Chem., 20, 1545 (1955).
433. Yu. S. Zal'kind and V. Pletts, Zhur. Obshch. Khim., 4, 1088 (1934).
434. R. Lespieau, A. Guillemonat, and M. Urion, Kolloid Z., 63, 86 (1933).
435. R. Vestin and A. Somersalo, Acta Chem. Scand., 3, 125 (1949).
436. T. H. Vaughan, J. Amer. Chem. Soc., 55, 4771 (1933).
437. W. H. Carothers, R. A. Jacobson, and G. J. Berchet, ibid., 55, 4666 (1933).
438. A. D. Petrov, S. I. Sadykh-Zade, et al., Dokl. Akad. Nauk SSSR, 85, 1297 (1952); 93, 293 (1953); 115, 522 (1957); Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 722 (1954); 181 (1955).
439. K. Bouwden, E. A. Braund, and E. R. H. Jones, J. Chem. Soc., 948 (1946).
440. I. A. Shikheev, M. F. Shostakovskii, and L. A. Kayutenko, Dokl. Akad. Nauk Azerbaidzh. SSR, 14, 687 (1958).
441. A. A. Petrov and V. S. Zavgorodnii, Zhur. Obshch. Khim., 30, 1055 (1960).
442. I. N. Nazarov and N. V. Torgov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 495 (1947).
443. German Pat. 740 988; Chem. Zentr., I, 961 (1944).
444. K. Adler and H. Brachel, Annalen, 608, 195 (1957).
445. I. N. Nazarov and A. N. Elizarova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 189 (1940).
446. I. M. Gvartsiteli, Dokl. Akad. Nauk SSSR, 72, 891 (1950).
447. W. H. Carothers and R. A. Jacobson, J. Amer. Chem. Soc., 55, 1097 (1933).
448. I. M. Heilbron, A. W. Johnson, E. R. H. Jones, and R. A. Raphael, J. Chem. Soc., 266 (1943).
449. A. N. Nazarov and L. B. Fisher, Zhur. Obshch. Khim., 20, 1114 (1950).
450. W. H. Carothers and G. J. Berchet, J. Amer. Chem. Soc., 55, 1095 (1933).
451. I. N. Nazarov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 683 (1938).
452. I. N. Nazarov, T. D. Nagibina, and I. I. Zaretskaya, ibid., 444 (1940).
453. I. N. Nazarov and I. I. Zaretskaya, ibid., 529 (1946).
454. M. Bertrand Compt. rend., 247, 824 (1958).
455. I. N. Nazarov and Kh. N. Pinkina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 633 (1946); Zhur. Obshch. Khim., 20, 2009 (1950).
456. I. N. Nazarov and M. S. Burmistrova, Zhur. Obshch. Khim., 20, 2021 (1950).
457. I. N. Nazarov and T. D. Nagibina, ibid., 23, 801 (1953).
458. I. N. Nazarov, L. I. Ukhova, and B. A. Rudenko, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 498 (1953).
459. I. N. Nazarov and I. V. Torgov, ibid., 129 (1943).
460. I. N. Nazarov, L. I. Ukhova, and V. A. Rudenko, ibid., 730 (1953).
461. I. N. Nazarov, A. I. Kuznetsova, and I. A. Gurevich, Zhur. Obshch. Khim., 20, 376 (1950).
462. I. N. Nazarov and A. I. Kakhinashvili, ibid., Suppl. 2, 905 (1953).
463. A. I. Nogaideli and K. Ya. Dzagnidze, ibid., Suppl. 2, 1632 (1953).
464. I. N. Nazarov and S. A. Vartanyan, ibid., 20, 1829 (1950).
465. I. N. Nazarov, S. A. Vartanyan, and V. N. Zhamagortsyan, ibid., 24, 1953 (1954).
466. S. A. Vartanyan and V. N. Zhamagortsyan, ibid., Suppl. 2, 363 (1953); Izv. Akad. Nauk Armyansk SSR, 11, 99 (1958); 12, 45 (1959).
467. A. G. Terezyan, Zhur. Obshch. Khim., 23, 1346 (1953); Izv. Akad. Nauk Armyansk SSR, 6, 35 (1953).
468. P. Karrer and P. Schneider, Monatsh., 81, 111 (1955).
469. K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, J. Chem. Soc., 44 (1946).
470. I. N. Nazarov and M. V. Kvarzina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 677 (1938).
471. J. L. H. Allan, E. R. H. Jones, and M. C. Whiting, J. Chem. Soc., 1862 (1955).
472. I. A. Favorskaya and L. V. Fedorova, Sint. Org. Soed., 2, 152 (1952).
473. I. N. Nazarov and E. A. Mistrikov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 335 (1958).
474. D. D. Coffman, J. Amer. Chem. Soc., 57, 1978 (1935).
475. S. A. Vartanyan, G. A. Chukhadzhyan, and V. N. Zhamagortsyan, Izv. Akad. Nauk Armyansk SSR, 12, 107 (1959).
476. I. N. Azerbaer, Zhur. Obshch. Khim., 15, 412 (1945).

