CCXIV.—*Sorption of Ammonia on Chabazite.*

By MEREDITH GWYNNE EVANS.

MANY workers have investigated the sorption of gases and vapours by the zeolite group of minerals, of which chabazite is a member. Rinne (*Z. Krist.*, 1924, **60**, 65) and Friedel (*Bull. Soc. franç. Min.*, 1896, **19**, 14, 94) showed that dehydrated chabazite was capable of sorbing many gases and vapours, including bromine, iodine, and mercury; and Seeliger, using a torsion-balance method (*Physikal. Z.*, 1921, **22**, 563), has made a detailed study of the sorption of gases on this mineral.

Chabazite was used as a sorbent for two reasons: (1) The time taken for sorption to reach equilibrium is very short, and this was a great advantage since it was desired to measure heats of sorption; (2) the crystalline nature of the zeolites made it probable that some information might be obtained by an *X*-ray examination of the crystals before and after sorption.

The Sorbent.—There has been much conflict of opinion as to the true nature of "zeolitic water." Rinne (*loc. cit.*) and Tammann (*Z. physikal. Chem.*, 1898, **27**, 323) have shown that the dehydration curves of the zeolites do not indicate the existence of definite hydrates, the vapour pressure varying continuously with the water content of the crystals. It has been shown also that the optical properties of the zeolites change continuously during dehydration, and are completely restored on rehydration. Beutell and Blascke (*Centr. Min.*, 1915, **142**, 195) and Stocklossa (*Neues Jahrb. Min., Beil.-Bd.*, 1917, **42**, 1), on the other hand, have obtained dehydration curves for the zeolites which indicate the existence of a large number of hydrates.

In view of this uncertainty concerning the nature of zeolitic water, and because of the important influence of moisture on the sorption process, the dehydration and rehydration processes of chabazite were examined. A quartz-fibre balance (see McBain, *J. Amer. Chem. Soc.*, 1926, **48**, 690) was used to follow the loss or regain of water by the chabazite, and the curves obtained by plotting this change of water content (1) against temperature at constant pressure of water vapour, or (2) against pressure of water vapour at constant temperature, were perfectly smooth and gave no indication of hydrate formation. Moreover, the rehydration was a complete reversal of the dehydration process at the same temperature, there being no hysteresis.

From these results it is considered probable that the water in chabazite is present in a very loosely bound condition, and not in any definite chemical combination, especially as Vegard and Schelderup (*Ann. Physik*, 1917, **54**, 160) have shown that the removal of water from chabazite only changed the intensities, and not the positions, of the lines in an *X*-radiogram.

EXPERIMENTAL.

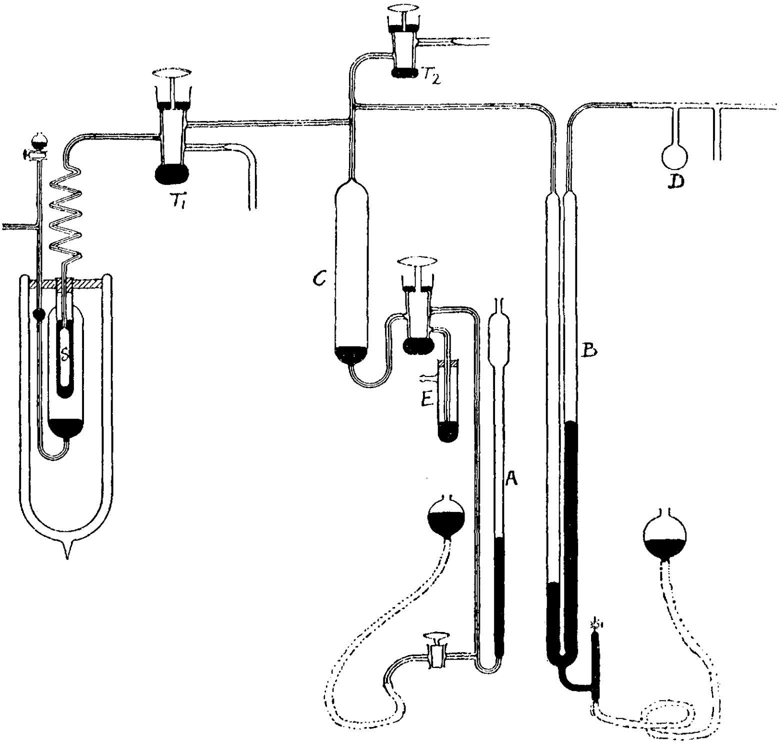
The apparatus is shown in Fig. 1, and is of the same design as that described by Herbert (*Trans. Faraday Soc.*, 1930, **26**, 118). It consists essentially of a gas-measuring system, burette and manometer, *B*; a compensating bulb, *C*, and burette, *A*, to maintain a constant pressure throughout a sorption experiment; and a sorption bulb *S*. This bulb was made of Jena glass and was joined to a spiral of glass tubing which was bathed in ice during an experiment, thus ensuring that the gas entering the sorption bulb was at 0°.

