

Ionic Exchange and Sorption of Gases by Chabazite

IN experiments on the sorption of gases by zeolites, it has been shown¹ that, of seven samples of chabazite found in different localities, one showed a much smaller power of sorption than all the others. It was supposed that the cause of this peculiar behaviour of this one sample might be sought in its higher univalent ion (K^+ , Na^+) content, in contrast to the probable higher Ca^{++} -content of the other chabazites. We have therefore tried to find the relation between the power of sorption of chabazite

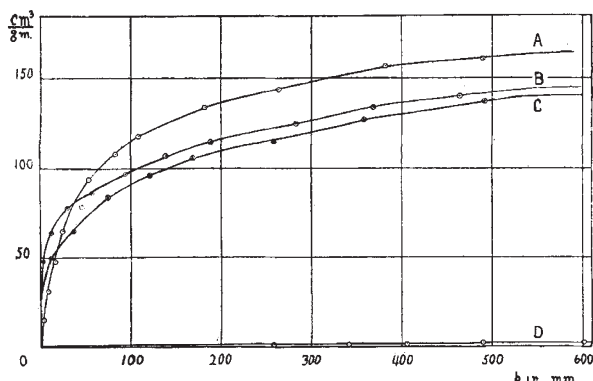


FIG. 1. Sorption isotherms of chabazite for hydrogen at $-190^{\circ}C.$ in c.c. per gm. dehydrated mineral (dehydrated at $500^{\circ}C.$). A, Na-chabazite; B, Ca-chabazite; C, Ca-chabazite reconverted from the K-chabazite; D, K-chabazite.

and its ionic content. This was done by comparing the sorption of different gases by samples of natural chabazite from Rübendörfel (near Aussig, Czechoslovakia) which had been boiled for two hundred hours in solutions containing K^+ , Na^+ , Ca^{++} , Sr^{++} , Ba^{++} , Cd^{++} , or La^{+++} -ions, in which way we hoped to obtain chabazites containing these ions. The sorbing power of samples so treated differed markedly from that of the original mineral, especially in the case of Na- and K-preparations.

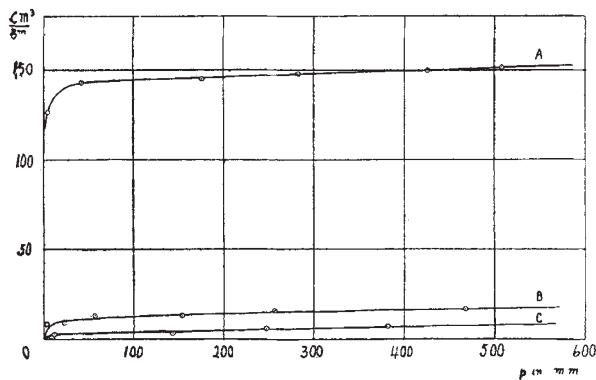


FIG. 2. Sorption isotherms of chabazite for nitrogen at $-190^{\circ}C.$ in c.c. per gm. dehydrated mineral (dehydrated at $500^{\circ}C.$). A, Ca-chabazite; B, Na-chabazite; C, K-chabazite.

Figs. 1 and 2 show the sorption isotherms for hydrogen and nitrogen at $-190^{\circ}C.$, for Ca-chabazite, Na-chabazite and K-chabazite. (The natural chabazite from Rübendörfel contains principally Ca^{++} -ions, and shows, too, a sorption nearly exactly equal to that of the Ca-chabazite.) From Figs. 1 and 2 it is obvious that the exchange of the calcium ions for sodium ions alters the sorptive power for hydrogen very little (slight increase), as contrasted

with the large decrease for nitrogen. The sorption of nitrogen by the K-chabazite is decreased still more than for the Na-chabazite; and this time, the sorption of hydrogen is practically zero.

That the change of sorptive power is reversible, is indicated by the fact that sorption curves of the Ca-chabazite, prepared by reconvertng the K-compound, are nearly identical with the original Ca-chabazite curves (Fig. 1).

These results show that the replacement of one Ca^{++} -ion ($r = 1.06 \text{ \AA.}$) by two Na^+ -ions ($r = 0.98 \text{ \AA.}$) decreases the sorption space of the crystals for nitrogen, but leaves it unaltered for hydrogen; further, the substitution of two K^+ -ions ($r = 1.33 \text{ \AA.}$) for one Ca^{++} -ion appears to close up the sorption space in the crystal even for molecules so small as hydrogen. The experiments with the divalent ions Ca^{++} , Sr^{++} , Ba^{++} ($r = 1.06 \text{ \AA.}$ to $r = 1.43 \text{ \AA.}$) show differences in sorption from that of the original mineral of not more than ± 10 per cent. (Only the Cd-chabazite showed a decrease of 30 per cent for hydrogen and 50 per cent for nitrogen.) That there really was an exchange of ions was shown by an analysis of the Ba-chabazite, which was found to contain 16 per cent barium. So we are able to say that a replacement of Ca^{++} -ions by an equal number of other divalent ions with radii up to 1.43 \AA. does not alter the sorption power for nitrogen and hydrogen.

It is known that the sorption of vapours by natural chabazite is limited by the size of their molecules; for example, ether and benzene, etc., are not sorbed at all. It is possible that in the Ba- and Sr-chabazites, the upper limit of the molecular diameter of a gas which will be sorbed is lower than that for the calcium compound. Our experiments show only that this limit is still larger than the diameter of the nitrogen molecules. In the case of Na-chabazite, the limiting size of the molecules sorbed seems to lie between that of nitrogen and hydrogen, and in K-chabazite this limiting size must be less than that of the hydrogen molecule.

Details concerning the apparatus, sorption isotherms, and samples will be published elsewhere.

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¹ E. Rabinowitsch, *Z. phys. Chem.*, B, 16, 43; 1932.

Tunny in the North Sea

AMONG the notes in the "Calendar of Nature Topics" in NATURE of July 15 are two paragraphs on the occurrence of tunny in the North Sea. This fish seems, indeed, to have become much more common there in recent times than it was some decades ago. A fisherman here, now concerned with Indian fishery investigations, recently told me that he remembers perfectly well that it was in the year 1911 (well-known also by an exceptionally heavy storm) that the big creatures, hitherto unknown, first came under the attention of those engaged in herring fishing on the North Sea. This particularly interested me, as 1911 was an exceptional year in its very warm and dry summer. My plankton investigations on the light-vessel *Haaks* off Den Helder, during the years 1910-1912, showed that the influence of this heat period was great also on the temperature of the sea and the development of the plankton. Diatoms, peridinians,