34. *Sorptive and Molecular-sieve Properties of a New Zeolitic Mineral.*

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The synthetic zeolitic mineral described in the preceding paper has been used in an investigation of sorption phenomena involving among other sorbates the rare gases (He, Ne, A, and Kr), the permanent gases (O_2 and N_2), ammonia, and hydrocarbons (CH_4, C_2H_6, C_3H_8, n-C_4H_{10}).

The sorbent behaved as a molecular sieve in the same manner as chabazite. Thus it did not occlude *iso*paraffins (C_4H_{10}, C_5H_{12}, C_8H_{18}), aromatic hydrocarbons (C_6H_6), or molecules such as $CHCl_3$ and CCl_4; it sorbed the *n*-paraffins propane and butane and such molecules as CH_2Cl_2 slowly, and methane, ethane, and molecules of smaller cross section very rapidly. By means of this selectivity quantitative separations were effected of *n*- from *iso*-paraffins and aromatic hydrocarbons, the behaviour again recalling that of chabazite.

Isotherms and isobars were obtained, and sorption heats derived for many sorbates. These heats decreased in a characteristic manner as the amount of gas sorbed increased, and owing to the interstitial position of the sorbed molecule were frequently considerable, particularly for *n*-paraffins.

Propane and *n*-butane diffused slowly into the dehydrated crystal lattice by a process of activated diffusion ($D = D_0\,e^{-E/RT}$), and the rate constant for the sorption as expressed by the "parabolic" diffusion law decreased with the fraction θ of saturation of the mineral at first linearly, $D = D_1(1 - \theta)$, and then, after a relatively sharply defined value of θ, much more slowly.

Comparison isotherms using chabazite showed that the sorptive power of the new mineral was of the same order as that of chabazite. Thus, synthetic crystalline zeolites can be made whose performance as sorbents is comparable with that of the best natural zeolites. Both chabazite and the synthetic zeolite show a greater selectivity in sorbing certain of the rare gases than does charcoal, and the data suggest that separations of helium and neon would be possible at temperatures higher than those needed when using charcoal, and so more conveniently accessible on a large scale.

In the preceding paper the preparation of a new mineral was described, from analcite, leucite, and gels. This mineral normally contained salt such as barium chloride in interstitial solid solution. From it, by extraction of barium chloride, the salt-free aluminosilicate was obtained which was found to be an excellent zeolitic sorbent. The present paper gives an account of the observed sorptive properties.

The molecular-sieve properties of various gas-absorbing zeolites fall into at least three classes, each of which can effect a variety of separations of molecular mixtures (Barrer, *J. Soc. Chem. Ind.*, 1945, **64**, 130). The molecules of some components may be too large to enter the interstices of the molecular sieve, while those of others are small enough to do so freely. It was accordingly of importance to determine the molecular-sieve properties of the synthetic zeolite, and to compare it with other zeolites. This comparison was made, not only as regards selectivity, but also as regards isotherms, and energetics and kinetics of sorption, in which the new mineral showed unusual behaviour.

The technical possibilities of sorbents such as charcoal, silica gel, ferric oxide, activated alumina, and the like have been well explored. These cheap materials have a permanent place as general purpose sorbents. Nevertheless, there may be a real but unexplored place for special purpose sorbents capable of quantitative molecular-sieve actions, such as the one now to be described.

Experimental.

Substances used as sorbates included those mentioned in the summary. The four noble gases were obtained from the British Oxygen Co., helium and neon being spectrally pure, while the krypton contained 4% of xenon. Impure argon was purified as follows: it was passed over Cu–CuO mixture at 300°, to remove hydrogen and some oxygen, and through soda-lime to absorb carbon dioxide. It was then dried over phosphoric oxide, and passed over red-hot magnesium to remove nitrogen and residual oxygen. The whole process of purification was repeated once. The hydrocarbons CH_4, C_2H_6, C_3H_8, and n-C_4H_{10} were prepared by decomposing with water the Grignard compounds formed from the redistilled alkyl bromides, with subsequent drying and fractionation of the hydrocarbons. High-boiling propyl and amyl ethers were used as solvents for forming the Grignard compounds in order to simplify the separation of the hydrocarbon from the ether. In the case of methane, however, diethyl ether was suitable. Pure *iso*butane, *iso*pentane, and *iso*octane were supplied in small quantity by the Shell Marketing and Refining Co.

Oxygen gas was obtained by heating outgassed A.R. potassium permanganate in a vacuum. Nitrogen from a cylinder was passed over Cu–CuO mixture at about 300° (to remove oxygen and hydrogen), and over phosphoric oxide to remove water. Ammonia was liberated by the action of concentrated sodium hydroxide solution upon A.R. ammonium chloride in an evacuated vessel. The ammonia was dried in transit through a tube of freshly ignited quick-lime. Other potential sorbates included pure carbon tetrachloride, chloroform, and methylene chloride.

Sorption equilibria were measured by using the static method, and the apparatus was similar to one already described (Barrer and Ibbitson, *Trans. Faraday Soc.*, 1944, **40**, 195, 206).

Four different samples of the barium chloride-free aluminosilicate mineral were prepared as described in the preceding paper. These were outgassed before use at 300—360° for periods lasting up to 24 hours, a mercury diffusion pump backed by a " Hyvac " pump being used. The mineral was found to retain its sorptive power indefinitely at these temperatures, so it is a robust three-dimensional network lattice of stability to be compared with that shown by mordenite, gmelinite, or chabazite.

Low temperatures were attained by using liquid nitrogen (— 195°), liquid air (— 186°), dry ice (— 78°), and ice. Temperatures intermediate between these fixed points were obtained by a device already described (Barrer, *Proc. Roy. Soc.*, 1937, **161**, *A*, 497, Fig. 1). Vapour-pressure thermometers were employed to register these low temperatures as follows: oxygen, from — 183° to — 210°; ethylene, from — 104° to — 150°; carbon dioxide, from — 78° to — 110°; ammonia, from — 34° to — 77°; sulphur dioxide, from — 10° to — 53°. The thermometers were sensitive and quick-acting and their use permitted a satisfactory manual control of temperature.

For higher temperatures electric furnaces were used, made by winding nichrome wire on asbestos-covered glass tubes. These were placed coaxially in metal cylinders of greater diameter, and the annular space filled with kieselguhr. Temperatures of from 60° to 400° were readily obtained with suitable series resistances, and temperatures in this range were registered with mercury-in-glass thermometers calibrated against standard thermometers.

