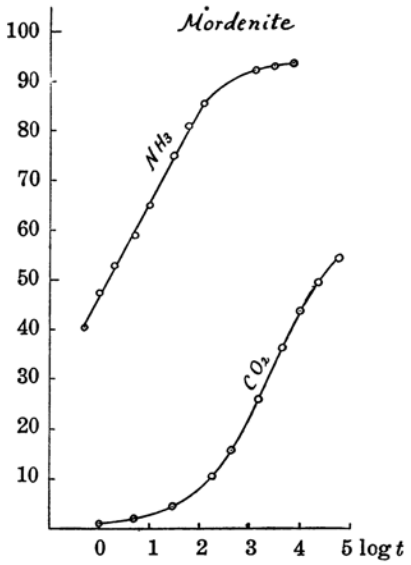

Fig. 2.

Table 9.

Sorption of Gases by Mordenite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of mordenite in c.c.
NH_3	0.5	751.4	117.76
	3	751.4	130.37
	7	751.4	133.29
	60	751.4	133.91
	480	750.8	134.16
	1200	760.2	135.17
CO_2	1	762.4	6.23
	4	762.4	10.65
	13	762.4	16.10
	32	762.4	23.63
	60	762.4	33.75
	186	763.4	51.02
	612	765.0	69.49

Table 9.—(*Concluded*)

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of mordenite in c.c.
SO_2	0.5	763.6	10.65
	3	763.6	29.00
	7	763.6	38.93
	12	763.6	46.06
	30	763.6	55.20
	60	763.6	61.29
	125	763.3	67.69
	480	763.9	70.09
	1415	751.1	72.01
C_2H_2	0.5	753.3	0.09
	4	753.3	0.68
	40	753.2	2.98
	120	752.4	5.31
	252	753.3	8.10
	545	754.5	11.52
	721	754.7	13.03
	1410	764.4	14.70
O_2	0.5	759.0	5.01
	4	759.0	6.87
	11	759.0	7.98
	60	759.0	8.45
	195	759.0	8.73
	625	758.1	9.04
	1448	756.7	9.88

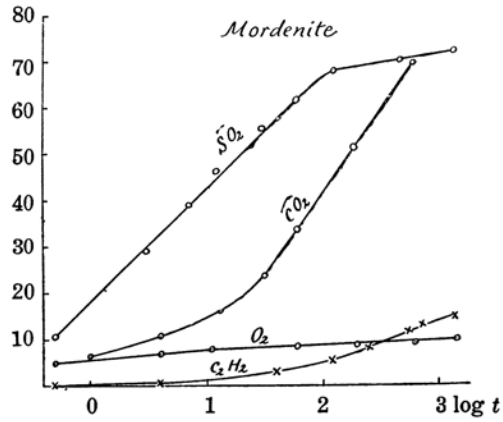

Fig. 3.

We see from these tables and figures, that the mordenite sorbs various kinds of gases. In this respect, mordenite resembles chabazite and differs from heulandite, laumontite and stilbite. The mechanism of sorption is, therefore, the same as that in the case of chabazite. It is a process of entering gas molecules into the molecular cavities of solid and forms a homogeneous solid solution.[6] Thus we have found another substance which have the great capacity of sorbing various gases in addition to charcoal, silica gel, chabazite and meerschaum. Indeed, mordenite may be the second example to chabazite which forms the crystalline molecular sieve.

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

Natrolite. The composition of natrolite is $Na_2O \cdot Al_2O_3 \cdot (SiO_2)_3 \cdot 2H_2O$. The mineral from Tezuka in Nagano Prefecture is used in the experiment. It consists of radial groups of white crystals.

The mineral was dehydrated by heating to 300°C. for 2.5 hours under evacuation. The loss of weight by this treatment was 11.45%. Sorptions of various gases by this substance were measured. The results are given in Table 10.

Table 10.

Sorptions of Gases by Natrolite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of natrolite in c.c.
NH_3	0.5	761.0	0.57
	3	761.0	1.20
	10	761.0	1.90
	65	760.7	3.98
	210	758.3	6.70
	365	757.5	8.37
	1440	755.6	15.75
CO_2	1490	760.4	1.08
SO_2	1440	761.0	0.97
C_2H_2	1380	759.2	1.78
O_2	1320	755.0	0.10
H_2	2880	767.4	0

The natrolite sorbs ammonia slowly, and no other gases. So probably it combines chemically with ammonia.

Apophyllite. The composition of apophyllite is said to be $(H_{14}K_2)O_8 \cdot Ca_8O_8 \cdot (SiO_2)_{16} \cdot 9H_2O$. The mineral from Maze in Niigata Prefecture was used.(7) The mineral was dehydrated by heating to 300°C. for 2.5 hours under evacuation. The decrease in weight was 11.17%. The results of the measurements of sorption on this substance are given in Table 11.

