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IONIC EXCHANGE AND SORPTION OF GASES BY CHABASITE.

By E. Rabinowitch and W. C. Wood.

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Chabasite crystals have a skeleton lattice formed by the ions Si^{4+}, Al^{3+} and O^{2-}. The hollows are occupied by positive ions, chiefly Ca^{2+}, and by neutral molecules, usually H_2O. Calcium can be exchanged for other divalent or monovalent ions, water for other molecules of appropriate size.

In a previous paper [1] several dehydrated chabasite samples from different localities, were found to possess about the same power of sorption; one, however—that from Richmond (Victoria)—sorbed three or four times less gas than all the others. Data available in Dölter's *Handbuch der Mineralogie* indicate that this chabasite is abundant in alkali ions, and we thought that this might be the reason of its low sorptive power. We therefore investigated the sorption by a number of chabasites in which calcium was exchanged for a series of different ions.

[1] E. Rabinowitch, *Z. physik. Chemie*, 1932 (*B*), **16**, 43, further quoted as "Paper I."

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Experimental.

1. Preparation of the Samples.—The purest crystals of chabasite from Rübesdorfel (Czechoslovakia) were washed in CCl_4 and ground. Portions of 3 gm. were mixed with 30 c.c. of 10 per cent. chloride solutions, and kept at about 100° C. for 200 hours, during which the solutions were replaced three times. The samples were then left exposed to the air for several days to allow them to acquire their "natural" water content, and analysed.

2. Analyses of the Samples.—We investigated samples treated with NaCl, KCl, $MgCl_2$, $CdCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ and $LaCl_3$. Approximately 0·5 g. were dissolved in 400 c.c. of conc. HCl for the separation of SiO_2. The treatment of the deposits with H_2SO_4 and HF (for the separation of SiO_2 from traces of barium, calcium, etc.), was omitted; the SiO_2 values given in the following tables may therefore be a little too high.

A complete ionic exchange took place with NaCl, KCl and $BaCl_2$, and a partial one with $SrCl_2$ and $CdCl_2$. The $MgCl_2$ sample contained only 2-3 per cent. MgO; that treated with $LaCl_3$ was practically identical

TABLE I.—Composition of Different Substituted Chabasites.

	Original Mineral.	Chabasite treated with the Chloride of				
		Sr.	Ba.	Cd.	Na.	K.
SiO_2	47·5	45·6	42·95	46·7	48·95	48·25
Al_2O_3	19·2	19·2	16·9	18·6	19·2	18·5
CaO	9·15	7·25	1·6	5·55	0·95	0·25
SrO	—	7·15	—	—	—	—
BaO	—	—	18·55	—	—	—
CdO	—	—	—	8·35	—	—
Na_2O	1·1	0·5	0·6	0·8	9·35	1·0
K_2O	1·55	0·9	0·75	0·75	1·25	13·8
H_2O	21·7	19·7	18·9	19·7	20·55	17·8
	100·2	100·3	100·25	100·45	100·25	99·6

TABLE II.—Equivalent Composition of the Chabasites.

	Original Mineral.	Chabasite treated with the Chloride of				
		Sr.	Ba.	Cd.	Na.	K.
SiO_2	4·2	4·05	4·3	4·25	4·35	4·4
Al_2O_3	1	1	1	1	1	1
CaO	0·85	0·65	0·15	0·5	0·1	0
SrO	—	0·35	—	—	—	—
BaO	—	—	0·75	—	—	—
CdO	—	—	—	0·35	—	—
Na_2O	0·1	0·05	0·05	0·10	0·8	0·1
K_2O	0·1	0·05	0·05	0·05	0·1	0·8
Total valency of the cations	8·1	8·2	7·9	8·0	8·0	7·8
H_2O	6·4	5·8	6·3	5·9	6·05	5·4

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with the original material (a spectroscopic test revealed the presence of about 1 per cent. of lanthanum). The sample treated with $CaCl_2$ was also unchanged; the small quantities of Na_2O and K_2O present in the original mineral were not exchanged for CaO. These three preparations were discarded for the sorption experiments. The composition of the other five, together with that of the original material (which is a typical Ca chabasite), is given in Tables I. and II. Table II. shows that the molecular composition of the samples can be represented by the formula :—

$$Al_2\,X\,(SiO_2)_4\cdot 6H_2O,$$

X standing for one mol. of bivalent or two mols. of monovalent ions. The ionic exchange takes place in a strictly stoichiometric way.