Molecular-sieve Characteristics.—The class of molecular sieve was determined, as in the case of chabazite, gmelinite, mordenite, and the like (Barrer and Ibbitson, *loc. cit.*; Barrer, *Trans. Faraday Soc.*, 1944, **40**, 555) by using certain molecules as yardsticks to determine the dimensions of the interstitial channels permeating the crystal lattice of the dehydrated zeolite and distributed along which the sorbed molecules are found.

The mineral was exposed after thorough outgassing and at various temperatures to these typical molecules, and it was established that: (*a*) *iso*Butane and benzene were not occluded, and it may be presumed that these molecules are of too great a cross-section to enter the lattice. (*b*) *n*-Butane and propane were slowly sorbed at room temperature or above, by a process of activated diffusion (p. 140). (*c*) Methane and ethane and all smaller molecules were sorbed very rapidly at all temperatures.

Comparison with the established behaviour of chabazite and gmelinite shows that the behaviour of the new mineral is the same as noted there (Barrer, 1945, *loc. cit.*), and that these are the characteristics of a Class I molecular sieve.* As required for Class I molecular sieve sorbents it was then further shown by bathing the mineral at higher temperatures (about 160°) in vapours of *iso*pentane, *iso*octane, chloroform, and carbon tetrachloride that none of these sorbates was occluded by the new mineral; but that methylene dichloride was slowly taken up by the zeolite.

After the above qualitative experiments, the separation of mixtures was attempted, the molecular-sieve property being used. The zeolite was brought into contact with binary mixtures of known composition, of which one constituent was first shown not to be occluded, and the other to be totally sorbed, under the conditions of the experiment. The fall in pressure of the mixture as sorption proceeded was then measured, and when equilibrium was established it was found that the final pressure was quantitatively equal to that of the non-sorbed components, and the fall in pressure to the amount of occlusible component. Especially in separations at room temperature, van der Waals adsorption of the non-sorbed component upon *external* crystallite surfaces of the powder was sometimes appreciable (distinguished by its small amount and nearly instantaneous occurrence; see Fig. 7). In separations where this surface adsorption was measurable, the sorbent was first bathed in the vapour of the non-sorbed component, and the equilibrium pressure p_1 read. A known pressure of a sorbable component was then added by means of a Toepler pump, giving a pressure $(p_1 + p_2)$, and the pressure fall followed as before. The pressure then fell in all cases until the pressure p_1 was again recorded. As an illustration, an experiment on the separation of *n*-butane from benzene may be described. The sorbent bathed in benzene vapour at 160° came to equilibrium when the benzene pressure p_1 was 2·66 cm. *n*-Butane was then introduced, the momentary pressure being 7·92 cm. The pressure fell slowly, however, and in a day had reached a final value of 2·66 cm. again, thereafter remaining unaltered.

The typical separations carried out were: *n*-C_4H_{10} from *iso*-C_4H_{10} at 160°, *n*-C_4H_{10} from *iso*-C_5H_{12} at 160°, *n*-C_4H_{10} from C_6H_6 at 160°, C_3H_8 from *iso*-C_4H_{10} at 160°, C_2H_6 from *iso*-C_4H_{10} at room temperature, NH_3 from *iso*-C_4H_{10} at 160°. Parallel separations can also be carried out by using chabazite (Barrer, 1945, *loc. cit.*), from which the new zeolite does not so far appear to differ in any way in its molecular sieve action.

Isotherms and Isobars.—Isotherms obtained at various temperatures and for a number of gases are shown in Figs. 1, 2, and 3. The isotherms for oxygen, nitrogen, and argon determined on sample 1 of the mineral (Fig. 1) show that little selectivity in sorption may be expected as between these gases at — 78°. There are differences, for example in the sorption of nitrogen, between the three specimens of the new zeolite used which reflect variations in the purity of the preparations,† the best of which probably was not more than 70—80% pure. Comparison isotherms of nitrogen in chabazite are also shown in Fig. 1(*d*).

Methane and ethane were sorbed at room temperatures with great rapidity; propane and butane more slowly. Isotherms for propane are shown in two sorbent samples containing the new mineral, one being clearly in higher yield than the other. Sorption of propane by chabazite (Barrer and Ibbitson, *loc. cit.*), gmelinite (Barrer, 1944, *loc. cit.*), and the synthetic zeolite, at similar temperatures of 235°, 225°, and 220°, respectively, is compared in Fig. 2(*e*). It is seen that at low pressures the synthetic

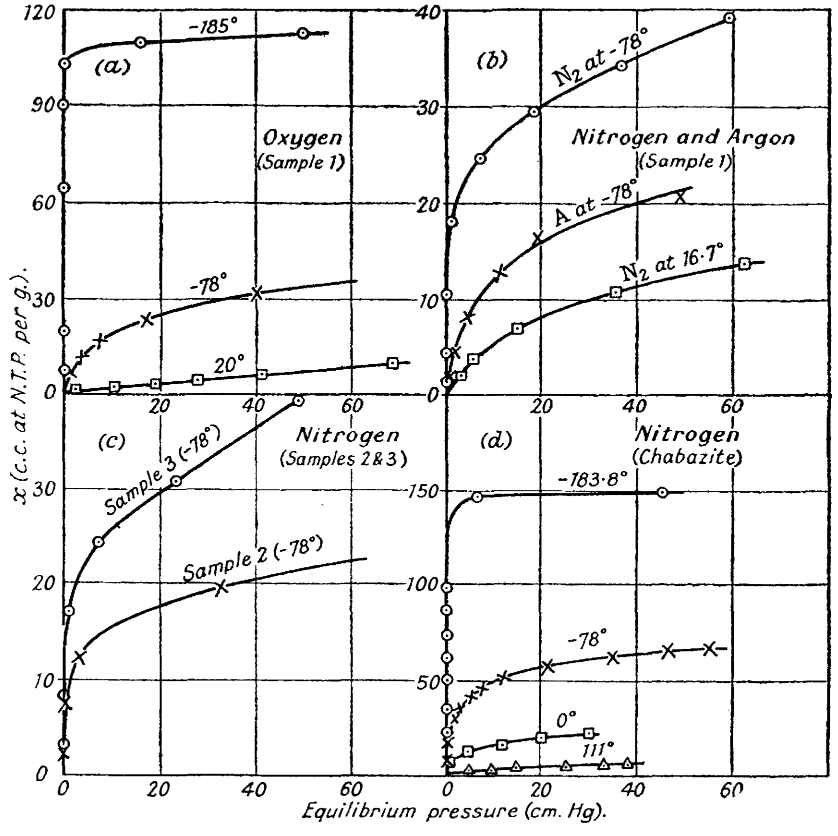
* A Class I sieve does not occlude aromatic hydrocarbons and *iso*paraffins under any conditions; it occludes *n*-paraffins slowly at room temperatures and above; and sorbs methane, ethane, and small molecules rapidly at all temperatures where sorption is appreciable.