Lensovet Technological Institute,
Leningrad

MOLECULAR SIEVES — PREPARATION, PROPERTIES, AND APPLICATIONS

V. Ya. Nikolina, I. E. Neimark, and M. A. Piontkovskaya

CONTENTS

Introduction 509

The structure and composition of zeolites. Classification 510

The preparation of synthetic zeolites 512

The sorptive properties of zeolites 514

The separation of mixtures by molecular sieves 517

Methods of altering the selectivity of zeolites 518

Possible technical applications of molecular sieve 519

INTRODUCTION

The sorptive properties of sorbents depend chiefly on the area and chemical nature of the surface, the pore structure, and the distribution of effective pore radius.

The adsorption potential, which determines the amount of adsorption, can vary greatly with change in the geometrical shape of the internal surface; it is much greater in narrow pores and channels of molecular dimensions, owing to the superposition of the fields of the opposite walls, and this effect is more marked the finer the pores of the adsorbent[1]. The free adsorptive surface of an adsorbent also depends on the dimensions of the molecules of the substance being adsorbed, since some of the finest pores may be inaccessible to large molecules. This leads to the so-called ultraporosity effect.

Some sorbents are known to have pore diameters approximately equal to molecular dimensions. Only very small molecules can penetrate into these fine pores. McBain has called this phenomenon "persorption"[2].

Fine pores are also present in activated charcoal, silica gel, and other technical sorbents, so that each shows the ultraporosity effect to some extent. The surface area cal-

culated from the sorption isotherms for gases or dyes always depends on the dimensions of the molecules of the adsorbed substance.

Adsorbents with fine pores can be regarded as molecular sieves. The fact that the cross-sections of these pores are of molecular dimensions makes it possible to separate gaseous and liquid mixtures by making use of differences in the size and shape of the component molecules. Such sorbents can sift out molecules of different sizes (hence the name "molecular sieves")[3,4,5]. Examples include zeolites, Saran charcoal, porous glasses, etc.

Zeolites are aluminosilicate polyhydrates of general composition

$$(R'_2, R)O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O,$$

where R' is a univalent cation (Na^+, K^+, Li^+) and R a divalent cation (Ca^{2+}, Sr^{2+}, Ba^{2+}, etc.). If the water molecules are removed from the zeolite crystals, other substances can be adsorbed in their place.

The molecular-sieve properties of zeolites have been known since 1925 [2], when Weigel and Steinhoff[6] discovered that the mineral chabazite exhibits selective sorption. They found that the vapours of water, methyl and ethyl alcohols, and formic acid were adsorbed rapidly on chabazite but that those of acetone, ether, and benzene were not. However, natural zeolites have not been used for the separation of mixtures.

Other natural zeolites with molecular-sieve properties are known (faujasite, gmelinite, mordenite) but they occur only in rare and poor deposits.

In the past twenty years methods have been developed in other countries for the preparation of synthetic zeolites and they are now produced on a large scale by Linde Air Products (USA). In a review of sorption processes up to 1957 [7] it was noted that the introduction of synthetic molecular sieves for practical purposes was one of the most important achievements in the application of adsorption in the preceding decade.

The industrial production of molecular sieves was preceded by extensive research, particularly in England by Barrer and his school. Barrer is the author of the first patents on the preparation of synthetic zeolites and their use for the separation of mixtures.