The water content of all the substituted chabasites is about the same, that of the potassium chabasite being, however, somewhat lower.[2]

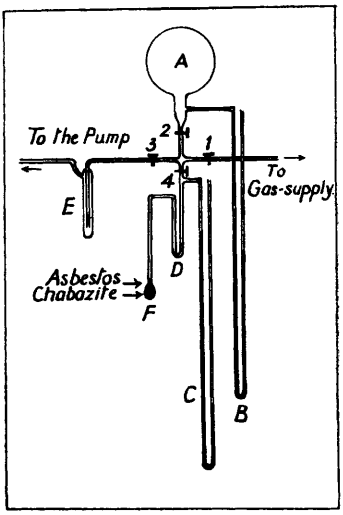

FIG. 1.

3. Sorption Experiments.—For each experiment 1 g. chabasite powder was placed in the hard glass tube F (Fig. 1), covered with asbestos wool to prevent sputtering and then heated to 500° for 2 hours, under constant pumping by a mercury pump. Traps D and E were immersed in liquid air (in experiments with CO_2 and C_3H_6 in solid carbon dioxide) to protect the chabasite from mercury and grease vapours. Gases were introduced in small portions from the container A, into the tube F, the quantity introduced being determined by the drop of pressure in A (manometer B), the resulting pressure in F by the manometer C. The quantity of

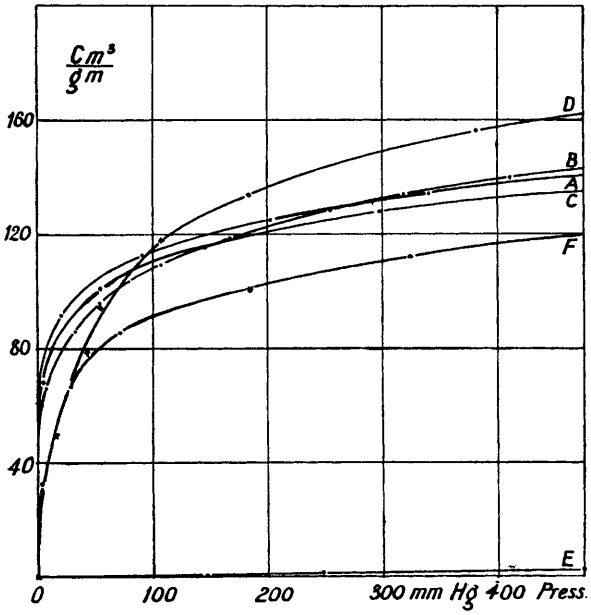

FIG. 2.—H_2 Sorption at − 190° C.

A	Sr-Chabasite.	D	Na-Chabasite.
B	Cu- ,,	E	K- ,,
C	Ba- ,,	F	Cd- ,,

[2] E. Gruner (*Z. anorgan. Chemie* (1933), **211**, 385) assumes $7H_2O$ in the calcium chabasite and $5H_2O$ in the alkaline chabasites.

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gas sorbed was calculated by subtracting from the total quantity admitted into F the small quantity filling the tubing FD. The same sample was used for experiments with all gases, as it was shown that repeated heating had no effect on its sorbing capacity.

Experimental Results.

A set of successive pressure measurements with increasing gas quantities served to determine a sorption isothermal. In accordance with previous experience, the isothermals obtained with H_2 and N_2 were well reproducible; it was, however, difficult to reproduce measurements with CO_2 to more than 10 per cent. and in the case of C_3H_6 deviations of 50 per cent. were quite possible. This is due to the great velocity with which the equilibrium is reached in the case of H_2 and N_2, the pressure becoming constant a few seconds after the introduction of the gas. With CO_2 one has to wait for an hour or more (at the higher pressures), and a day or more is necessary with C_3H_6. The results obtained with C_3H_6 (Fig. 5), are therefore not very reliable. The sorption values obtained with the natural calcium chabasite were practically identical with those found in Paper I.