† As shown in the preceding paper, there is some tendency to decomposition and recrystallisation during extraction of barium chloride from interstitial solid solution in the framework of the zeolite.

mineral is the most vigorous sorbent, the performance of which is striking since, as pointed out above, the synthetic product was not 100% pure. The isotherms for ammonia [Fig. 2(*f*)] illustrate the great affinity which polar gases may show for this zeolite, since even at 300° there is substantial occlusion. At room temperatures the mineral became heated following the admission of a dose of ammonia. The energetic sorption of water was also demonstrated by adding the dehydrated mineral to a little water, which became hot. This behaviour was also observed with mordenite, harmotome, and especially with chabazite.

Like oxygen and nitrogen, all the rare gases were sorbed very rapidly, freely permeating the dehydrated crystal lattice. Hence, selectivity in sorbing these smaller atoms both in chabazite and in the synthetic zeolite does not depend upon those molecular-sieve effects which permit separation for example of *n*- and *iso*-paraffins by the same zeolites, but instead depends solely upon differences in van der Waals and polarisation forces exerted on the sorbate within the lattice. Helium was sorbed only weakly, but the affinity of the rare gases for the zeolites can be seen to increase sharply with increasing atomic weight (Fig. 3).

Fig. 1.

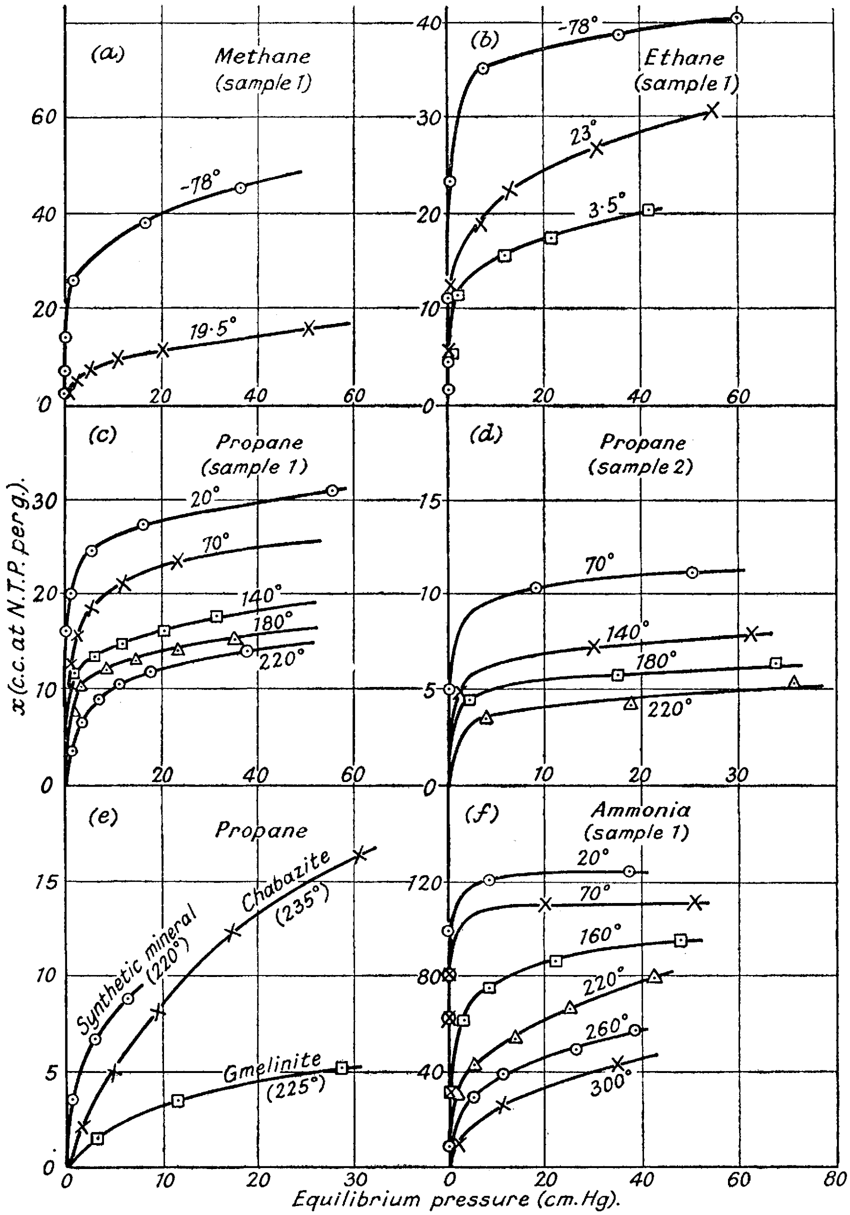


Sorption isothermals for oxygen, nitrogen, and argon on various samples of the new mineral, and for nitrogen on natural chabazite. Note that different scales have been used for the ordinates in the several sections of the diagram.

The hydrocarbon–zeolite and noble gas–zeolite equilibria when plotted as curves of log x/p against log x were often, in the case of the new zeolite, characteristic in form with a point of inflexion. These curves then provide some evidence that in the new zeolite there may be two principal groups of sorption site available. Further evidence of this arises from the energetics and kinetics of sorption (p. 140, and Fig. 8).

These curves are useful also for estimating saturation values in some instances, saturation corresponding to a vertical log x/p–log x curve (Barrer, *Proc. Roy. Soc.*, 1938, **167**, *A*, 392, 406). Apparent saturation values may in some instances be estimated from the flattening of isobars at low temperatures (Fig. 4); or directly from isotherm data, especially when these data approximate to the Langmuir isotherm. In the latter event the slope of the graph of p/x against p gives the saturation value. These methods of deriving saturation values are in order denoted by the numbers 1, 2, and 3 given in parenthesis in Table I. For a gas like neon, where sorption is measured well above the liquefying point, and so a long way from saturation of the sorbent, method 3 can give only a lower limit, for there is partial occupation merely of sites of greatest sorption potential, those of lesser potential being virtually unpopulated. The saturation value from the slope of the p/x–p curve must therefore refer only to an

FIG. 2.