THE STRUCTURE AND COMPOSITION OF ZEOLITES. CLASSIFICATION

Like many silicates, zeolites are made up of SiO_4^{4-} tetrahedra, which are cross-linked via common O^{2-} ions to form complex anionic radicals[8,9]. In the aluminosilicates some of the Si^{4+} ions are replaced by Al^{3+} ions, so that the lattice has a residual negative charge. The cations neutralising this charge in the anionic framework are situated in the internal spaces in the lattice, and this gives the zeolites ion-exchange properties[10]. The cations in the zeolite lattices usually have a large ionic radius and low charge, for example Na^+, K^+, Ca^{2+}, Ba^{2+}, and less frequently, Rb^+ and Cs^+. The Al:Si ratio in the lattice is variable but one univalent cation is present for every Al^{3+} ion, to neutralise the excess negative charge.

The structure of the zeolite crystal is determined by the magnitude of the forces acting along the three mutually perpendicular directions in the anionic framework. If these forces are equal, the crystals form a stable three-dimensional lattice structure. If the lattice forces are greater in two of the directions than in the third, a layer lattice structure is produced, and if the forces in two of the directions are weaker than that in the third, a "fibrous" or "chain" structure is formed. Zeolites can thus be divided into three classes[11,12]: 1) crystals with a rigid lattice; 2) layer structures; and 3) semi-rigid structures. A characteristic feature of all zeolites is the presence of weakly-held water molecules, which under appropriate conditions may be reversibly removed or replaced by molecules of certain other substances. Unlike water of crystallisation, zeolite water is removed continuously on heating, and not step wise[13]. Zeolites contain interconnected internal channels through which water and certain other "foreign" molecules are able to move.

All zeolites used as molecular sieves (chabazite, faujasite, mordenite, etc.) have a rigid three-dimensional framework formed by rings of SiO_4 and AlO_4 tetrahedra, and this is not distorted on dehydration[14-17]. For example, in the mineral faujasite, which has the highest sorptive capacity, the stable cubic lattice includes large, many-sided holes or "super-cages". The shape of these cages resembles that of a sphere with sections cut off, the perimeter of each "cut" being formed by a ring of many tetrahedra[18].

Fig. 1 illustrates a structure showing the arrangement of hexagonal prisms characteristic of chabazite, and Fig.2 shows the superposition of cubo-octahedra characteristic of faujasite[19].

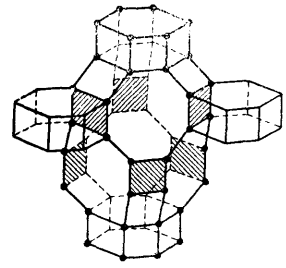


Fig. 1. Arrangement of hexagonal prisms characteristic of chabazite.

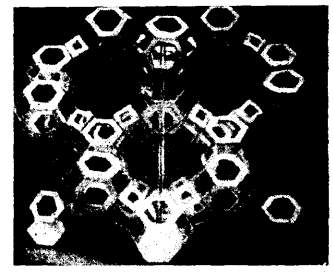


Fig. 2. Superposition of cubo-octahedra, characteristic of faujasite.

TABLE 1. Characteristics of some natural molecular sieves.

Property	Chabazite	Gmelinite	Levynite	Faujasite	Mordenite	Reference
Approximate chemical composition	$(Ca,Na_2)\cdot O\cdot Al_2O_3\ 4SiO_2\cdot 6H_2O$	$(Na_2,Ca)\cdot O\cdot Al_2O_3\ 4SiO_2\cdot 6H_2O$	$CaO\cdot Al_2O_3\ 3SiO_2\cdot 5H_2O$	$(Na_2,Ca)\cdot O\cdot Al_2O_3\ 5SiO_2\cdot 10H_2O$	$(Ca,K_2;\ Na_2)\cdot O\cdot Al_2O_3\cdot 10SiO_2\cdot 6.6H_2O$	22
System	trigonal	pseudotrigonal	trigonal	cubic	monoclinic	22
Crystal form	rhombohedra	hexagonal, sometimes trigonal	rhombohedra	octahedra		8
Specific gravity	2.08—2.16		2.09—2.66	1.92	2.15	8
Hardness	4—5			5	4—5	8
Volume occupied by water, $cm^3\ g^{-1}$	0.214	0.211	0.184	0.281	0.135	22
Sources	Czechoslovakia, Iceland, Australia (near Melbourne)	regions of volcanic activity		very rare, found near Baden	Morden-Kings (USA)	8

TABLE 2. Characteristics of some synthetic molecular sieves.

