SORPTION OF GAS BY MINERAL. I. HEULANDITE AND CHABAZITE.

By Jitsusaburo SAMESHIMA.

Received March 20, 1929. Published April 28, 1929.

It is already known that the minerals of zeolite group have some special chemical properties.(1) G. Tammann(2) observed that the dissociation pressures of zeolite minerals change continuously with the change of their water contents. By the dehydration of them over sulphuric acid no change was perceptible on the appearance as well as the transparency of the crystals. Tammann attributed this to the formation of solid solution of the hydrated and the dehydrated minerals.(3) G. Stoklossa,(4) however, stated that the water evaporates somewhat step by step. The sorption capacities of chabazite was measured by R. Seeliger,(5) F. Simon,(6) O. Schmidt(7) and others,(8) of gases, O. Weigel and E. Steinhoff(9) of organic vapours.

I have measured the quantities of gases sorped by heulandite and chabazite. The procedure of the measurement is as follows. A known quantity of the air-dry mineral is put in a glass tube, which is then connected to a phosphorus pentoxide tube and a Toepler vacuum pump successively. The tube is heated to 360–400°C. and evacuated simultaneously until no evolution of vapour is perceptible. Now the tube is hermetically sealed and weighed. The tube is then filed and opened, and the dehydrated mineral is transferred into the measuring apparatus. The emptied glass

---

(1) Doelter, "Physikalisch-Chemische Mineralogie" (1905), p. 168 or "Handbuch der Mineralchemie" II, 3 (1921).
(2) Tammann, *Z. physik. Chem.*, **27** (1898), 323.
(3) See O. Weigel, *Chem. Abstracts*, **17** (1923), 3151.
(4) Stoklossa, *Neues Jahrb. Mineral. Geol., Beilage-Band*, **42** (1919), 1.
(5) Seeliger, *Physik. Z.*, **22** (1921), 563.
(6) Simon, *Z. physik. Chem.*, **132** (1828), 456.
(7) Schmidt, *Z. physik. Chem.*, **133** (1928), 263.
(8) For earlier literatures, see Doelter's books.
(9) Weigel and Steinhoff, *Z. Krist.*, **61** (1924), 125.

tube and the pieces of glass are weighed and subtracted from the former value, the correction for the bouyancy of air being applied. Thus the weight of the dehydrated mineral can be known exactly.

From the weight decrease, the percentage content of volatile matter in the air-dry mineral can be estimated. These volatile matter has not been analysed, so its composition is not known, but it can be supposed from the composition of mineral that the volatile matter is composed mostly of water. If the mineral is contaminated with $CaCO_3$, $MgCO_3$ etc., then carbon dioxide may be contained in the evolved vapour. I have selected transparent well defined pure crystals for the experiments.

The measuring apparatus is the same which was described in this Bulletin, 2 (1927), 2, except the measuring burette. In the present experiment, an ordinary 100 c.c. gas-burette has been used instead of the special burette used on that time.

Now the vessel containing the mineral is evacuated and heated to 300°C. by an electric furnace. After a thermostat was brought in place of furnace, the vessel is communicated to the gas-burette which contains a known quantity of gas. The room temperature and the barometric pressure are noted. The temperature of the mineral has been fixed to 25.0°C. The volume of gas sorped has always been reduced to those at 0°C. and 760 mm. pressure, and the values thus calculated are recorded in the present paper.

Heulandite. The composition of heulandite is considered to be $CaAl_2Si_6O_{16}5H_2O$(1) The mineral from Ogasawara-jima, Japan, has been used.(2) The mineral has an appearance like mica, and the crystal is translucent and easily separable in thin, colourless, transparent lamellæ from the cleavages.

On the dehydration by heating to 350°C., the crystal became somewhat opaque and white. 0.8459 gr. air-dry heulandite gave 0.7543 gr. dehydrated substance by evacuation and heating to 350°C. Percentage of the water evaporated is 10.8, or one gram of dehydrated substance combines with 0.0067 mol H_2O, assuming the volatile matter is consisted merely of water.

The amounts and the velocities of sorptions of ammonia, carbon dioxide and ethylene have been measured and the results are shown in the following tables.

By the sorption of ammonia, the mineral becomes chalky in its appearance and expands its volume. After the first measurement had been finished, the vessel was evacuated and heated to 300°C. By this treatment,

---

(1) Doelter, "Handbuch der Mineralchemie" II, 3 (1921), p. 188.

(2) K. Jimbo, *J. Coll. Sci. Imp. Univ. Tokyo*, **11** (1899), 278.

the expanded mineral has given up its sorped ammonia and shrinked and collapsed into small pieces. Then ammonia has been fed again, and measured the sorption capacity, the result of which is given in Table 2.

Table 1.

Sorption of ammonia by heulandite at 25.0°C.