(a) ⎫ *Isothermals on sample* 1 *of*
(b) ⎬ *the new minerals.*
(c) ⎪
(f) ⎭

(c) ⎫ *Comparative isothermals of propane on two different samples of the new mineral.*
(d) ⎭

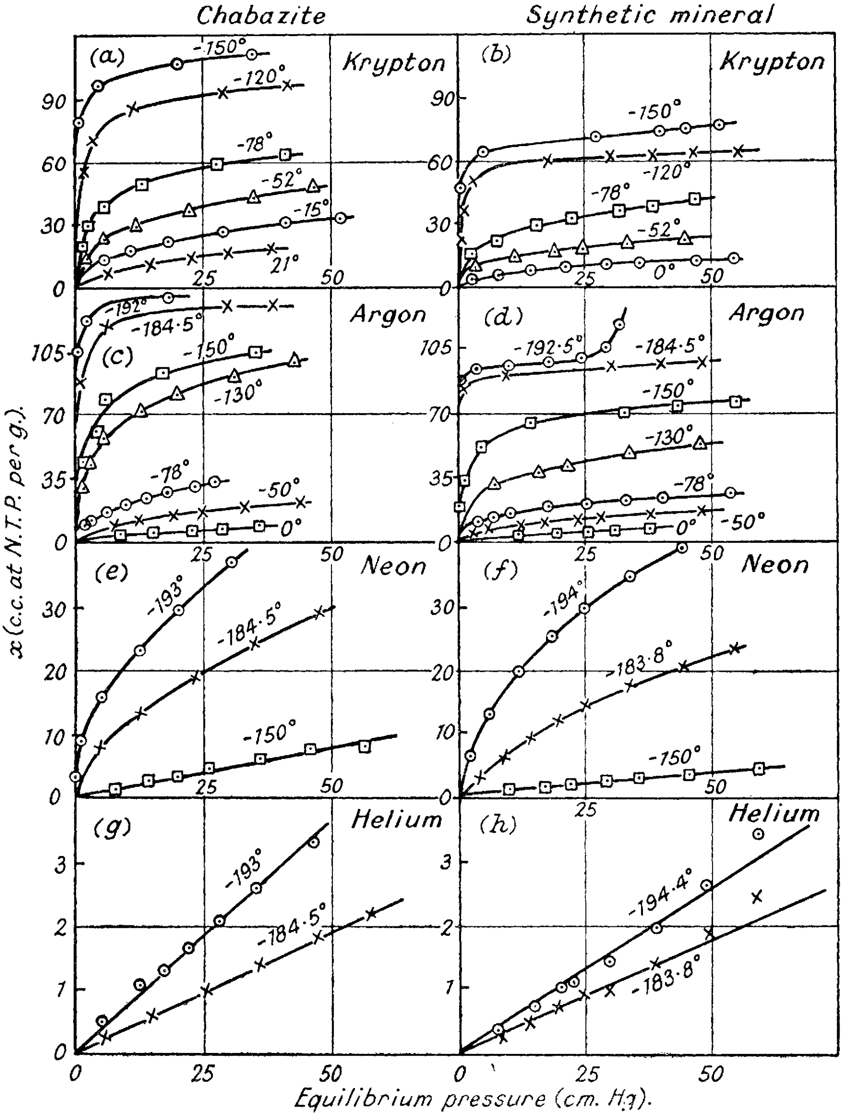
(e) *Comparative isothermals for propane on the new mineral, on natural chabazite, and on gmelinite.*

Note that different scales have been employed in the several sections of the diagram.

arbitrary range of the sites of greatest potential. The figures are unavoidably not very accurate, but the three methods lead to fairly consistent results. The saturation value given for argon in chabazite is rather lower than one already given (*idem, ibid.; Ann. Reports*, 1944, **41**, 31—46), but this value depends on the thoroughness of outgassing (Barrer and Ibbitson, *loc. cit.*; Lamb and Woodhouse, *J. Amer. Chem.*

Soc., 1936, **58**, 2637). Both the zeolites of Table I were outgassed under the same conditions as, but milder than, those for the sample of chabazite used previously. Referred to unit mass, the new zeolite shows saturation values about 65—75% of the corresponding figures for chabazite. The greater values for chabazite are partly due, however, to the greater density of the synthetic mineral, which contains the heavy element barium, and partly due to the lesser purity of the samples of the synthetic product.

FIG. 3.



Sorption isothermals for the noble gases on natural chabazite and on the new mineral. To avoid confusion in the cases of argon and krypton several isotherms determined at temperatures between — 50° *and room temperature have been omitted from the diagrams. For the same reason many experimental points at the low-pressure ends of the isotherms have had to be omitted. Note that different scales have been employed for the ordinates for the different gases.*

Referred to unit *volume* of the *pure* minerals, there may be little difference in the saturation capacity, and hence in the interstitial sorption volumes within a c.c. of each zeolite.

The two zeolites show a greater selectivity than charcoal in sorbing some of the noble gases. At — 194·7°, per g. of sorbent at an equilibrium pressure of 10 cm., sample 4 of the synthetic zeolite sorbed 17·5 c.c. at N.T.P. of neon and 0·5 c.c. of helium, giving a separation factor of 35-fold. In chabazite this factor was 27-fold; while on an active charcoal under the same conditions it was only 5-fold (Fastovskii and Girskaya, *J. Chem. Ind. U.S.S.R.*, 1937, **14**, 358). It therefore seems likely that these zeolites could act more effectively than charcoal in separating neon and helium at temperatures readily available on a large scale (— 194° to — 210°).