Adsorbent	Cell dimensions, Å	Free diameter of the largest cage	Type of "window" connecting the largest cage	Free diameter of the "windows", Å	Largest molecules penetrating the dehydrated crystal	Maximum number of molecules accommodated by the largest cage	Free pore volume (cm^3 per cm^3 of crystal)
Chabazite, calcium form	$a=13.78, c=14.97$ (hexagonal)	7.5 by 11.5 (oblong cage)	8-membered rings, 6 per cage	3.9 6 per cage	normal paraffins ($d=4.9$ Å)	12—14 H_2O 6 A; N_2; O_2	0.46
Linde synthetic zeolite 5A	12.27 (cubic)	~11.8	ditto	~4.2; 6 per cage	ditto	~29 H_2O; 12 A; O_2	0.46
Synthetic adsorbent similar to faujasite	24.8 (cubic)	~12	12-membered rings, 4 per cage	9—10 Å 4 per cage	Readily occludes n-, iso-, and neo-paraffins, aromatics, and naphthenes. Largest molecule not determined	32 H_2O 17—19 A, N_2, O_2 ~4.5 n-C_5H_{12} ~2.8, iso C_5H_{12} ~5.4 C_6H_6 ~4.1 cyclohexane	0.53

The group with semi-rigid structures includes the "fibrous" zeolites (the natrolite group) formed by chains of (Si—Al)—O tetrahedra[20]. Dehydration leads to displacement of the atoms around the spaces holding the water, but the chain length is not shortened appreciably. In zeolites of the heulandite group (heulandite, phillipsite, etc.), the planar lattice layers are separated by water molecules and cations which hold the anionic layers together. The dehydration of layer zeolites is accompanied by a considerable decrease in volume in one direction. Sorption in fibrous and layer zeolites is much weaker than in zeolites with a rigid lattice: the former can occlude only polar molecules such as H_2O or NH_3, with an increase in volume.

Table 1 gives data for natural zeolites with molecular-sieve properties. The unit cell of the Linde molecular-sieve lattice is a cubo-octahedron. These are joined in sixfold coordination in the Linde type A adsorbents and in tetrahedral coordination, like the diamond structure, in the type X adsorbents (Table 2)[8,21].

The most open lattice structure is shown by synthetic zeolites analogous to the mineral faujasite (molecular sieve 13 X). Electron microscopy has shown that the powdered material is made up of small cubes[23]. Various derivatives can be prepared from the sodium form of faujasite by cation exchange with salts of potassium, ammonium, methylamines, magnesium, calcium, strontium, barium, etc. (molecular sieve 10 X is the calcium form of faujasite). The sodium form has the composition $Na_2O\cdot Al_2O_3\cdot 2.67SiO_2\cdot mH_2O$, where m depends on the moisture content of the air. According to Barrer and Sutherland's data[24], faujasite crystals (at a relative pressure $P/P_0 = 0.25$) adsorb a volume of sorbate (calculated as the liquid) equal to approximately half the volume of the adsorbent (from 0.54 for nitrogen to 0.41 for isooctane). The number of molecules occluded by one faujasite 24.8 Å cell varies between 254 (for water) and 22 (for isooctane).

The composition of zeolites may vary, even in material from the same deposit, as a result of partial substitution of one cation by another and by changes in the $Al_2O_3:SiO_2$ ratio, which in chabazite, for example, can vary from 1:2.3 to 1:6.[17,25]

In the zeolites used as molecular sieves the relative volume occupied by the cavities in the lattice is very large. Barrer[22,26] gives the following values for this volume, as percentages of the total zeolite volume:

faujasite	56	levynite	40
chabazite	47—50	mordenite	28—33
gmelinite	50		

The considerable inter-lattice volume gives molecular sieves high sorptive capacity. The stable three-dimensional lattice of zeolites of this type enables them to withstand prolonged heating at 300°—450° and reduced pressure without undergoing any significant structural changes. Evacuation in this way is used to remove the water inside the crystals before using the mineral as a sorbent.

Barrer[22] has classified molecular sieves into 4 categories, depending on the minimum cross-sectional area of the channels:

Class A (faujasite) has the largest channel cross-section and readily absorbs normal and iso-paraffins (up to isooctane) and all molecules which can be occluded by the other classes: the free channel diameter is approximately 6 Å* [27].

Class B (chabazite, gmelinite, and the synthetic zeolite $BaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot H_2O$) has a minimum channel diameter of ~4.9 Å, does not adsorb iso-paraffins or aromatic hydrocarbons, adsorbs methane, ethane, and smaller molecules rapidly, and normal paraffins from propane to heptane slowly [29].