Sorption of:	R (c.c./gm.).	R and W (c.c /gm.).
(1) N_2 (at − 190° C., p = 400 mm.) .	170	163
(2) H_2 (same conditions) . . .	130	130
(3) CO_2, (p = 100 mm., t = + 20° C.)	110	115

The changes in the sorption power caused by ionic exchange are *reversible*. By treating a sample of potassium chabasite with a solution of $CaCl_2$, we recovered a calcium chabasite which sorption isothermals were practically identical with those of the original mineral. The results of the sorption measurements are given in Figs. 2, 3, 4 and 5.[3]

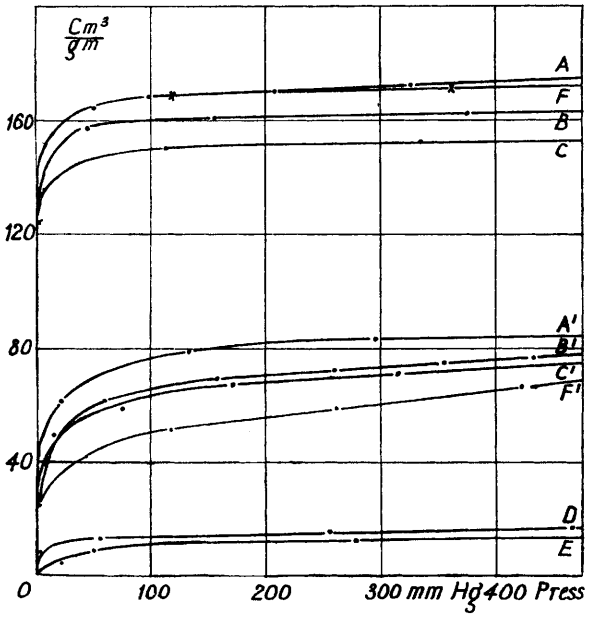

FIG. 3.—N_2 Sorption.

A Sr-Chabasite
B Ca-Chabasite
C Ba- ,,
D Na- ,,
E K- ,,
F Cd- ,,
} − 190° C.

A'
B'
C'
F'
} − 80° C.

[3] The numerical data underlying Figs. 2-5 can be found in the dissertation by W. C. Wood, University of Göttingen, 1934.

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The conclusions which can be drawn from these isothermals are as follows :—

(*a*) The three *alkaline earth chabasites* have practically identical sorption properties (the differences observed in experiments with C_3H_6 are not certain enough for discussion).

(*b*) *Cadmium chabasite* isothermals run somewhat below those of the alkaline earth products, indicating a lower sorption energy. It is, however, probable that the saturation values are the same. The unchanged water content supports this assumption.

(*c*) *Sodium chabasite* is characterised by a very small sorption capacity for *nitrogen*. H_2, CO_2 and H_2O are, however, strongly sorbed. The corresponding isothermals rise at first slower than those of the other chabasites, indicating a smaller initial sorption energy, but attain ultimately even somewhat higher values. The water content is, however, the same, indicating that the saturation values (and thus the sorption space), may be unchanged in this chabasite too.

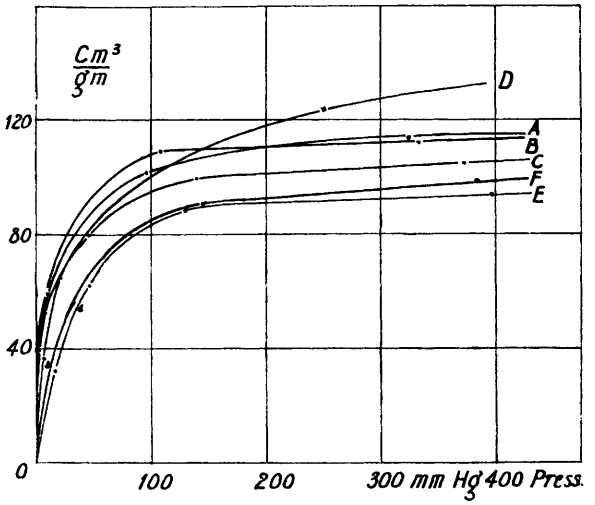

FIG. 4.—CO_2 Sorption at 20° C.

