SORPTION OF VAPOUR BY CHABAZITE.

By Tositomo BABA.

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The fact that a partially dehydrated chabazite has the striking property of sorbing a very considerable amount of gases such as ammonia, carbon dioxide and ethylene, etc., has already been examined and confirmed by many investigators.(1) In the case of vapours, however, it was reported by O. Weigel and E. Seinhoff,(2) and O. Schmidt(3) that this property was not so much marked as in the case of gases, and moreover in certain cases, say ether and benzene, etc., it could not be observed entirely. Schmidt concluded in his paper that this unexpectancy might be due to the great magnitude of their molecular dimentions comparing with the small pores or cavities presumably existing in the crystal of a dehydrated chabazite, into which gases and vapours are sorbed. Further studies on the sorptions of vapours by chabazite may decide whether his conclusion be right or not, and may give us some information about the mechanism of sorption by solid adsorbent. In the present experiments both the sorption amounts and velocities of the vapours of some organic substances have been measured.

Material. The mineral, chabazite, from Izu in Japan(4) has been crashed into small pieces together with mother rock, and the transparent well defined crystals of 0.5~1.5 mm. have been carefully picked up. After dehydration by heating to 370°C. and highly evacuating, the crystals have kept their appearance unaltered, 0.5736 gr. of air-dry sample gave 0.4640 gr. of dehydrated substance, so the water evaporated was 19.1%.

Experimental Procedure. The apparatus used for this experiment is schematically shown in Fig. 1. The whole apparatus is made of glass, and the cocks are of mercury sealed type. Part A is the same with the apparatus ordinarily used for the volumetric measuring of both the sorption amount and velocity at constant pressure,(5) bulb E, cock K_3, burettes B_1 and B_2, and mercury reservoir H_1 being provided for this purpose. In order to overcome the difficulties which are met with, when we treat liquid vapour instead of gas, – preventions of condensation and leaking through the cocks of vapour – parts B and C are attached. Part B, nothing but a manostat which keeps the whole apparatus at a constant low pressure, consists of a manometer M, a large bottle V, a cock K_5 and a mercury reservoir H_2 etc. M serves not only as U-formed manometer but also as the pressure regulator

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(1) R. Seeliger, *Physik. Z.*, **22** (1921), 563; F. Simon, *Z. physik. Chem.*, **132** (1928), 456; O. Schmidt, *Z. physik. Chem.*, **133** (1928), 263; J. Shameshima, this Bulletin, **4** (1929), 96.

(2) O. Weigel and E. Steinhoff, *Z. Krist.*, **61** (1924), 125.

(3) Loc. cit.

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

(5) For example, Sameshima, this Bulletin, **2** (1927), 2.