Class C (sodium mordenite) [channel dia 4.0 Å (Ed. of Translation)] does not adsorb aliphatic hydrocarbons beyond ethane; methane and ethane are occluded slowly, and N_2, CO, H_2O, and smaller molecules are adsorbed fairly rapidly.

Class D (levynite, potassium mordenite) has a minimum channel diameter of ~3.8 Å, occludes nitrogen and molecules of smaller cross-section; argon, HCl, and NH_3 are adsorbed slowly; hydrocarbons and their derivatives are hardly adsorbed at all.

THE PREPARATION OF SYNTHETIC ZEOLITES

Before considering methods for preparing synthetic molecular sieves, we must examine the origin of natural zeolites. It has been suggested [30] that they have been formed by the prolonged mineralising action of solutions (the so-called hydrothermals) on rocks at high temperatures (100°–350°) and relatively high alkalinity. Chabazite is most frequently found in cavities in basalts, and is deposited in the outflow from some hot springs. Gmelinite occurs in many regions of volcanic activity. Mordenite deposits are generally richer, and large quantities are found in the Morden-Kings basalts (USA).

Most methods for preparing synthetic zeolites imitate the natural geochemical processes, since zeolites and clays can be formed in superheated aqueous solutions under pressure [31-33].

Under laboratory conditions the hydrothermal synthesis of zeolites is carried out in small stainless-steel autoclaves; in some cases a silver vessel is placed inside [31,34-40]. The starting materials are usually a solution of sodium aluminate and an aqueous suspension of silicic acid containing some alkali [41]. This mixture yields an aluminosilicate gel of the required composition. A weighed specimen of gel is placed in the autoclave, water is added, followed in some cases by a slight excess of alkali, the autoclave is hermetically sealed and placed in an air thermostat with heater. After the necessary time interval, the autoclave is cooled, the product is washed with water at ~100° and dried. Before the adsorptive properties are studied, the zeolite is heated at 350° under reduced pressure for several hours.

Many syntheses have been carried out to examine the effect of such factors as temperature, duration of reaction, alkalinity of the medium, quality of the original gel, and occlusion of salts. The crystallisation temperature of the zeolite varies over a wide range from 60° to 450° [31]. The optimum temperature for the formation of mordenite, for example, is 265°–295° [41], and a mineral similar to chabazite has been obtained at 150° [25].

The duration of the reaction can vary over very wide limits: the alkali-metal aluminosilicates crystallise fairly rapidly, sometimes in a few hours, but gels containing calcium or barium cations crystallise slowly, sometimes requiring several weeks [31]. In some cases (for example, the crystallisation of mordenite in a strongly alkaline medium) a good yield of zeolite is obtained in 24 h, and after 2 days recrystallisation is observed, with the formation of a different phase which is more stable under the given conditions.

In a paper on the hydrothermal synthesis of potassium aluminosilicates Barrer and Baynham [42] reported that the time required for crystallisation with high yield increased as the reaction temperature was lowered. At 300° and above not more than 16 h was necessary, but 3–4 days were necessary for some crystallisations below 150°.

It has been assumed that the formation of highly-hydrated materials such as zeolites requires a high water-vapour density, so that increased pressure favours the synthesis. The pressure in the autoclaves has been raised to several hundred atmospheres, but since the temperature was below the critical temperature, water was always present in the liquid state and acted as mineraliser. The crystals often separated very slowly and, once formed, did not grow any further [30].

The success of the hydrothermal crystallisation depends to a great extent on the conditions of preparation of the aluminosilicate gel. In a study of the laboratory synthesis of mordenite Barrer [41] examined the influence of dehydration of the silica gel on the yield of zeolite. Good yields of mordenite were obtained irrespective of the rate of evaporation on a water bath. Drying above 110° makes the aluminosilicate gel insoluble and leads to unsatisfactory crystallisation. Later, Barrer and Baynham [42] omitted the evaporation of the water, since it was found that this preliminary ageing retards the crystallisation at temperatures below 200° (the evaporation was not omitted in the synthesis of mordenite, which crystallises above 200°). The effect of gel drying was not significant, however, when the hydrothermal crystallisation was carried out at high temperature (above 350°) or in strongly alkaline medium [43].