A Sr-Chabasite. D Na-Chabasite.
B Ca- ,, E K- ,,
C Ba- ,, F Cd- ,,

(*d*) *Potassium chabasite* sorbs as little nitrogen as the sodium product, and practically no hydrogen at all (at −190° C.). H_2O, and CO_2 are still strongly sorbed, although also to a somewhat smaller degree than by all other chabasites. C_3H_6 is only very weakly sorbed both by the sodium and by the potassium chabasite.

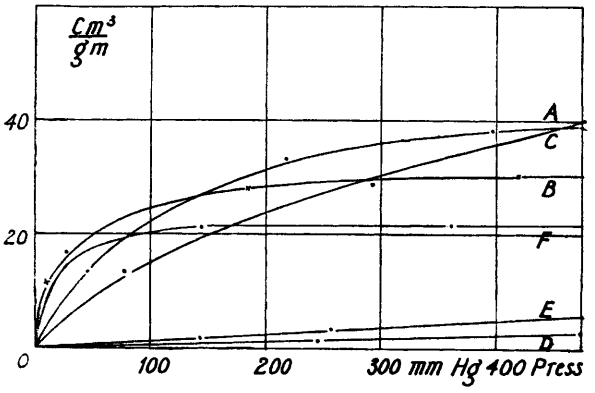

FIG. 5.—C_3H_6 Sorption at 20° C.

A Sr-Chabasite. D Na-Chabasite.
B Ca- ,, E K- ,,
C Ba- ,, F Cd- ,,

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Discussion.

In general, the above results are in agreement with our assumption. The replacement of divalent by monovalent ions actually decreases the sorptive capacity of the crystals. The influence of the larger K^+ is more pronounced than that of the smaller Na^+ ions.

It is, however, difficult to interpret satisfactorily the details of the experimental results. The unchanged capacity for sorbing water and carbon dioxide indicates that space for sorption is not, or not essentially, decreased by the introduction of alkaline ions. The slightly smaller H_2O and CO_2 content of K-chabasite may be due to the space occupied by the K^+-ions becoming unavailable for sorption. (The number of additional monovalent ions—about 0·8 mols. according to Table II. —is nearly equivalent to the decrease in the number of water molecules). This effect is, however, absent in the Na chabasite; and in the case of K^+ it may also be due to an incomplete saturation, *i.e.* to a smaller sorption energy. In any case, the small difference in the space available for sorption cannot account for the strong differences observed in sorption experiments with H_2 and N_2. They must be due to *energetical* conditions. The results obtained with the *potassium chabasite* are consistent with an assumption that the sorption energy both for hydrogen and nitrogen is decreased in the relation of about 5 : 1 (as compared with calcium chabasite). The sorption energies for carbon dioxide and water are also decreased, but to a much smaller degree.

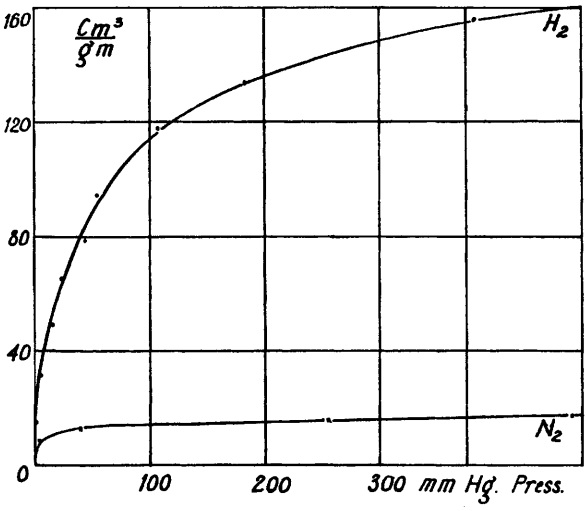

FIG. 6.—Sorption by sodium-chabasite at − 190° C.