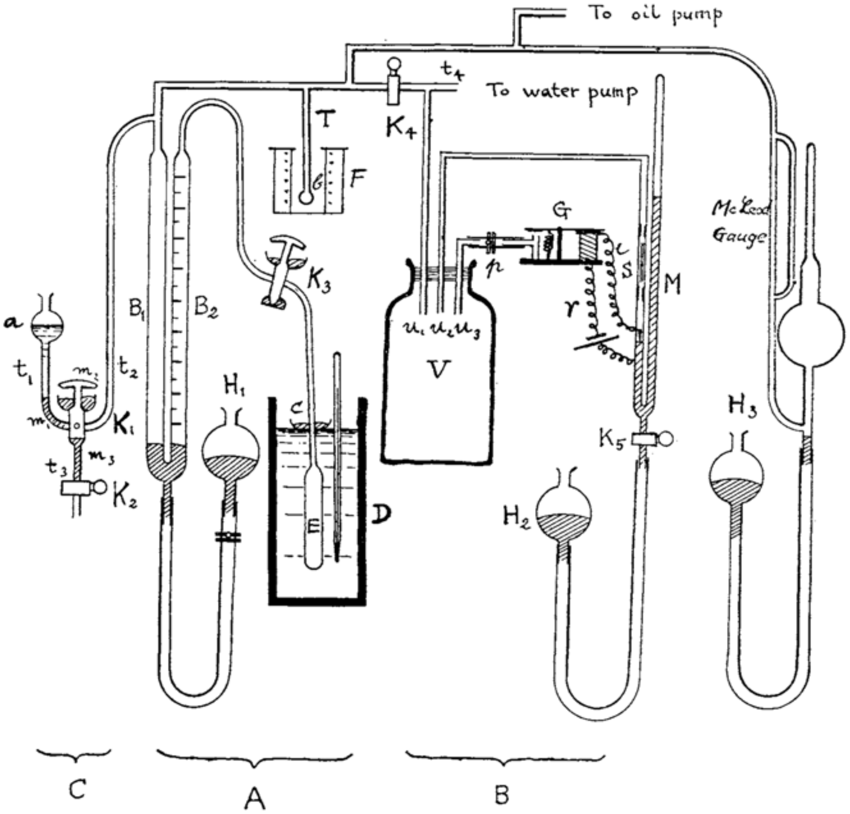

Fig. 1.

in which the quantity of mercury can arbitrarily be adjustable by the use of K_5 and H_2. The bottle V has a capacity of about 10 litres and serves as a preventer of a sudden change of pressure, the pressure in which is kept constant automatically by means of a device composed of a lever G, an electro-magnet i and an accumulator r. The lever G has an iron stick on one end and a rubber piece on the other and can open or close the mouth of bottle by the action of electric current which may be self-explainable by the figure.

The bottle is constantly evacuated by a water pump through tube t_4. By the proper adjustment of the power of water pump and screw cock p, the pressure has been able to keep constant within 0.1–0.2 mm. Hg. S is a safety device which consists of a glass tube packed with copper wires of about 20 cm. long for the accidental explosion causing from the electric sparks between the mercury surface and the platinum pointer.

An attached part designated by C is a specially deviced introducer for liquid vapours, which is a bottomless hollow cock K_1 with one hole, a turning of which causes communication of tubes t_1 to t_3, or t_2 to t_3, but not

t_1 to t_2. At first the parts m_1, m_2 and m_3 are sealed with mercury, and cock K_1 is evacuated together with the whole apparatus through tube t_2. Then the liquid under investigation is poured into bulb a, and cock K_1 is turned to tube t_1, when the liquid partially rushes into the hollow space of cock K_1 with the mercury in m_1. On turning cock K_1 to tube t_2 again, the liquid in the cock vapourizes at once into the whole apparatus through tube t_2. This method enables us to introduce liquid vapours into the apparatus without any difficulty or trouble even in the case of methyl amine whose boiling is -6°C., by the use of solid carbon dioxide.

To carry out the experiment, ground joint c is disconnected, the weighed fresh crystals of chabazite are placed in sorption bulb E, then the ground joint is restored to the former position. The mercury level in the burettes B_1 and B_2 is opened, cock K_4 being closed, cock K_1 is turned to tube t_2 and mercury-sealed. Now, electric furnace F is brought around the bulb E and heated to 350~370°C. and then all the parts of the apparatus are highly evacuated by an oil pump. Both heating and evacuating are continued for two hours. Then electric furnace F is substituted by thermostat D, the temperature of which being always kept at 25.0°C. and the manostat is also brought into action at the same time. Cock K_3 is then closed, the mercury level in the burettes is raised a little and the liquid vapour is introduced into the apparatus for the first time. Cock K_4 is opened and the reading of burette B_2 is recorded, keeping the mercury level in burettes B_1 and B_2 at the same height, and then opening cock K_3, the changes of readings are recorded with the time and the room temperature, the latter being necessary for the corrections of the readings afterwards.