The alkalinity plays a particularly important part in the hydrothermal crystallisation of zeolites, and their crystals grow best at a pH of 8–12. For this reason, Barrer and coworkers maintained the ratio

$$\frac{(R^{II}, R^{I}_2)O}{Al_2O_3} = 1$$

in the synthesis of aluminosilicates. Layer-lattice aluminosilicates of the kaolin or montmorillonite type are formed at lower alkalinity [31]. When the alkalinity is reduced, the crystallisation is retarded, probably due to the insufficient solubility of the gel, and fewer, finer crystals are formed [41]. From a large number of experiments, Barrer concluded that in hydrothermal reactions the pH is as important as temperature and composition. In laboratory experiments the pH has usually been 8–10.5. In the synthesis of mordenite increase in the pH above 10.0 facilitates recrystallisation to analcite [43].

Table 3 gives some of Barrer's experimental data on the preparation of mordenite [41], and Table 4 gives the

* One patent reports that faujasite dehydrated at 250° under reduced pressure can be used to separate molecules with an effective diameter of ~14 Å from molecules with a larger cross-sectional area [28].

TABLE 3. Composition of gel: $Na_2O.Al_2O_3.10.9SiO_2.nH_2O$.

Reaction conditions		pH of cold mother liquor after reaction	Reaction product
temp., °C	duration		
~295	2 days	~10	good yield of mordenite and some analcite
~290	ditto	9.5—10	mordenite, some analcite
~295	»	~9	excellent yield of mordenite
~295	»	~7.5	mordenite, some analcite; poor crystallisation
~280	»	10—10.5	few mordenite crystals, corroded; some analcite
~290	24 h	~10.5	good yield of mordenite and some analcite
~280	17 h	—	good yield of mordenite

TABLE 4. Composition of original gel: $K_2O.Al_2O_3.nSiO_2$.

Temperature, °C	pH	n	Reaction product
150	>10.5	1—2	moderate yield of zeolite of composition $K_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 3H_2O$
150	>10.5	3	moderate yield of above zeolite or chabazite (depending on the alkalinity)
150	>10.5	4—6	good yield of chabazite
85	>10.5	7—8	good yield of phillipsite, $K_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 3H_2O$, and chabazite

experimental conditions used by Barrer and Baynham for the preparation of potassium chabazite[42].

Comparison of the X-ray diffraction patterns of synthetic specimens with those of natural chabazite converted to the potassium form by ion exchange shows that the specimens of highest silica content (approximate composition $K_2O.Al_2O_3.4.15SiO_2.4.4H_2O$) have structures closest to that of natural chabazite.

Molecules of the salts NaCl, KCl, KBr, $BaCl_2$, etc., present in high concentration in the mother liquor, often enter the inner channels of the growing crystals as "fillers", facilitating the formation of a very open aluminosilicate lattice. These "foreign" molecules can sometimes be removed by hydrothermal extraction with water, without breakdown of the lattice[31].

Barrer[30,44,45] used this method to prepare a new material, with molecular-sieve properties, from analcite or aluminosilicate gel, with barium chloride or bromide as mineraliser. Data from the most successful experiments are given in Table 5. The original mineral or gel was ground to a powder, mixed thoroughly with solid barium chloride ($BaCl_2$: mineral volume ratio = $\frac{1}{2}$ to $1\frac{1}{2}$) after which water was added (water : solid volume ratio = $\frac{1}{2}$ to 1). The use of saturated or almost saturated barium salt solutions is recommended. Analogous exchange can be carried out with calcium[46].

After extraction of the excess salts with water, the specimens of the new product were found to be extensively hydrated, with a stable three-dimensional lattice similar to that of mordenite or chabazite[44]. Study of the adsorption by the new mineral of substances with different molecular dimensions confirmed that they belonged to the chabazite class. This zeolite has a particular affinity for polar gases, and ammonia is adsorbed strongly even at 300°.

Molecular sieves can thus be prepared not only by direct synthesis, but also by recrystallisation of certain minerals in concentrated salt solutions.

The American worker Sensel[47] recommends, for the hydrothermal synthesis of a hydrated aluminosilicate corresponding to molecular sieve 4A, the maintenance of a stoichiometric component ratio corresponding to the formula $Na_2O.Al_2O_3.2SiO_2$ (a small excess of alkali is permissible), a temperature in the range 65°–160° (best results at 105°–140°), and a reaction duration of 4–24 h. The weight of water should be 80–90% of the total autoclave charge, and the optimum dehydration temperature is 150°–315°. Three-fold treatment with concentrated $CaCl_2$ solution (5 N) at the boil leads to replacement of up to 80% of the sodium cations by calcium, and the zeolite first obtained is converted to an adsorbent of molecular sieve type 5A.