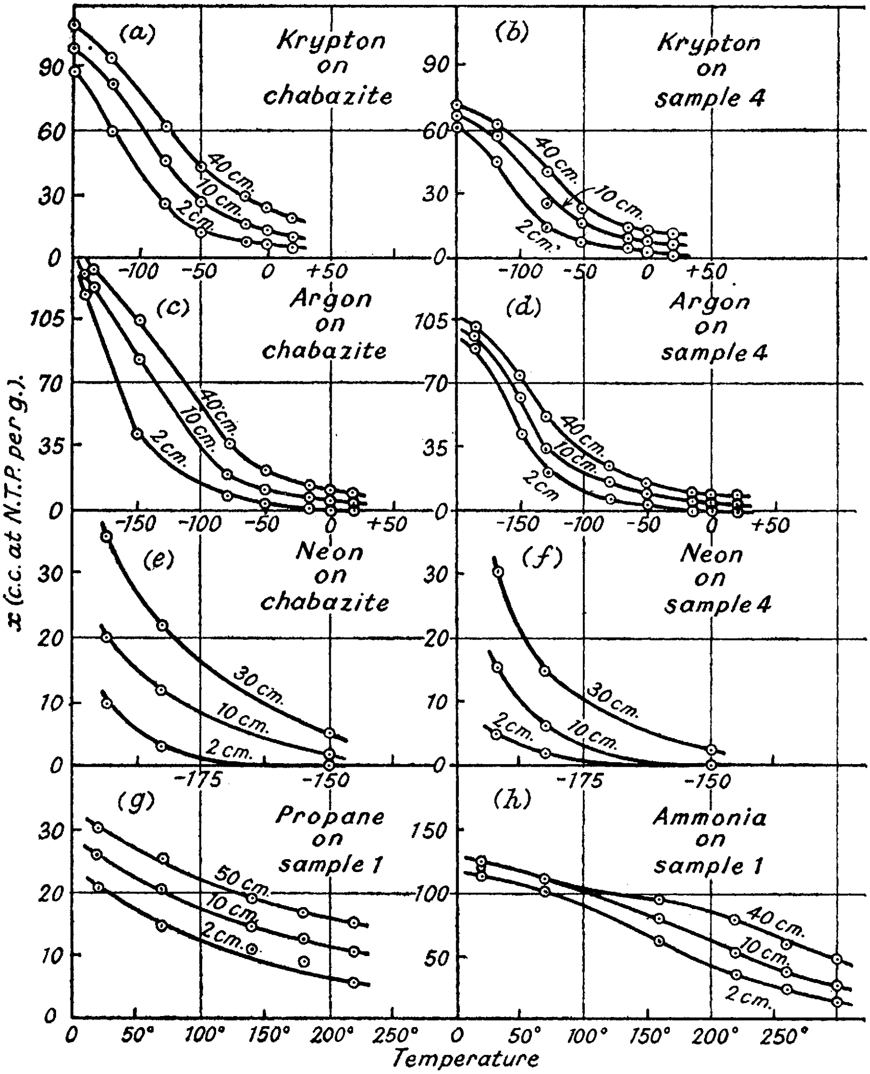
TABLE I.

*Some apparent saturation values in chabazite and in the synthetic zeolite.**

Gas.	Saturation value (c.c. at N.T.P./g.).	
	Synthetic zeolite.	Chabazite.
Ne	>53(3)	>50(3)
A	115(2), 106(1), 105(3)	141(1), 135(3)
Kr	80(1), 78(2), 73(3)	112(1), 105(3)
O_2	115(3), 120(1)	—
C_2H_6	90(1)	—
C_3H_8	70(1)	—
NH_3	140(1), 140(2)	—

* The saturation values for C_2H_6, C_3H_8, and O_2 refer to sample 1 of the synthetic zeolite; those for the noble gases to sample 4.

FIG. 4.



Some sorption isobars on natural chabazite and on the new mineral.

Energetics of Sorption.—From the variation of the sorption equilibrium with temperature the heats of occlusion were determined. This heat can be obtained by plotting log p against $1/T$ for a given charge of gas, x, p being the corresponding equilibrium pressure. Then

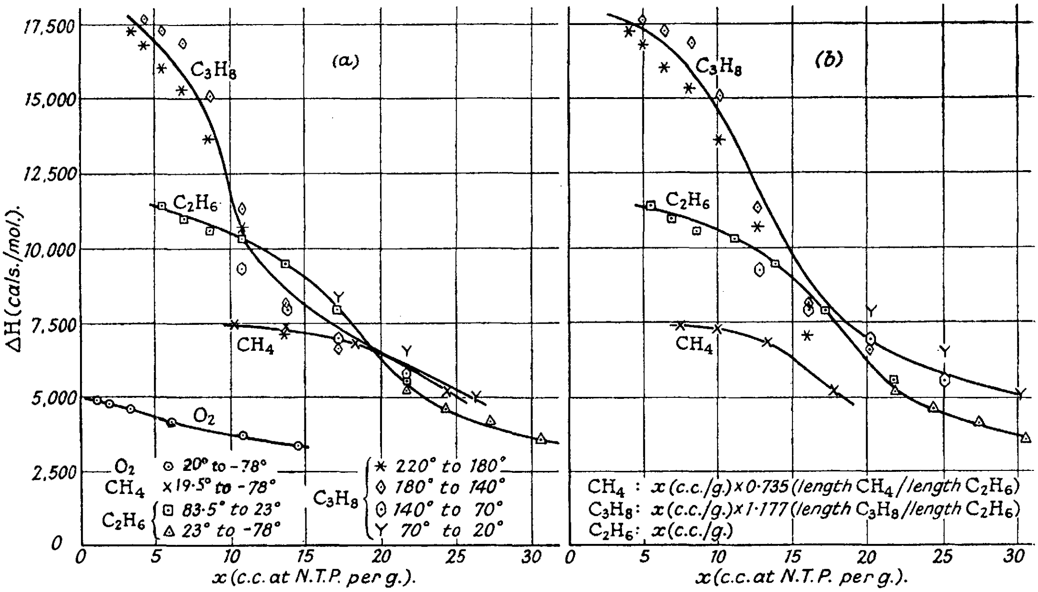
$$2{\cdot}303R\frac{\partial \log_{10} p}{\partial (1/T)} = \Delta H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Alternatively, on integration between two temperatures T_1 and T_2 the Clapeyron equation gives

$$2{\cdot}303R\left(\log_{10}\frac{p_1}{p_2}\right)\frac{T_2T_1}{T_1 - T_2} = \Delta H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

ΔH was determined by equation (1) for some of the noble gases on chabazite, and from equation (2) for oxygen and several hydrocarbons and noble gases on the synthetic mineral. By measuring ΔH at a series of different values of x, the variation in the heat of sorption as x increases can be obtained. These data are presented in Fig. 5(*a*) for O_2, CH_4, C_2H_6, and C_3H_8 in sample 1 of the new mineral, and in Figs. 6(*a*) and (*b*) for the noble gases in chabazite and in sample 4 of the synthetic zeolite, respectively. For chabazite there is a continuous asymptotic decrease in ΔH as x increases (Barrer and Ibbitson, *loc. cit.*; Barrer, 1938, *loc. cit.*), while for both samples of the synthetic sorbent the ΔH–x curve shows a tendency to be divided into two parts. This behaviour could mean that there are mainly two kinds of site available in this sorbent, but a continual variability in the sites in chabazite.