Tube T is used for the measuring of the water content of the mineral, and in this case, the weighed sample in bulb b is heated to 360~370°C. in a high vacuum for two hours as before, hermetically sealed, and the net decrease of the weight of the mineral is measured as usual. This tube T is also used for the introduction of carbon dioxide by connecting it with the gas generator.

Experimental Results. The sorption amounts and velocities of the following fifteen substances have been measured: pentane, benzene, ether, chloroform, carbon tetrachloride, acetone, ethyl acetate, methyl alcohol, ethyl alcohol, methyl amine, ethyl amine, propyl amine, butyl amine, carbon bisulphide, and carbon dioxide(1). The last have been measured for the purpose of comparison with the results obtained by Prof. Sameshima recently. The results obtained by the author are shown in Table 1.

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(1) In the cases of methyl amine and carbon dioxide the atmospheric pressure served conveniently as the natural manostat.

Table 1

Substance and pressure of vapour in mm. Hg	Time in min.	Sorbed volume of vapour at 25.0°C. by 1 gr. dehydrated chabazite in c.c. (N.T.P.)
Pentane C_5H_{12} p=404	0	0.0
	10	0.0
	40	0.0
Benzene C_6H_6 p=71	0	0.0
	60	0.0
	120	0.0
Ether $(C_2H_5)_2O$ p=374	0	0.0
	20	0.0
	40	0.1
	60	0.1
Chloroform $CHCl_3$ p=120	0	0.0
	0.5	0.1
	1.5	0.2
	10	0.2
	20	0.2
Carbon tetrachloride CCl_4 p=76	0	0.0
	0.5	0.1
	30	0.1
Acetone $(CH_3)_2CO$ p=116	0	0.0
	10	0.0
	30	0.0
Ethyl acetate $CH_3COOC_2H_5$ p=60	0	0.0
	0.5	0.2
	1.5	0.3
	3.5	0.4
	5	0.4
	10	0.5
	15	0.6
	31	0.6
	42	0.7
	60	0.7
Methyl alcohol CH_3OH p=73 (1st observation)	0	0.0
	0.33	3.5
	1	5.3
	3	9.0
	5	13.0
	10	27.1
	21	60.8
	41	107.9
	60	129.9
	95	144.9
	120	148.2
	180	149.5
Methyl alcohol CH_3OH p=73 (2nd observation)	0	0.0
	0.5	5.7
	1	7.0
	3	11.4
	5	1.51
	10	28.5
	20	57.7
	40	101.5
	60	122.6
	90	131.3
	120	134.8
Ethyl alcohol C_2H_5OH p=35	0	0.0
	0.5	1.1
	1	1.4
	3	1.6
	5	1.6
	10	1.7
	20	2.3
	30	2.7
	40	3.1
	62	4.0
	100	5.2
	162	5.8

Table 1.—(*Continued*)

Substance and pressure of vapour in mm. Hg	Time in min.	Sorbed volume of vapour at 25.0°C. by 1 gr. dehydrated chabazite in c.c. (N.T.P.)
Methyl amine CH_3NH_2 p=754	0	0.0
	0.5	4.7
	1	5.8
	2	6.9
	3	8.8
	5	10.2
	10	12.8
	15	14.6
	21	16.4
	30	19.0
	40	20.8
	60	24.5
	120	31.3
	180	37.5
	300	44.8 (p=755)
	2549	74.4 (p=763.5)
Ethyl amine $C_2H_5NH_2$ p=585	0	0.0
	0.5	2.2
	1.33	2.5
	2	2.8
	5.25	3.1
	11	4.2
	20	4.5
	40	5.6
	60	6.2
	120	7.0
	256	7.6
Propyl amine $C_3H_7NH_2$ p=174	0	0.0
	0.5	0.5
	1	0.8
	2	1.1
	3	1.2
	5	1.6
	10	1.9
	20	2.3
	40	2.7
	60	2.9
	90	3.2
	180	4.2
	250	5.2
	1215	7.2
Butyl amine $C_4H_9NH_2$ p=52	0	0.0
	0.58	1.0
	1	1.1
	2.17	1.2
	4	1.3
	8	1.5
	18	1.7
	30	2.0
	61	2.6
	120	3.3
	192	4.2
	320	4.9
	1295	5.5
Carbon dioxide CO_2 (1st sorption) Case I p=768.8	0	0.0
	0.42	23.3
	1	36.8
	1.5	41.6
	2	44.1
	3	45.9
	5	47.8
	10	51.0
	20	54.3
	42	59.1
	60	60.9
	120	64.2