Time after the contact of subst. to gas in min. t	Vol. of NH_3 sorped by 1 gr. of dehydrated subst. in c.c. (N.T.P.) x	Pressure of gas in mm. Hg.
0.5	8.1	770.0
1	13.2	,,
2	20.9	,,
3	28.5	,,
5	36.1	,,
10	51.6	770.0
15	61.9	,,
20	69.4	,,
30	80.1	,,
45	91.0	,,
60	98.6	770.0
90	108.2	,,
1340	134.8	765.3
2730	137.6	751.2

Table 2.

Second sorption of ammonia by heulandite at 25.0°C.

Time after the contact of subst. to gas in min. t	Vol. of NH_3 sorped by 1 gr. of dehydrated subst. in c.c. (N.T.P.) x	Pressure of gas in mm. Hg.
0.5	26.6	754.0
1	40.7	,,
2.7	74.3	,,
5	97.7	,,
10	120.5	,,
15	128.2	754.0
20	131.9	,,
47	137.6	,,
60	138.3	,,

These values are depicted in Fig. 1. In this figure the logarithm of time in minutes is taken in abscissa and the sorped volume of ammonia in

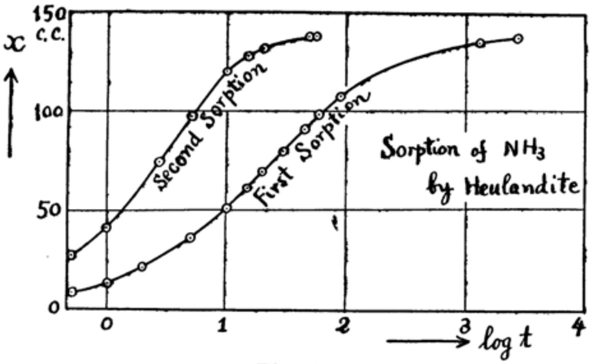

Fig. 1.

c.c. in ordinate. We see, from the figure, that the first sorption proceeds more slowly than the second one. As has already been described, the first sorption is done by the crystallised mineral while the second by the powdered one, so the difference in sorption velocities is expected. The sorption amounts, however, are quite the same in both cases.(1)

The sorption amounts by heulandite of carbon dioxide and ethylene have been measured. But it has sorped no considerable amounts of these gases. One gram of dehydrated heulandite sorped 0.5 c.c. of carbon dioxide and 0.2 c.c. of ethylene in 60 minutes under nearly one atmosphere and at 25.0°C. respectively.

From the fact that the dehydrated heulandite absorbs only ammonia in large amount, this substance may combine chemically with ammonia. There are numerous cases where the ammonia combine with dehydrated salt, for example calcium chloride, copper sulphate or cobalt chloride, etc.

One gram of our dehydrated mineral absorbs 138 c.c. of ammonia at normal temperature and pressure, or 0.0062 mol NH_3. This value is identical with the number of mols of water (0.0067) combines with the same quantity of dehydrated mineral, some allowance for the volatile matters other than water being made. Thus we have known that H_2O can be replaced by the same number of mols of NH_3 in the molecule of heulandite. The composition of the substance obtained in the present experiment may be $CaAl_2Si_6O_{16}\cdot 1.5H_2O\cdot 3.5NH_3$. Or if we assume the formula of heulandite to be $Ca_2Al_4Si_{12}O_{32}.11H_2O$,(2) then the substance corresponds to $Ca_2Al_4Si_{12}O_{32}\cdot 4H_2O\cdot 7NH_3$. It may be interesting to study from the standpoint of the silicate complex theory that whether any molecule of water can be replaced by ammonia or not, or how many ammoniacal heulandites can be synthesised.

---

(1) Cf. Sameshima, this Bulletin, **2** (1927), 5.

(2) Stoklossa, *Neues Jahrb. Mineral. Geol., Beilage-Band,* **42** (1919), 1.

Chabazite. The composition of chabazite is considered to be $(CaNa_2)Al_2Si_4O_{12} \cdot 6H_2O$. The minerals from Mitaka in Izu(1) and from Takashima in Hokkaido have been used. The former is transparent crystals of 1–2 mm. and the latter translucent crystals of 3–5 mm. On dehydration by heating to 350–400°C. the crystals do not change their appearance. Thus the transparent crystals keep their transparency unaltered.

0.2089 gr. air-dry chabazite from Izu gave 0.1669 gr. dehydrated substance by evacuation and heating to 400°C. Percentage of the water evaporated is 20.1. The amounts of sorptions of carbon dioxide, ethylene and ammonia have been measured and the results are shown in Table 3.

Table 3.

Sorption of gases by chabazite from Izu at 25.0°C.

Gas	Time after the contact of subst. to gas in min. t	Vol. of gas sorped by 1 gr. of dehydrated subst. in c.c (N.T.P.) x	Pressure of gas in mm. Hg.
CO_2	0.25	75.4	769.5
	1	109.0	,,
	2	115.4	,,
	5	116.4	,,
	23	116.8	,,
	30	117.4	,,
	60	117.7	,,
C_2H_4	0.25	7.1	768.5
	1	11.9	,,
	3	19.7	,,
	5	23.1	,,
	10	29.8	,,
	15	33.8	768.5
	30	40.3	,,
	60	46.7	,,
	90	50.3	,,
	1270	57.7	765.5
NH_3	0.25	129.3	764.5
	1	175.5	,,
	2	196.8	,,
	5	205.8	,,
	10	207.7	764.3
	30	209.3	764.0
	70	211.0	763.5
	360	212.3	761.3
	1460	213.0	760.2

---

(1) K. Jimbo, *J. Coll. Sci. Imp. Univ. Tokyo*, **11** (1899), 279.