FIG. 5.



Variation of sorption heat with amount sorbed for methane, ethane, propane, and oxygen on the new mineral.

In Fig. 5(*a*), the ΔH–x curves cross for the hydrocarbons at larger values of x. This apparently surprising behaviour is considered, however, to be due to the smaller amount of the larger molecule C_3H_8 needed to saturate the interstitial sorption volume than of the smaller molecules C_2H_6 or CH_4. It has been pointed out (Barrer and Ibbitson, *loc. cit.*) that if two chain molecules x_1 and x_2 of lengths L_1 and L_2 are occluded in a zeolite, the relative saturation values shown will be approximated by

$$\frac{\text{Saturation value of } x_1}{\text{Saturation value of } x_2} = \frac{L_2}{L_1}$$

The appropriate relative dimensions of CH_4, C_2H_6, and C_3H_8 stand in the ratio 0·735 : 1·00 : 1·18. According to the above relationship, if the amounts of methane, ethane, and propane are multiplied by 0·735, 1·00, and 1·18 respectively, these abscissæ are proportional to θ, the fraction of sites occupied, and the constant of proportionality is the same. This has been done in Fig. 5(*b*), when it is seen that the ΔH–θ curves will no longer cross.

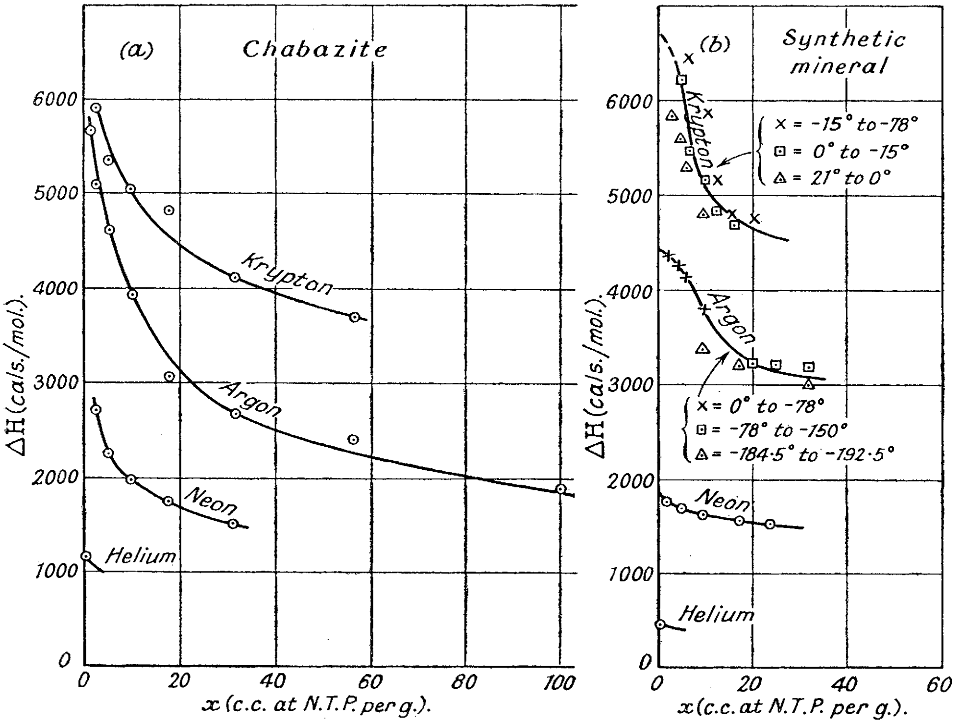
When the heats of sorption were measured at a series of temperatures, no definite evidence could be obtained of any systematic trend in ΔH with temperature, apart from random fluctuations due to experimental inaccuracy (Table II). The experimental accuracy is of the order of $\pm$ 600 cals. A similar insensitiveness of ΔH to temperature has been noted in other studies (Barrer and Ibbitson, *loc. cit.*; Barrer, 1938, *loc. cit.*).

TABLE II.

Sorption heats of C_3H_8 *in sample* 1 *of synthetic zeolite at different temperatures* (in °K.)

Amount sorbed, c.c. at N.T.P./g.	ΔH (cals./mol. sorbed).			
	293—343°.	343—513°.	513—553°.	553—593°.
3·44	—	—	—	17,300
4·35	—	—	17,700	16,800
5·00	—	—	17,300	16,100
6·90	—	—	16,900	15,400
8·64	—	—	15,200	13,700
10·9	—	9,330	11,300	10,700
13·7	—	8,160	8,200	7,200
17·3	8,330	6,950	6,700	—
21·7	6,560	5,700	—	—
26·1	5,000	—	—	—

FIG. 6.

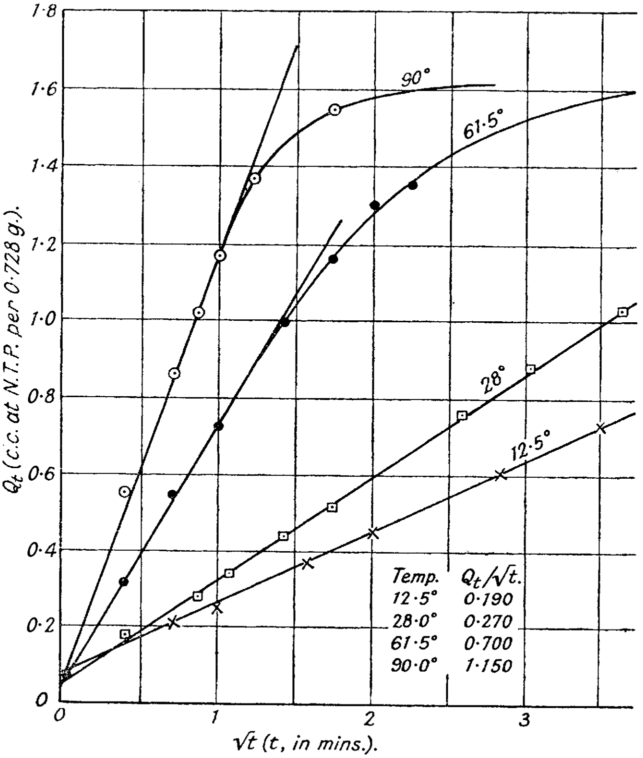


Variation of sorption heat with amount sorbed for the noble gases on (a) *natural chabazite,* (b) *new mineral.*

Some calculations of the standard free energies and thence entropies of occlusion in typical instances, by methods already given (Barrer and Ibbitson, *loc. cit.*; Barrer, *Trans. Faraday Soc.*, 1944, **40**, 374), led to the conclusion that the sorbate molecules behave not very differently from three-dimensional oscillators in both sorbents. Thus they may possess an amount of freedom comparable with liquids when sorbed interstitially.