Table 1.—(*Continued*)

Substance and pressure of vapour in mm. Hg	Time in min.	Sorbed volume of vapour at 25.0°C. by 1 gr. dehydrated chabazite in c.c. (N.T.P.)
Carbon dioxide CO_2 (2nd sorption) Case II p=772	0	0.0
	0.45	38.6
		57.2
	2	70.4
	3	75.1
	5	77.6
	10	80.2
	20	82.4
	45	85.3
	80	87.8
	120	89.3
	180	90.8
	1200	96.2 (p=764)
Carbon dioxide CO_2 (3rd sorption) Case III p=760.9	0	0.0
	0.45	45.2
	1	60.2
	2	69.6
	3	74.0
	5	76.9
	10	79.8
	20	81.9
	40	84.9
	80	86.0
	120	88.2 (p=760)
	2640	102.8 (p=760)
Carbon dioxide CO_2 Another sample of chabazite Case IV p=762	0	0.0
	0.33	68.1
	0.75	81.3
	1.5	96.6
	2.25	98.5
	3	101.1
	5	103.5
	10	104.5
	15	104.7
	20	105.2
	40	106.0
	65	106.3
Carbon bisulphide CS_2 p=200	0	0.0
	0.5	41.3
	1	51.1
	2	59.5
	3	63.0
	5	67.1
	10	70.9
	15	72.5
	20	73.4
	42	75.3
	100	77.4
	2440	85.1

As seen from the above table, chabazite has almost no tendency to sorb pentane, benzene, ether, chloroform, carbon tetrachloride, acetone and ethyl acetate, while it sorbs methyl-, and ethyl alcohol, methyl-, ethyl-, propyl-, and butyl amine. By the first sorptions of alcohols, amines and carbon dioxide, chabazite seems to have little change in its transparent and colourless appearance, but to become more or less fragile in its crystal structure. If these fragile crystals again or repeatedly sorb methyl alcohol, methyl amine or ethyl alcohol, sorption amount of which being considerable, they show a tendency to collapse partially into small pieces even in the course of sorption, and if we try to drive off these vapours from the crystals by heating and evacuating, they readily become fine powders. This phenomenon, however, is not observed in the case of carbon dioxide.

Differing from these substances, carbon bisulphide is found to be a very interesting substance against chabazite because the mineral, strange to observe, takes appearance of pure yellow colour on the sorption of this vapour, evolving simultaneously hydrogen sulphide which is easily detectable from its characteristic addled egg-like odour and the sensitive reaction with lead salts. It is evident that carbon bisulphide is decomposed catalyticaly on the course of sorption by chabazite, free sulphur and hydrogen sulphide being produced as some of the decomposition products. Though the true mechanism of this decomposition may not be hoped for until the other decomposition products have been brought to light, it is highly probable that the other reactant is the water in crystals which cannot be expelled by the above mentioned treatment of dehydration, the hydrogen in the hydrogen sulphide having been considered not to come from any other source than the water.