The most difficult to understand are the results with *sodium chabasite*, in which the initial sorption energy for hydrogen appears to be reduced only by a factor 0·7, whereas the sorption energy for N_2 is diminished roughly in a relation 3 : 1. Sodium chabasite can be described either as possessing an abnormally high sorptive capacity for hydrogen, or an especially low sorptive capacity for nitrogen (Fig. 6).

We may recall that the natural chabasite from Richmond (Victoria) which led to this investigation, had a sorptive capacity uniformly reduced (in the relation 3 : 1) for all the three gases H_2, N_2 and CO_2. This result illustrates the variety of the sorption effects occurring in alkali substituted chabasites.

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Sorption Formulæ.

The experimental results described above are not sufficiently complete to be used for quantitative representation by sorption formulæ as was done with the sorption isothermals of the natural chabasite in Paper I. We can here, however, improve the theoretical treatment given in that paper. Two possible states of the molecules sorbed by chabasite were mentioned there: (*a*) that of a "gaseous" sorbate, with molecules freely moving about in the cavities of the crystal, and (*b*) that of a "solid" sorbate, with molecules fixed to definite crystallographical positions. The first picture does not exclude the existence of periodical variations in the potential, or of more or less high "potential barriers" in certain lattice positions, thus accounting for the slowness of diffusion of the sorbate. The second picture must account for the existence of diffusion by assuming accidental interchanges of molecules between adjoining sorption centres. In this way, the two extreme hypotheses converge towards an intermediary picture of a "partially fixed" sorbate, which is probably nearest to the truth.

The actual state of a given sorbate, however, may be nearer to the one of the two pictures. It is therefore useful to have sorption formulæ for both limiting cases.

(a) Gaseous Sorbate.—The formulæ for the distribution of molecules between a gas phase and a zeolite was given in Paper I. as follows:

$$\frac{N_a}{N_g} = \frac{(V_a - bN_a)}{V_g} e^{\phi/RT} \quad . \quad . \quad . \quad . \quad (1)$$

N_a is the number of molecules of the sorbate in the solid phase, N_g that in the gas phase, V_a the "sorption volume" of the crystal, b the volume required by a single molecule, V_g the volume of the gas phase, ϕ the sorption energy (per mol.). Supposing b to be independent of the degree of saturation, we may assume $V_a = bN_{\text{max.}}$, where $N_{\text{max.}}$ is the maximum number of molecules which can find place in the crystal. Hence

$$\frac{N_a}{N_g} = \frac{(N_{\text{max.}} - N_a)b}{V_g} e^{\phi/RT}. \quad . \quad . \quad . \quad (1')$$

For constant concentration of the sorbate $\left(\frac{N_a}{N_{\text{max.}} - N_a} = const.\right)$ the following *vapour pressure formula* (3) is derived from (1)

$$\log_e p_{\text{atm.}} = -\frac{\phi}{RT} + \log_e T + \log \frac{N_a}{N_{\text{max.}} - N_a} - \log_e N_A T_0 b \quad (2)$$

where N_A is the number of molecules in c.c. of the gas at $t = 0°$ C. and $p = 1$ atm.[4]

(b) Solid Sorbate.—The statement in Paper I. that "formula (1) holds also for the case of a fixed number of sorbing centres, b meaning in this case the volume of each centre and V_a that of all of them together" requires correction. The distribution of molecules between

[4] M. H. Hey, (*Mineralogical Magazine*, 1935, **24**, 99) derived, by kinetic considerations, a vapour pressure formula very similar to (2) (but with slightly different meaning of some constants). Some constants in his formulæ are, however, related to the special mechanism of evaporation and condensation which he uses for derivation—a result not in accordance with thermodynamics, which requires that a formula describing an equilibrium shall contain nothing about the mechanism by which this equilibrium is reached.