Kinetics of Sorption.—An investigation of the kinetics of sorption of propane and of butane was made. These gases are sorbed slowly at room temperature, but more rapidly when the temperature is raised, by a process of diffusion within the crystal lattice. Over a considerable fraction of the total sorption the rate of uptake was a linear function of $\sqrt{t}$ (t = time), so the " parabolic " diffusion equation is clearly applicable. Fig. 7 shows this relationship, as well as the large temperature coefficient in the diffusion velocity. The small " foot " appearing along the axis of Q_t is to be interpreted as an initial rapid adsorption upon *external* surfaces of the powdered mineral, as distinct from the slower occlusion process. In accordance with this hypothesis, the foot diminishes somewhat as the temperature rises, corresponding to the exothermal character of adsorption. The slope $Q_t/\sqrt{t}$ of the linear portion of the sorption rate curve is proportional to $C_0\sqrt{D}$, where D is the diffusion constant * and C_0 is the concentration of sorbate just inside the external surface of the sorbent particles. Now C_0 for the exothermal sorption of propane decreases, if anything, as the temperature rises, but nevertheless the overall rate of sorption increases with increasing temperature. It follows that the largest temperature coefficient resides in D. Table III gives values for $Q_t/\sqrt{t}$ for propane and n-butane; when log $Q_t/\sqrt{t}$ is plotted against $1/T$, the points fall near to straight lines, with slopes corresponding to an apparent energy of activation, E_a, of 10·3 k.-cals. for propane and 11·4 k.-cals. for n-butane. There is no doubt, therefore, that sorption occurs by an activated diffusion process ($D = D_0\,\mathrm{e}^{-E/RT}$). The above apparent energies of activation may be smaller than the true energies, E, because the values of C_0, the concentration just inside the external surface of the particles of sorbent, will, if less than the saturation value, decrease as the temperature rises owing to the exothermal character of the occlusion.

FIG. 7.



Sorption kinetics of propane on the new mineral and the parabolic diffusion law.

TABLE III.

Temperature coefficients in the kinetics of sorption.

Propane.				n-Butane.			
Temp.	$Q_t/\sqrt{t}$.	Temp.	$Q_t/\sqrt{t}$.	Temp.	$Q_t/\sqrt{t}$.	Temp.	$Q_t/\sqrt{t}$.
12·5°	0·190	61·5°	0·700	17·5°	0·0333	86°	0·270
28	0·270	90·0	1·150	68	0·218	142	0·660

* If the diffusion equation $\partial C/\partial t = D(\partial C^2/\partial x^2)$ is integrated for the boundary condition $C = C_0$ at $x = 0$ for all t and the time interval is small enough for the inside of the particles not to have any appreciable content of occluded gas, then the solution, when the sorbing medium is initially gas free, is

$$C = C_0\,\left(1 - \frac{1}{\sqrt{\pi}}\int_0^{x/2\sqrt{Dt}} \mathrm{e}^{-y^2}\,\mathrm{d}y\right)$$

$$= C_0\left[1 - \frac{2}{\sqrt{\pi}}\left(\frac{x}{2\sqrt{Dt}} - \frac{x^3}{3\,.\,1'\,.\,(2\sqrt{Dt})^3} + \frac{x^5}{5\,.\,2'\,.\,(2\sqrt{Dt})^5} - \ldots\right)\right]$$

whence $$Q_t = -\int^t D\left(\frac{\partial C}{\partial x}\right)_{x=0} = C_0\frac{\sqrt{Dt}}{\sqrt{\pi}}$$

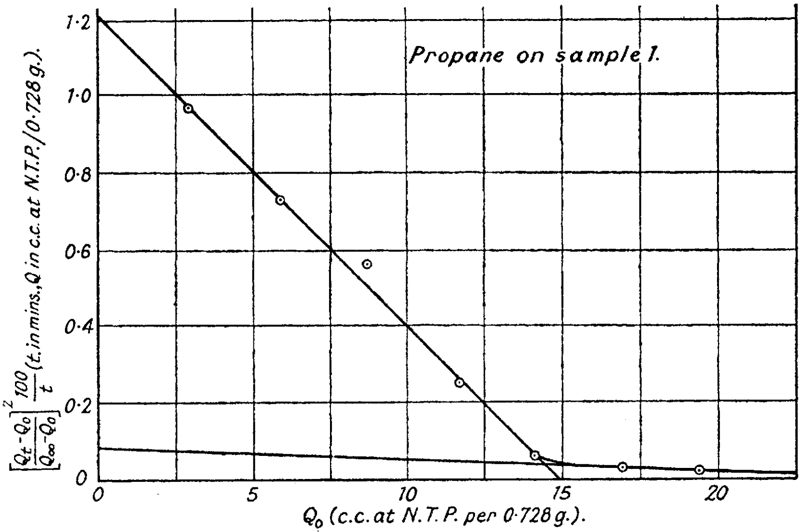
Ammonia, the noble gases, methane, ethane, oxygen, and nitrogen, by contrast to C_3H_8 and n-C_4H_{10}, were sorbed so rapidly that the rate-controlling step was almost certainly governed by the liberation of the heat of sorption, followed by the dissipation of this heat, and a settling in of the sorbed gas as the sorbent approached thermal equilibrium with its surroundings once more.