Similar conditions are used in a method for the preparation of molecular sieves described in McCormick and Westerland's patent[48]. A solution containing silicate, aluminate, and metal ions is heated to 80°–100°, mixed thoroughly, and kept for at least 5 h until the zeolite crystal lattice has formed. This method was used to prepare molecular sieves of composition $(0.9 \pm 0.2)M_{2/n}O.Al_2O_3.(2.5 \pm 0.5)SiO_2.(0-8)H_2O$ and $(1 \pm 0.2)M_{2/n}O.Al_2O_3.(1.85 \pm 0.5)SiO_2.(0-6)H_2O$.

A patent by Milton[49] describes the preparation of an aluminosilicate of the 4A type, with composition $Na_2O.Al_2O_3.1.85SiO_2.5.1H_2O$. An aluminate gel enriched with alumina, obtained from a mixture of $NaAlO_2$, Na_2SiO_3, and NaOH solutions, was heated at ~100° for periods varying from 15 min to 90 h. In the same way a gel with increased silicic acid and sodium oxide content yielded a zeolite of type X, with approximate composition $0.9Na_2O.Al_2O_3.2.5SiO_2.6.1H_2O$, close to that of the mineral faujasite.

TABLE 5. Conditions for the hydrothermal synthesis of barium zeolite[45].

No.	Aluminosilicate component	Hydrothermal treatment conditions	Temp., °C	Yield of mineral
1	natural analcite	5 successive treatments with fresh portions of $BaCl_2$ and H_2O, for 12 h each	270	excellent
2	synthetic analcite $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$	6 treatments with $BaCl_2$ and water for 24 h each	210	excellent
3	aluminosilicate gel $K_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$	heated for 6 days with one portion of H_2O and $BaCl_2$	180	excellent
4	gel $BaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$	heated for 3 days with $BaCl_2$ and H_2O	235	good
5	gel $BaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$	ditto	270	moderate
6	synthetic analcite	two successive treatments with fresh portions of H_2O and $BaBr_2$ for 48 and 30 h	205	excellent
7	gel $BaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$	heated for 1 day with a concentrated $BaCl_2$ solution at 210°, then for 2 days at 197°	210—197	good

Extraction

Product No.	Water : mineral ratio	Number of extractions	Extraction conditions
2	15 : 1	10	24 h each at 210°
7	15 : 1	7	36 h each at 208°

X-Ray powder methods have shown that the structures of synthetic and natural zeolites are closely similar. For example, the spacings and relative intensities of the lines for natural mordenite are close to those for synthetic sodium mordenite and sodium mordenite prepared by ion exchange[41]. Complete agreement in such cases is not to be expected, since chance inclusions and partial replacement of cations are possible in the natural materials.

In 1949 an experimental study of the synthesis of zeolites was begun in the Linde research laboratory, where a large number of specimens were synthesised, including zeolite "X" of composition $M_{86/n}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 267H_2O$ (where n is the valency of the cation), with lattice structure similar to that of faujasite[50]. Workers in the same laboratory also synthesised a few cubic zeolites, with unit-cell composition corresponding to the formula $Na_{12}[(AlO_2)_{12} \cdot (SiO_2)_{12}] \cdot 27H_2O$ and effective pore diameter 4.2 Å [51,52]; the spaces within the crystals after dehydration made up 45% of the volume. Replacement of ~30% of the Na^+ cations by Ca^{2+} increases the effective pore size of the zeolite to 5 Å and the free pore volume accessible to water reaches 48%. The calcium form of type A (sieve 5A) occludes straight-chain hydrocarbons up to and including tetradecane.

Work has also been carried out recently in the USSR on the synthesis of zeolites and the study of their adsorptive properties[53,54].