Theoretical Consideration of the Mechanism of Sorption. Consistent with Schmidt's idea, it may be plausible to consider that vapours which have large molecular volumes are, in, general, impossible or difficult to be sorbed by chabazite, comparing with those which have small molecular volumes. Thus pentane, benzene, chloroform, etc. which are nearly not sorbed have molecular volumes greater than 70 except acetone, while alcohols, amines, carbon bisulphide, carbon dioxide, etc, which are more or less considerably sorbed, have molecular volumes smaller than 70 except higher homologous of amines. Though any definite relation is not as yet found between the sorption amount and molecular volume, the sorption amount may decrease distinctly with the increase of molecular volume or molecular weight in homologous compounds, and it is very noteworthy that the substitution of methyl group by ethyl group causes instantaneously a remarkable decrease in the sorption amount as in the cases of alcohols and amines.

As regards the sorption velocities, it was already pointed out by Prof. Sameshima that carbon dioxide and ammonia are sorbed very rapidly, while ethylene is sorbed rather slowly. These characteristic sorption phenomena against different substances have also been observed in the present experiment; the sorption velocities of methyl amine, methyl alcohol, and ethyl alcohol, etc. are very small in comparison with those of carbon dioxide, and of carbon bisulphide. These circumstances are more distinctly shown in the following graphs in which the sorption amount x at time t has been plotted against t.

Any mathematical formula to express these curves will be hoped for, yet unfortunately, this has been done only in the cases of alcohols where the velocity curves are not fully but approximately expressible by the equations somewhat like those of autocatalytic reactions.

$$\log\frac{b+x}{a-x}=kt+h \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(A)}$$

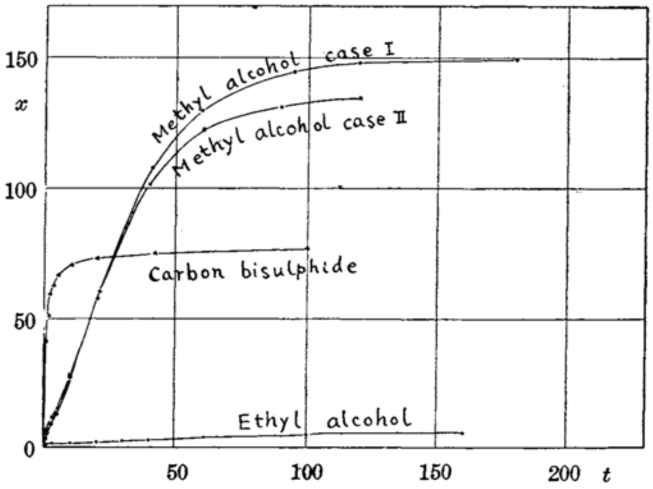

Fig. 2.

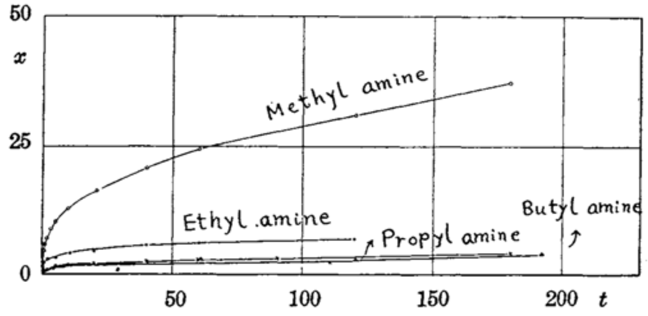

Fig. 3.

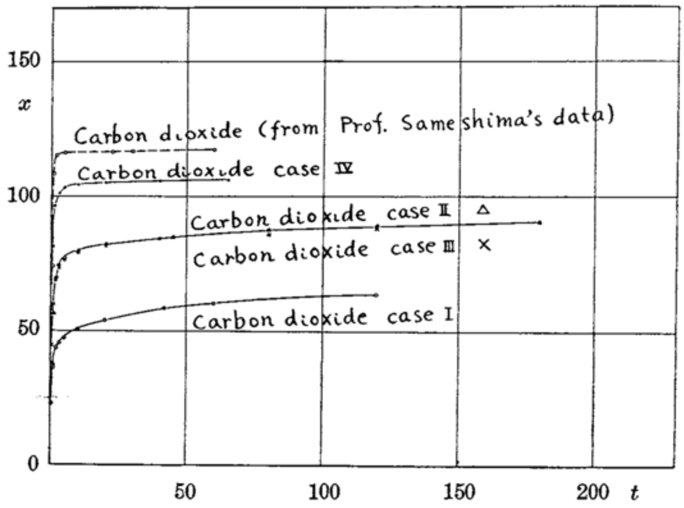

Fig. 4.