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gas phase and a fixed number of sorption centres depends on the *number* of unoccupied centres only, and the notion of the "volume of a sorption centre" is an unnecessary complication. Moreover, law (1) does not apply unchanged to a distribution of this kind. In passing from the gaseous state into that of a *solid* sorbate, the molecules lose not only their potential energy of sorption ϕ but also their kinetic energy. The distribution law is therefore more complicated. The probability of finding a molecule in the gas phase (volume V_g, temperature T) is, according to quantum statistics:

$$P_{\text{gas}} = \int_{E=0}^{\infty} V_g \frac{4\sqrt{2}\pi m^{\frac{3}{2}} E^{\frac{1}{2}}}{h^3} e^{-E/kT} \mathrm{d}E.$$

The probability of finding the molecule in the solid sorbate is:

$$P_{\text{solid}} = (N_{\text{max.}} - N_a) e^{\phi/RT}$$

and the distribution law is therefore

$$\frac{N_a}{N_g} = \frac{N_{\text{max.}} - N_a}{V_g} \frac{h^3 N_A{}^3}{(2\pi MRT)^{\frac{3}{2}}} e^{\phi/RT} \quad . \quad . \quad . \quad (3)$$

a formula which differs essentially from (1) by the occurrence of the factor $T^{\frac{3}{2}}$, and by the molecular weight M replacing the molecular volume b in the rôle of a characteristic constant of the sorbate.

The vapour pressure formula derived from (3) is:

$$\log_e p_{\text{atm.}} = -\frac{\phi}{RT} + \frac{5}{2}\log_e T + \log_e \frac{N_a}{N_{\text{max.}} - N_a} + \log_e \frac{(2\pi RM)^{\frac{3}{2}}}{h^3 N_A{}^4}. \quad (4)$$

Equation (4) differs from the ordinary quantum theoretical vapour pressure formula of a homogeneous ideal solid body by the occurrence of the characteristic "saturation term"

$$\log \frac{N_a}{N_{\text{max.}} - N_a}.$$

(c) Vibrating Sorbate Molecules.—Since the sorption energies are not greater than 30,000 Cals. per mol., the quanta corresponding to the vibrations of the molecules around their equilibrium positions must be of the order of 1000 Cals. (300 cm.$^{-1}$) or smaller and these vibrations are by no means "frozen" at temperatures above 100°$_{\text{abs.}}$ (which were used in most sorption experiments). The law of distribution of molecules between gas and sorbate is in this case:

$$\frac{N_a}{N_g} = \frac{(N_{\text{max.}} - N_a)}{V_g} \sum_v e^{-E_v/RT} \frac{h^3 N_A{}^3}{(2\pi MRT)^{\frac{3}{2}}} e^{\phi/RT} \quad . \quad . \quad (5)$$

and the corresponding vapour pressure formula:

$$\log_e p_{\text{atm.}} = -\frac{\phi}{RT} + \frac{5}{2}\log_e T + \log_e \frac{N_a}{N_{\text{max.}} - N_a} - \log_e \sum_v e^{-E_v/RT} + \log_e \frac{(2\pi RM)^{\frac{3}{2}}}{h^3 N_A{}^4} \quad (6)$$

In these formulæ, E_v is the vibrational energy (per mol.) corresponding to the state with the vibrational quantum number v.