By means of tap T_1 the sorption bulb could be either connected to the gas-measuring system, or evacuated by means of mercury-vapour pumps and a charcoal bulb immersed in liquid air.

The manometer and gas burette were of the usual U-tube type, the burette being graduated in tenths of a c.c. The other limb of the manometer was evacuated, and the vacuum preserved by means of the charcoal bulb *D*; a constant check was kept on the vacuum in the manometer head by means of a McLeod gauge in this part of the system.

A glass scale divided in millimetres was placed in front of, and as close as possible to, the limbs of the gas-measuring system, and the whole was enclosed in a jacket through which water was circulated from a thermostat.

FIG. 1.



The pressure was maintained constant by decreasing the volume of the dead space of the apparatus as the sorption process proceeded. Known volumes of mercury were admitted to the compensating bulb *C* from the burette *A*. Mercury could be withdrawn from *C* by applying suction to *E*. On the upper stem of the compensating bulb a reference mark was etched so that it was possible to calculate the volume of the dead space in C. Tap T_2 connected the system to the gas train.

The burettes, and all connecting tubes, were calibrated by means of mercury before assemblage, and the diameters of the two limbs of the pressure-measuring system were determined at 2-cm. intervals along their lengths so as to correct for changes in capillary effect due to changes in diameter.

Calibration of the Sorption Bulb.—Seeliger (*loc. cit.*) found that dehydrated chabazite was capable of sorbing even inert gases, such as argon, to a small extent. The following methods were used to determine the volume of the dead space of the sorption bulb.

(1) The density of the chabazite was determined, so enabling us to calculate the dead-space volume.

(2) The volume of the dead space was determined by means of nitrogen before the chabazite was dehydrated, it being assumed that hydrated chabazite did not sorb this gas to any appreciable extent. No time effect was observed during these measurements, equilibrium being instantly attained, and the same value of the dead space was given by measurements made at different pressures.

(3) It was considered desirable, however, to measure the dead space volume after the chabazite had been degassed. This was done by admitting quantities of nitrogen to the chabazite at successively higher constant pressures, the disappearance of gas being due to the sorption effect and the dead-space volume. The low-pressure experiments showed a time effect of about 24 hours before equilibrium was reached, but at the higher pressures the process was instantaneous. In the later high-pressure experiments it was assumed that the chabazite was sorbing very little nitrogen, and that the gas disappearing could be accounted for by the volume of the dead space. In this way a value of the dead-space volume of the sorption bulb could be determined, and the results showed remarkable agreement with the values given by the other methods.

It was now possible to calculate the true relationships between sorption and time or pressure for nitrogen on chabazite dehydrated at 350°.

The Bunsen Ice Calorimeter.—The design of this calorimeter was the same as that described by Griffiths (*Proc. Physical Soc.*, 1913—14, **26**, 1). The calorimeter (Fig. 1) was suspended in a transparent vacuum vessel and surrounded for 2 or 3 days by a well-lagged vessel packed with ice, the ice sheath being then formed by starting crystallisation by means of a small amount of solid carbon dioxide. The desired size of sheath could be obtained by blowing air through ether; it was very uniform and enabled reproducible measurements of heat to be made.

Drift.—After the formation of the ice sheath, the calorimeter usually exhibited a freezing drift which continued for a day or two; it then remained in a steady condition for 24 hours, during which heat measurements could be made without disturbing the equilibrium of the calorimeter. The insulating effect of the vacuum vessel reduces the drift of the calorimeter and in most cases eliminates it entirely. Occasionally, heat measurements were made when the calorimeter showed a slow constant freezing drift, and it was always possible to attain the same constant drift at the end of the heat exchange. It was found inadvisable to make heat measurements when the calorimeter was showing a slow thawing drift (compare Foresti, *Gazzetta*, 1923, **53**, 487; 1925, **55**, 185).

It was convenient to measure the change of volume due to the melting of the ice by following the movement of the mercury along a capillary tube, since we desired to follow the relationship between time and heat of sorption, as well as between time and sorption. The capillary tubes were selected and calibrated with great care and no serious trouble due to sticking was experienced.

The calorimeter was calibrated electrically in a way similar to that employed by Griffiths (*loc. cit.*).