where x is a sorption amount at time t; and a, b, k, and h are empirical constants. Fig. 5 shows the linear relationship between $\log\frac{b+x}{a-x}$ and t, the constancy of k being also shown in Table 2.

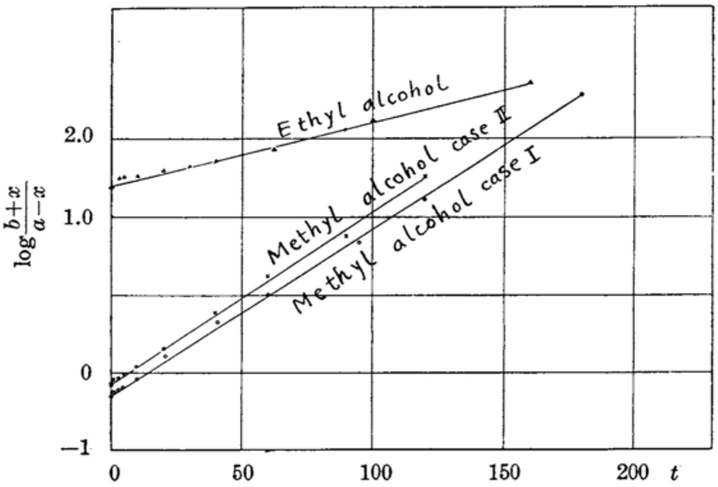

Fig. 5.

Table 2.

Vapour	Time in min.	Sorbed vol. of vapour at 25° by 1 gr. dehydr. chabazite in c.c. (N.T.P.)	Constant k
Methyl alcohol (1st observation) $a=149.56$ $b=77.0$	0	0.0	—
	1	5.3	(0.0355)
	5	13.0	0.0214
	10	27.1	0.0218
	21	60.8	0.0228
	41	107.9	0.0221
	60	129.9	0.0218
	95	144.9	0.0207
	120	148.2	0.0209
	180	149.5	0.0215
			mean 0.0216
Methyl alcohol (2nd observation) $a=135.5$ $b=100$	0	0.0	—
	1	7.0	(0.0524)
	5	15.1	0.0224
	10	28.5	0.0211
	20	57.7	0.0219
	40	101.5	0.0226
	60	122.6	0.0228
	90	131.3	0.0208
	120	134.8	0.0211
			mean 0.0215
Ethyl alcohol $a=6.1$ $b=150$	0	0.0	—
	1	1.4	(0.1172)
	5	1.6	(0.0253)
	10	1.7	0.0137
	20	2.3	0.0106
	30	2.7	0.0087
	40	3.1	0.0079
	62	4.0	0.0077
	100	5.2	0.0084
	160	5.8	0.0082
			mean 0.0092

To deduce the above formula following two assumptions have been made.

(i) The sorption velocity is proportional to the area of the entrances of pores or cavities into which vapours are sorbed, and to the degree of unsaturation of sorption capacity, namely, the amount sorbed after infinite time minus the present amount sorbed.

(ii) The area of the entrances of pores or cavities is enlarged by their collision with the vapour molecules passing through them in such a way that the area increase per unit time is, for the first approximation, proportional to the number of molecules which pass through the pores or cavities per unit time.