(7) K. Jimbo, *Journal College Scierce, Imp. Univ. Tokyo, Japan,* **11** (1899), 276.

Table 11.

Sorption of Gases by Apophyllite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of apophyllite in c.c.
NH_3	0.5	762.3	0.30
	15	762.3	0.48
	140	762.3	1.17
	535	760.1	3.08
	1310	761.3	4.76
SO_2	1350	764.2	0.63
C_2H_2	1400	759.0	0.89
O_2	1260	752.6	0.64
H_2	1260	760.8	0.39

Sorption amounts of gases by apophyllite are thus comparatively small. It seems probable that ammonia combines with the dehydrated mineral, though the amount is lower than other zeolite minerals.

Analcite. The composition of analcite is $(NaAl)O_2 \cdot (SiO_2)_2 \cdot H_2O$. The mineral from Maze in Niigata Prefecture was used. It was dehydrated by heating to 300°C. for 2.5 hours under evacuation. The decrease in weight was 7.83%. The results of sorption measurements are given in Table 12.

Table 12.

Sorption of Gases by Analcite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of analcite in c.c.
NH_3	30	761.3	0.39
	450	761.3	0.41
	1440	759.8	0.44
SO_2	26	758.3	0.45
	180	758.5	0.82
	1140	759.1	1.01
C_2H_2	1	764.6	1.71
	120	764.4	1.89
	1280	771.3	1.95
O_2	1	764.9	0.32
	1200	756.8	0.32

As is seen from Table 12, no gas is sorbed in considerable quantity by the dehydrated analcite.

Inesite. The composition of inesite is $(Mn, Ca)_6O_6 \cdot (SiO_2)_6 \cdot 4H_2O$. Zambonini described that the mineral lose 3.85% water on heating to 202°C., while 5.98% on heating to 310°C. changing the colour of mineral.[8]

The mineral from Rendaiji Mine, Shizuoka Prefecture was used in the present experiments. It is an aggregates of radial groups of pink coloured crystals. The mineral has been dehydrated by heating to 200°C. for 1 hour under evacuation. The loss of weight was 4.84%. Sorptions of ammonia and carbon dioxide were measured. The mineral sorbs considerable amount of ammonia but no carbon dioxide as shown in Table 13.

Table 13.

Sorption of Gases by Inesite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of inesite in c.c.
NH_3	10	767.1	0.91
	60	766.9	1.84
	530	767.2	4.61
	1800	766.8	8.02
	4740	759.9	13.51
	11690	765.2	22.57
	20640	765.9	30.03
	30570	752.8	35.26
	55130	758.1	42.37
	66600	755.7	43.35
	80955	748.9	44.00
CO_2	0.5	756.9	0.15
	43	757.0	0.20
	1200	761.0	0.30

The sorption velocity of ammonia by inesite is rather slow. Non-sorption of carbon dioxide and the slowness of ammonia sorption indicate that the dehydrated inesite combines chemically with ammonia. The dehydrated inesite has nearly been saturated with ammonia after the period

(8) Doelter, "Handbuch der Mineralchemie," Bd. II, 1 Hälfte (1914), 758.

of two months as shown in Table 13. The amount of ammonia sorbed is about 45 c.c. or 0.0020 mol per 1 gram of mineral. The amount of water evaporated by the process of dehydration was 4.84% in our sample, or 0.0027 mol per 1 gram of mineral. Thus the number of mols of the ammonia sorbed is three fourth of that of the water evaporated. The composition of the ammoniacal inesite, therefore, may be $(Mn, Ca)_6O_6 \cdot (SiO_2)_6 \cdot 3NH_3$.

Bentonite. Bentonite is a sort of clay of exceedingly fine grain. It is mainly found in U. S. A. and Canada, and now widely used in industrial purposes. In water it forms a jelly-like mass. It has a strong adsorptive power in aqueous medium. Recently, a substance was found in Japan having similar chemical composition and similar properties with the American bentonite.[9] The locality of the substance is Yamamoto-mura in Yamagata Prefecture. It is a hard clay of light yellow colour. Sorptive capacities of gases of this Japanese bentonite were measured.

The substance was put in the large quantity of water, stirred and dispersed to form a colloidal solution. The undissolved sandy matter was rejected, and the colloidal solution was evaporated up on a water bath. The dried substance thus obtained, was powdered in an agate motor. The powdered bentonite was then dewatered by heating to 250°C. for 2 hours under evacuation. The sorption of gases were measured on this substance. The results are given in Table 14.

Table 14.