In a previous study of diffusion mechanisms (Barrer, *Trans. Faraday Soc.*, 1941, **37**, 590) it was pointed out that the diffusion " constant " D of a solute in interstitial solid solution within a homogeneous zeolitic sorbent should depend on the fraction θ of all available interstitial sites occupied, according to the expression $D = D_1(1 - \theta)$, so that when $\theta \rightarrow 1$, $D \rightarrow 0$. At constant C_0, the parabolic diffusion law becomes

$$(Q_t - Q_0)^2/t(Q_\infty - Q_0)^2 = kD_1\,(1 - \theta)$$

where Q_0, Q_∞, and Q_t are the amounts sorbed at time $t = 0$, $t = \infty$, and $t = t$, respectively, and k is a constant depending upon the particle size and number. The initial slopes of sorption rate curves according to the parabolic diffusion law should thus decrease linearly with θ, which is proportional to Q_0, the amount initially present in the sorbent. In testing this relation, successive doses of gas were admitted to the zeolite at room temperature, the sorbent becoming progressively filled with sorbed gas. The initial pressures, and so C_0, were kept constant, and the values of the left-hand side of the equation are given in Table IV. When this quotient is plotted against Q_0 (Fig. 8) the curve is seen to consist of two parts, suggesting two kinds of sorption site within the mineral to which there are different rates of access. The first group of sites requires about 15 c.c. of propane at N.T.P/0·728 g. of mineral to become saturated, and in this group sorption occurs much more rapidly than in the second group of sites. Some evidence, based upon the form of heat–charge curves particularly of hydrocarbons (*loc. cit.*, and Fig. 5) has already been given supporting the existence of two groups of sorption sites.

FIG. 8.



Curve showing variation of diffusion coefficient in zeolitic solids with increasing saturation.

TABLE IV.

Q_0	2·92	5·92	8·73	11·64	14·40	16·94	19·40
Q_∞	5·92	8·73	11·64	14·50	17·68	19·88	22·35
$\left(\frac{Q_t - Q_0}{Q_\infty - Q_0}\right)^2 \times \frac{10^2}{t}$	0·96	0·73	0·56	0·25	0·057	0·0262	0·0156

DISCUSSION.

In considering occlusion by zeolites it must be remembered that cations as well as sorbed molecules are simultaneously present in the same interstitial channels throughout the anionic network. Evidence has already been obtained which shows clearly that sorbate and cation are in close association (Barrer, *Trans. Faraday Soc.*, 1944, **40**, 555). The inhomogeneity of the sorbents, as revealed by the variation of ΔH with the charge of gas, can then be due to the following causes : (i) There may be at least two crystallographically distinct sets of interstices, each capable of occluding sorbate molecules. Each set then develops its own sorption potential, and the isotherm is the resultant of two or more isotherms of Langmuir type. (ii) There may be only one set of sites capable of accommodating sorbate molecules, but there may be partial exchanges such as Na^+ by K^+, Ca^{++} by Ba^{++}, $2Na^+$ by Ca^{++}, and so on, the sorption potential then varying with the type of ion in occupation in the interstice. Such exchanges are already known to modify strongly the energetics of sorption (*idem, ibid.*). (iii) There may be room for more than one small molecule in the same interstices as the cation, but whereas the first molecule is in contact with the cation, others, for steric reasons, are displaced from the cation and therefore bound in a field of modified potential. (iv) At high interstitial concentrations, the sorbate molecules may interact strongly enough to produce clustering, with dilute and concentrated phases in equilibrium.

When ΔH is plotted as a function of x, the charge of gas, the data show, over the investigated values of x, the following behaviour. For "active" analcite (Barrer and Ibbitson, *loc. cit.*; Barrer, 1938, *loc. cit.*) there was only a small dependence of ΔH upon x, and the sorption sites were therefore comparatively uniform. In natural mordenite, and more especially in chabazite (*locc. cit.*, 1938, 1944), ΔH decreases continuously with increasing x, but here the known chemical heterogeneity of these minerals could offer one explanation of the behaviour in accordance with (ii) above. The synthetic mineral now investigated shows a rather more definite break in the ΔH–x curve, which might be ascribed to the presence of two similar sets of interstitial sites. In this connection the kinetic evidence of Fig. 8 is the most convincing.

A tendency towards clustering of sorbate molecules has not yet been observed in gas–zeolite systems, and would be revealed by an *increase* in ΔH for larger values of x. Such behaviour was noted by Orr (*Proc. Roy. Soc.*, 1939, **173**, *A*, 349) when noble gases were sorbed on external surfaces of alkali halide crystals; while clustering of hydrogen atoms is well established in H_2–Pd systems and leads under certain conditions to an equilibrium between α- and β-phases (*e.g.*, Lacher, *ibid.*, 1937, **161**, *A.*, 525); and evidence for a variety of sub-phases has been adduced by Jura and Harkins (*J. Amer. Chem. Soc.*, 1946, **68**, 1941) and by Jura, Loeser, Basford, and Harkins (*J. Chem. Physics*, 1945, **13**, 535). First- or second-order phase changes may therefore eventually be found in the present zeolitic solid solutions, where only physical interactions occur.

A second point of interest arises in applying to molecular-sieve zeolites the rule of Gurwitsch (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 805)—that the saturation volumes expressed as c.c. of liquid sorbate are the same for all sorbates in a given sorbent. This rule may be considered valid only for sorbents with wide, easily accessible pores. It has been shown, however, that in several gel sorbents the saturation quantities expressed as moles decrease nearly inversely as the molecular volume of the sorbate, and this behaviour has been interpreted in terms of a range in pore sizes resulting in a continuous but only partial molecular-sieve action (Foster, *Nature*, 1946, **157**, 340; Broad and Foster, *J.*, 1945, 366). The zeolitic molecular sieves, however, constitute a third group. For very small molecules Gurwitsch's rule is a good approximation. For molecules of intermediate size an interesting behaviour appears. Some sorbates which are copiously occluded, may have molecular volumes equal to or greater than the molecular volumes of other sorbates which are not sorbed at all. For example, on the one hand *n*-heptane, *n*-pentane, and *n*-butane are copiously occluded by suitably activated chabazite, and on the other hand *iso*pentane, *iso*butane, chloroform, and benzene are totally excluded (Barrer, 1945, *loc. cit.*; Barrer and Ibbitson, *loc. cit.*). This is because it is molecular shape rather than molecular volume which decides whether sorption can occur. Clearly, in this intermediate range of molecular dimensions, it is quite impossible to apply Gurwitsch's rule indiscriminately. Finally come very large molecules towards which zeolites do not behave as sorbents.

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