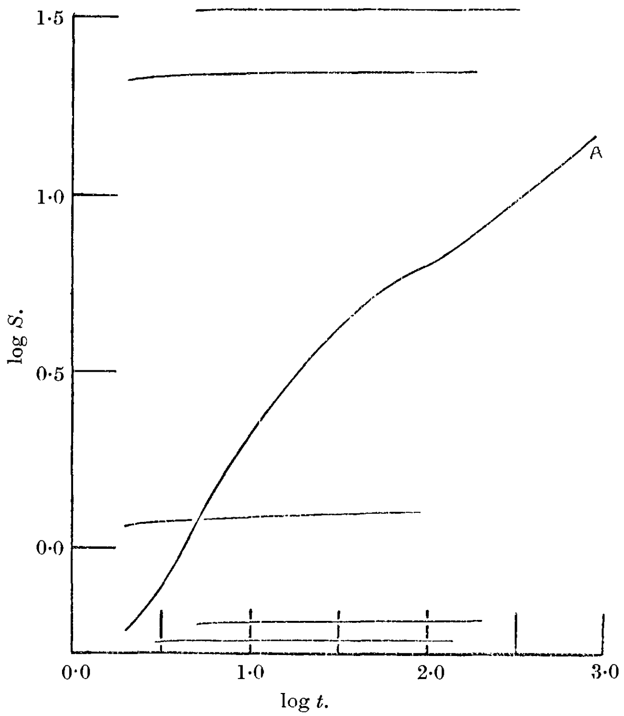
Procedure.—The chabazite was degassed for 3 days at 350°, and the calorimeter, after the formation of the ice sheath, was raised into position, and mercury (cooled to slightly below 0°) was poured into the inner tube of the calorimeter to ensure good contact between the sorption bulb and the calorimeter. A rubber stopper on the capillary tube above the sorption bulb fitted tightly into the neck of the calorimeter, and when the capillary scale was in position, the calorimeter and cooling spiral of the sorption bulb were well covered with ground ice.

The experimental procedure was the same as that described by Herbert (*loc. cit.*), except that heat–time readings were made concurrently with those of the rate of sorption. When, at any particular pressure, equilibrium was reached, more gas at a higher pressure was admitted to the sorption bulb. In this way it was possible to obtain a series of relationships between (i) sorption and time, (ii) sorption and pressure, (iii) heat of sorption and time, and (iv) heat of sorption and sorption.

Results.—The sorption rate of ammonia on hydrated chabazite was first determined, the result of one constant-pressure experiment being shown in Fig. 2, curve A. There is a peculiar bend in the log S–log t curve at log $S = 0{\cdot}8$, just where the general appearance of the curve begins to indicate an approach to equilibrium. A possible explanation of this peculiarity was discovered on removing the ice bath from the sorption bulb, for it was found that an appreciable amount of water had collected in the latter. Since the only possible source of this water is the chabazite, it is highly probable that it had been displaced therefrom by the ammonia.

As this peculiarity hampered measurements of sorption on hydrated chabazite, the sorbent was in all cases degassed at 350° for 3—4 days and used in this condition. Fig. 2 shows some of the log *S*–log *t* curves obtained at different constant pressures. It is seen that equilibrium is much more rapidly approached in the case of the dehydrated than in that of hydrated chabazite. The curves are very steep initially, and rapidly bend over, becoming nearly parallel to the log *t* axis. It was found that chabazite thus treated was in a steady state, the same equilibrium sorption values being obtained at any constant pressure, whether the gas was added at successively increasing pressures, or *ab initio* at the one constant pressure.

Fig. 2.



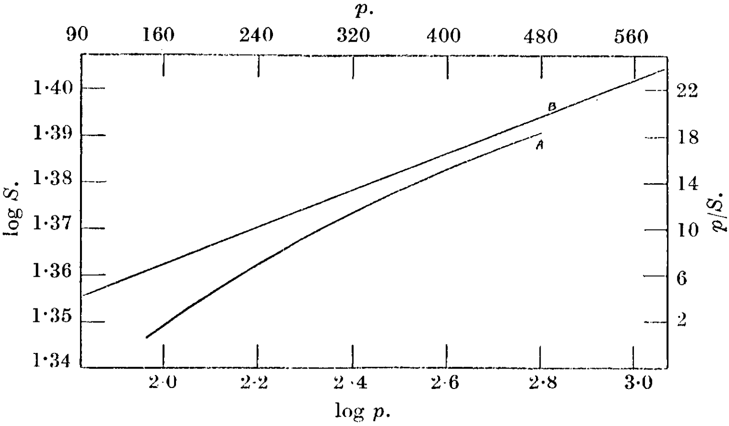
The change of rate of approach to equilibrium with pressure is seen from this series of curves. Equilibrium is approached more rapidly in the early (low-pressure) experiments than in those at a