Sorption of Gases by Bentonite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of elutriated bentonite in c.c.
NH_3	0.5	761.8	50.86
	3	761.8	69.16
	10	761.8	76.43
	35	761.0	79.10
	370	753.7	81.13
	1440	759.5	82.30
CO_2	0.5	758.5	4.54
	15	758.5	4.93
	433	758.6	4.95
	1140	758.6	4.98

(9) R. Shigemune, *Tokyo Kogyo Shikensho Hōkoku*, Vol. 25, No. 10, (1930).

Table 14—(*Concluded*)

Gas	Time in min.	Pressure of gas in min.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of elutriated bentonite in c.c.
SO_2	0.5	755.9	12.26
	12	755.9	14.20
	145	751.8	14.60
	1320	749.9	14.97
C_2H_2	0.5	767.8	2.41
	10	767.8	2.81
	185	766.5	2.93
	1542	766.0	3.09
O_2	1470	760.8	0.29

The bentonite was dispersed in water and the suspensoid was dialysed for 25 days using perchment paper as the dialysing membrane. The substance was evaporated, dried by heating to 250°C. for 2 hours under evacuation. Sorption of gases of this substance have been measured. The results are shown in Table 15.

Table 15.

Sorption of Gases by Dialysed Bentonite.

Gas	Time in min.	Pressure of gas in mm.	Vol. of gas (N.T.P.) sorbed at 25°C. by 1 gr. of substance in c.c.
NH_3	0.5	760.5	42.88
	3	760.5	76.76
	6	760.5	92.23
	30	760.5	104.75
	115	759.4	106 78
	571	762.3	108.48
	1260	763.6	110.39
CO_2	0.5	763.1	50.04
	3	763.1	89.19
	12	763.1	95.05
	90	763.0	97.00
	300	763.4	97.78
	707	762.9	98.08
	1442	761.6	99.16
SO_2	0.5	760 5	9.15
	3	760.5	11.16
	35	760.5	12.11
	605	760.7	12.93
	1400	766.6	13.23
C_2H_2	0.5	757.5	1.83
	11	757.5	2.11
	370	756.3	2.41
	1415	758.3	3.19
O_2	1140	764.9	0.87

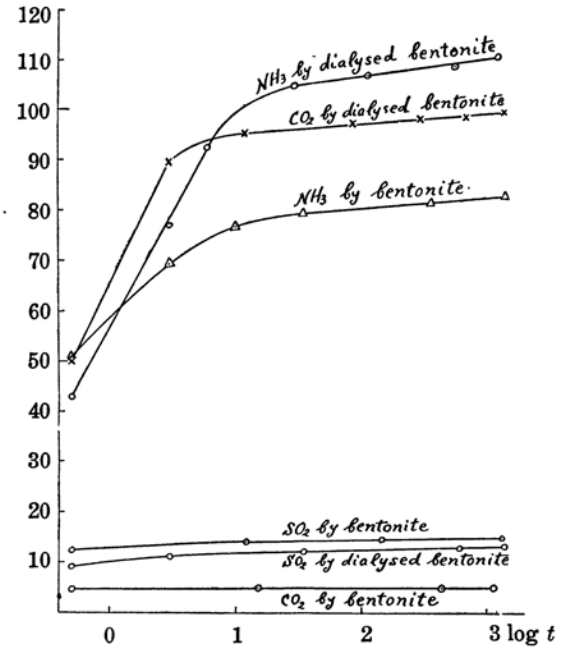

Fig. 4.

The sorption velocities of ammonia, carbon dioxide and sulphur dioxide are depicted in Fig. 4. The curves in the figure are composed of two sections, corresponding to the initial and final sorptions.[10] For the final sorption the following relation holds as shown in the figure:

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

where x denotes the sorption amount at time t, k and α being constants.

The expences connected with this investigation have been defrayed by grants from the Department of Education.

Summary.

1. The sorptions of ammonia, carbon dioxide, sulphur dioxide, acetylene, oxygen and hydrogen under one atmospheric pressure at 25°C. by the dehydrated samples of laumontite, stilbite, mordenite, natrolite, apophyllite, analcite, inesite and bentonite have been measured.

2. All samples except analcite sorb ammonia in considerable quantities.

(10) Sameshima, this Bulletin, **7** (1932), 177.

3. Mordenite sorbs ammonia, carbon dioxide, sulphur dioxide, acetylene and oxygen.

4. Bentonite sorbs ammonia, carbon dioxide and sulphur dioxide.

5. From the sorption amounts of gases and the forms of sorption velocity curves it is concluded that the ammonia combines chemically with laumontite, stilbite, natrolite, apophyllite and inesite.

6. Various gases which are sorbed by dewatered mordenite enter into the cavities among the molecular gratings of mordenite crystals, forming solid solutions. Thus we have found another sorbent of chabazite class.

7. Bentonite is one of the sorbent of silica gel class, being so-called amorphous or microcrystalline structure.

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