Granting the above two assumptions, we obtain two equations.

$$\frac{dx}{dt}=kA(a-x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(I)}$$

$$\frac{dA}{dt}=c\cdot\frac{dx}{dt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(II)}$$

where x is sorption amount at time t as above; A the area of the entrances of pores or cavities; a the saturation value of x; k and c proportional constants.

Integrating equation (II)

$$A=cx+A_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(III)}$$

where A_0 is the initial value of A, that is, the area of the entrances of the pores or cavities in the crystal, on which any vapour molecules have not yet been sorbed.

Eliminating A from equations (I) and (III)

$$\frac{dx}{dt}=k(cx+A_0)(a-x). \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(IV)}$$

This becomes by integration

$$\log\frac{\frac{A_0}{c}+x}{a-x}\cdot\frac{ac}{A_0}=\left(\frac{A_0}{c}+a\right)kct\,,$$

which can be easily rewritten in the form of equation (A).

In the case of carbon dioxide the variation of the sorption velocities in the alternative repetition of sorption and desorption has been observed. As Table 1 and Fig. 4 show, the sorption velocity accelerates about twice, when desorption and sorption have been repeated again (Case I and Case II), but further repetition causes no further increase (Case III). The large velocity in Case IV is probably due to the different treatment of the mineral before the experiment was commenced; or more correctly speaking, instead of taking the fresh mineral, the writer employed the mineral which had been exposed to the open atmosphere for several hours after the first dehydration, where it seems probable that a previous sorption of air and moisture occurs and consequently has a change of the sorption velocity in the next sorption of carbon dioxide. It is easily understood here that these facts are well consistent with the writer's assumptions made above, which indicate that the changes of the velocity are due to the enlargement of the pores or cavities in the mineral by the shock of bombardments of the sorbing gas or vapour molecules, and in the cases of alcohols and methyl amine, this enlargement of the pores or cavities is more conspicuous than in the case of carbon dioxide, so that in the former cases the crystal of chabazite may be much weakened in its structural nature, while in the latter case it is apparently unchanged, but vary in the sorption velocity when they sorbs the gas again.

In conclusion, the precise mechanism of sorption by chabazite might not be accounted for by mere consideration of the molecular volume of sorbing gas or vapour molecules as well as of the sorption velocity, however it may be sure that the sorption is much more related to the volume absorption than to the surface adsorption, otherwise disintegration of chabazite crystals or acceleration of sorption velocity would not take place in the above cases.

The present work has been done all through the experiments under the kindest guidance of Prof. J. Sameshima, to whom the writer wishes to express his hearty thanks.

Summary.

1. The sorption amounts and velocities by chabazite of fifteen substances have been measured at 25.0°C. by a statical method.

2. The sorption amounts of the vapours of pentane, benzene, ether, chloroform, carbon tetrachloride, acetone, and ethyl acetate have been found to be negligibly small, while those of methyl alcohol, methyl amine, carbon dioxide and carbon bisulphide have been found to be great. Ethyl alcohol, ethyl amine, propyl amine and butyl amine have been slightly sorbed.

3. No change in appearance of the mineral has been observed by the first sorption of alcohols, amines and carbon dioxide, but in the case of carbon bisulphide the crystal of chabazite have becomes yellow in colour,

probably indicating catalytic decomposition of this vapour into free sulphur, hydrogen sulphide and other decomposition products.

4. By the repeated sorptions of methyl amine, methyl alcohol and ethyl alcohol, the crystals of chabazite have become more or less fragile, and by heating and evacuating these fragile crystals have disintegrated themselves into fine powders.

5. The vapours which have large molecular volumes are generally difficult, if not impossible, to be sorbed by chabazite. The large gaps in sorption amounts between methyl and ethyl compounds in alcohol and amine series may be attributed to the same reason.

6. With regard to the sorption velocities of alcohols, the following formula has been applied which has some theoretical meaning:

$$\log\frac{b+x}{a-x}=kt+h$$

where x is the sorption amount at time t, and a, b, k and h the empirical constants.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.