TABLE I.

p.	*S*.	*h*.	*p*.	*S*.	*h*.	*p*.	*S*.	*h*.
92·2	22·20	16·68	164·4	23·10	17·03	373·0	24·08	17·39
111·7	22·52	16·80	219·1	23·46	17·16	398·1	24·15	—
125·9	22·65	—	251·2	23·60	—	585·0	24·53	—
157·4	23·03	16·99	295·8	23·82	17·31			

higher pressure. Sorbents such as charcoal, silica gel, and glass similarly require a longer time for equilibrium to be approached the higher the pressure. The sorption–pressure curves rise very steeply and rapidly bend over, becoming nearly parallel to the pressure axis. Fig. 3 (Curve A), in which log *S* is plotted against log *p*, shows the combined results (see also Table I); the curve is slightly concave to the log *p* axis, but an approximate estimate of the slope over a comparatively straight portion gives $\Delta \log p/\Delta \log S = 23$, whence the exponential in the Freundlich isotherm $1/n = 0{\cdot}044$, as compared with the value 0·06 obtained by Seeliger (*loc. cit.*). It was found that the sorption–pressure results obeyed Langmuir's equation $S = abp/(1 + ap)$, as shown in Fig. 3 (Curve B), where p/S is plotted against *p*. The values of the constants are $a = 0{\cdot}08$ and $b = 25{\cdot}0$. (The significance of this will be discussed in a subsequent paper.)

FIG. 3.



Simultaneously with these experiments, measurements of heat of sorption were carried out (see Table I). The curves showing its variance with time follow a course very similar to the sorption–time curves, and if we assume that there was very little time lag in the registering of heat by the calorimeter, we can correlate the heat and the sorption for the system as equilibrium is approached.

Since these values are not equilibrium values, the results cannot be treated thermodynamically, but we may obtain some idea of the change in "activity" of the sorbent as sorption occurs by considering the dh/dS values for such curves.

Fig. 4.

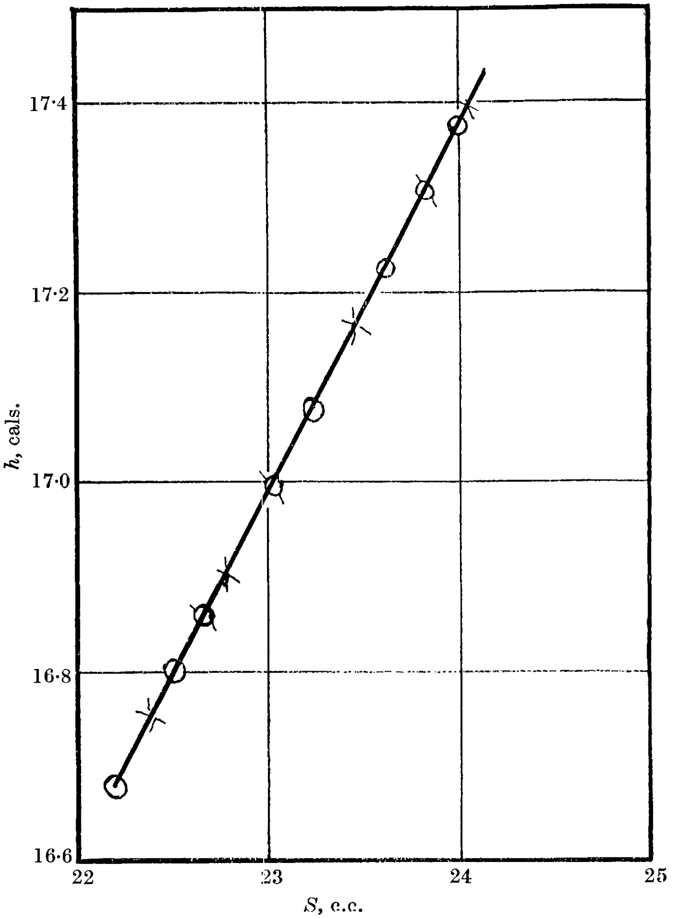


Fig. 4 shows the equilibrium values of the heat of sorption plotted against the sorption. This curve is composed of results obtained both by successive additions of gas and by sorption carried out *ab initio*.

It is seen that the value of dh/dS is constant over the range of sorption considered, a result which is to be expected from a system obeying the Langmuir isotherm.

Summary.

(1) The condition of the water in the zeolite chabazite is discussed.

(2) The rates of sorption of ammonia on hydrated and dehydrated chabazite have been studied.

(3) The pressure–sorption relationship obeys the Langmuir isotherm.

(4) The heat of sorption is a linear function of the sorption.

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