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(**d**) **Isothermals.**—From all the three formulæ (2), (4) and (6), we obtain the following isothermal equations:

$$\frac{N_a}{N_{\text{max.}} - N_a} = ap\,; \quad N_a = \frac{apN_{\text{max.}}}{1 + ap}(a = \text{const}) \quad . \quad . \quad (7)$$

A law of this form must hold for the sorption isothermals independently of the "gaseous," "solid" or "semi-solid" state of the sorbate, provided only that ϕ is a constant independent of the saturation $N_a/N_{\text{max.}}$

The experimental sorption isothermals of chabasite, however, never fulfil law (7). This shows clearly that the sorption energy is dependent on saturation. Two possibilities may be considered: the sorption energy may either decrease continuously with increasing sorption, or it may change in steps. In Paper I. we made the mistake of expecting that sudden changes of the sorption energy must reveal themselves by discontinuities or inflexions in the sorption isothermals. This is not true. If, for instance, the crystal contains two kinds of sorption centers, N_1 (with the energy ϕ_1), and N_2 (with the energy ϕ_2), then the distribution between gas phase and each set of centers will be independent of the existence of the second set and given by a formula of the kind (7). The total number of molecules in the sorbed state will be:

$$(N_a)_1 + (N_a)_2 = p\left(\frac{a_1(N_{\text{max.}})_1}{1 + a_1p} + \frac{a_2(N_{\text{max.}})_2}{1 + a_2p}\right) \quad . \quad . \quad (8)$$

This equation represents a smooth function without any discontinuities or inflections. Obviously, a continuous change of ϕ with $N_a/N_{\text{max.}}$ may be expected to occur in the case of a "gaseous" or nearly gaseous sorbate, whereas the existence of a discrete set of values ϕ_1, ϕ_2 . . . is more characteristic of a "solid" sorbate with a number of different crystallographic positions occupied by the molecules of the sorbate.

(**e**) **Saturation.**—In the case of a fixed number of sorption centers, the number of molecules corresponding to the saturation state must be the same for all kinds of sorbates, or, alternatively, only a few widely separated saturation values may be found, forming a small whole number series. This may occur either in the case of larger molecules occupying two or more centres, or in the case of a particular set of centers being unavailable for some kind of sorbate. In the case of a gaseous sorbate, the saturation values may vary continuously according to the size and shape of the molecules.

In Paper I. we used formula (1) for the representation of the isothermals, considered ϕ as a continuous function of the concentration and extrapolated individual saturation values for all gases investigated. In doing so, we practically adopted the hypothesis of the "gaseous" sorbate.

After the appearance of that paper, it has been, however, suggested [5] that chabasite possesses two crystallographical positions which are vacant in the dehydrated lattice. Under these circumstances, two different saturation values and two different sorption energies for each gas may be expected. Hey suggested that the saturation values extrapolated in our previous paper may be arranged in two groups—some being close to 330 c.c./gm. (corresponding to 12 molecules of sorbate per unit cell) and the others to about $\frac{1}{2}$ of this value. Fig. 8 in Paper I. shows that this interpretation is not incompatible with the experiments

[5] See A. Tiselius, *Z. physik. Chemie*, 1935, *A*, **174**, 401.

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made with natural calcium chabasite. The results obtained with the substituted chabasites and illustrated by Figs. 2-5 in this paper are, however, more difficult to reconcile with this scheme. To interpret them would require much more than two different kinds of centers. Besides the saturation values 330 and 165 c.c., those lying in the neighbourhood of 80 c.c. and 20 c.c. are suggested by the slope of some curves.

By assuming 4 or more different kinds of positions, each having its own characteristic sorption energy, one has in hand enough independent constants to be able to represent all the experimental isothermals. A representation of this kind is, however, of no great value in the actual state of the experimental material available. Fuller investigations of the sorption equilibrium may, however, give, with the help of the above derived formulæ, information about the state of the sorbates under different conditions.

The experimental part of this paper forms one part of the dissertation presented by Mr. W. C. Wood to the Faculty of Science of the University of Göttingen. Results of an investigation of the electrical properties of zeolites, which were included in this dissertation, were communicated on a previous occasion.[5]

The experiments were carried out in the Minerological Institute of the University of Göttingen, to whose Director, Professor V. M. Goldschmidt (now is Oslo), we are highly indebted for his kind interest in this work and many valuable suggestions. We also thank Dr. E. Thilo for valuable advice in the analytical part of this work.

[5] E. Rabinowitch and W. C. Wood, *Z. Elektrochemie*, 1933, **39**, 562.