0.3344 gr. air-dry chabazite from Hokkaido gave 0.2725 gr. dehydrated substance by evacuation and heating to 360°C. Percentage of the water evaporated is 18.5. The sorption amounts are shown in Table 4.

Table 4.

Sorption of gases by chabazite from Hokkaido at 25.0°C.

Gas	Time after the contact of subst. to gas in min. t	Vol. of gas sorped by 1 gr. of dehydrated subst. in c.c. (N.T.P.) x	Pressure of gas in mm. Hg.
CO_2	0.5	70.9	757.6
	2	105.2	,,
	5	111.6	,,
	10	111.7	757.7
	30	111.9	757.9
	60	112.0	758.2
C_2H_4	0.5	8.9	758.6
	2	13.9	,,
	5	18.9	,,
	16	26.9	758.7
	22	29.0	,,
	30	31.9	758.8
	60	37.0	759.0
	1200	53.7	760.7
NH_3	0.3	115.6	767.4
	1	149.1	,,
	2.5	181.7	,,
	5	194.9	,,
	10	197.2	767.3
	30	198.4	767.2
	68	198.5	767.0
	270	199.9	766.2
	1430	200.4	765.0

The data in Table 3 and Table 4 are depicted in Fig. 2.

The amounts of gases sorped by chabazite from Izu is a little larger than those by that from Hokkaido. These differences probably due to the purities of samples and the degrees of dehydrations. It is noteworthy that the carbon dioxide and the ammonia are sorped very rapidly, while ethylene is sorped rather slowly. The velocities of sorptions of carbon dioxide and ammonia are nearly the same with the velocity of sorption of gas by charcoal.(1) We see, in the paper of Seeliger(2) that the velocity of

---

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

(2) Seeliger, *Physik. Z.*, **22** (1921), 563.

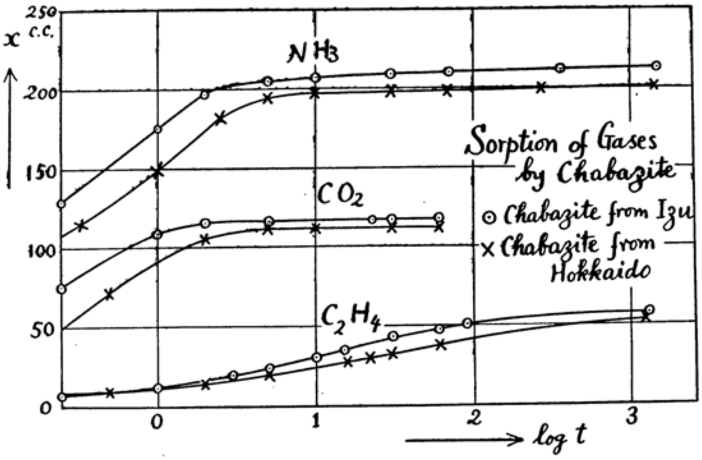

Fig. 2.

sorption by chabazite of acetylene is much smaller than those of ammonia, carbon dioxide and nitric oxide. Further studies on this point may give interesting results on the mechanism of sorption.

Seeliger described that one gram of his chabazite sorped 82.22 c.c. of hydrogen at 0°C., while Schmidt's chabazite(1) sorped only 1.5 c.c. of hydrogen at 20°C. The author measured the amount sorped by one gram of chabazite from Hokkaido at 25.0°C. of hydrogen and obtained the value 1.1 c.c. Thus our chabazite absorbs no considerable amount of hydrogen.

The author wishes to express his cordial thanks to Professor S. Tsuboi who kindly placed some of the minerals on the author's disposal, and identified some others by the mineralogical testing.

Summary.

1. The amounts and the velocities of sorptions by partially dehydrated heulandite of ammonia, carbon dioxide and ethylene have been measured.

2. It was known that the heulandite absorbs only ammonia in considerable amount.

3. The number of mols of ammonia sorped are nearly identical with that of water evaporated in the process of dehydration. So the ammonia is considered to combine chemically with the dehydrated heulandite. The composition of the substance obtained in the present experiment is probably $Ca_2Al_4Si_{12}O_{32}\cdot 4H_2O\cdot 7NH_3$.

---

(1) Schmidt, *Z. physik. Chem.*, **133** (1928), 263.

4. The amounts and the velocities of sorptions by dehydrated chabazites of carbon dioxide, ethylene and ammonia have been measured.

5. Chabazite absorbs carbon dioxide and ammonia rapidly, but ethylene slowly.

6. Chabazite absorbs hydrogen only in small quantity.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.