Barrer and coworkers have given data on the synthesis of a number of zeolites at comparatively low temperatures. Study of sodium aluminosilicate crystallisation fields at comparatively low temperatures[55] led Barrer and Baynham and others to the conclusion that since the zeolites are "filled" structures in which the filler is water, they should be more readily formed at low temperatures (in the absence of high pressures), because of the volatility of the filler. The laboratory experiments on the synthesis of zeolites in the range 60°–110° were carried out in sealed heat-resistant glass tubes; those at higher temperatures were carried out in stainless steel autoclaves, since under these conditions the aluminosilicate gel reacts with glass. The crystallisation often took place very readily and rapidly. A zeolite of the 4A type ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$) was obtained in good yield from a gel enriched with alumina, at 85°–110° after only 2–3 h. The time required for crystallisation increases with increase in the silica content of the gel. The gel crystallises more rapidly in the presence of a large excess of alkali, particularly at 60°–85°.

The Linde company supplies molecular sieves of the 4A (pore diameter ~4 Å), 5A, and 13X types in the form of powder or solid stable granules. The latter are made by mixing the powdered zeolite with a binder, moulding to the required shape, and drying. Binders used include clay, attapulgite[56], gelatinous aluminium hydroxide[57,58], starch, a high-molecular-weight fatty acid, a heavy metal stearate[59] or "sterotex" — a hydrogenated vegetable oil[47], which is burnt off in the dehydration process.

Barrer[19] has published a table giving the specific surfaces of crystals and other sorbents (Table 6).

THE SORPTIVE PROPERTIES OF ZEOLITES

The sorptive properties of zeolites differ sharply from those of other adsorbents[60].

1. They readily adsorb only those molecules which are able to penetrate into the uniform channels of the structure.
2. The adsorption potential is very high as a result of the superposition of the fields of the opposite walls of the narrow channels, so that the zeolite has a high adsorptive capacity at low adsorbate concentrations.
3. For the same reason, zeolites have a high adsorptive capacity at high temperatures.
4. Since zeolites are polar sorbents, they have a high affinity for polar molecules, particularly water molecules, and they also show selective adsorption of unsaturated organic compounds.

Adsorption on zeolites has been studied by many workers[61-66]. The shapes and dimensions of the adsorbate molecule and zeolite channels determine whether or not a given molecule will penetrate into the crystal. The cross-sectional area in the narrowest places should be greater than the corresponding critical dimensions of the sorbate molecules, which for spherical molecules will be equal to the diameter, and for other symmetrical molecules will be the maximum cross-sectional area perpendicular to their length. For an asymmetric molecule, the critical dimension will be the diameter of the circle which encloses the maximum cross-sectional area of the molecule in the plane perpendicular to its length[22]. Differences in the size and shape of molecules are illustrated in Fig. 3.

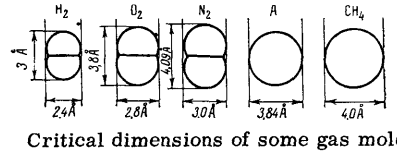


Fig. 3. Critical dimensions of some gas molecules.

TABLE 6. Specific surfaces of some porous materials.

Porous crystal	Specific surface, $m^2 g^{-1}$	Active sorbent	Surface, $m^2 g^{-1}$
Linde sieve 13X	1030	"Carbolac" carbon	1060
Linde sieve 10X	1030	Carbon black powder	770
Linde sieve 4A	~800		
Linde sieve 5A	750–800	Silica gel	610
Calcium chabazite	750		
		Activated alumina	230–380
Mordenite	440	Sepiolite	310 (max)
Methylammonium bentonite	160	Attapulgite	260 (max)
Dimethylammonium bentonite	150		
Trimethylammonium bentonite	130	"Vycor" porous glass	140
Tetramethylammonium bentonite	140		

The molecules of normal hydrocarbons have identical cross-sectional areas and all of them, up to heptane, penetrate into the channels of zeolites of type 5A, but the rate of adsorption decreases with increase in chain length[67-69]. Barrer used the experimental data to construct a table[22] characterising the selectivity of the occlusion of different substances by the three classes of zeolite (Table 7).

Barrer divided all the compound studied into groups[22,70] according to the nature of their sorption by molecular sieves. If the molecules of a given substance are adsorbed by a given sorbent, it would be expected that other molecules in the same group should also be occluded by

TABLE 7. Selectivity of molecular sieves of classes B, C, and D towards various materials.

Class of zeolite	Typical molecules occluded rapidly at room temperature or below	Typical molecules occluded at a moderate rate at room temperature or above	Typical molecules not occluded appreciably at room temperature or above
B	He, Ne, A H_2, N_2, O_2 CO, CO_2, COS, CS_2 H_2O, HCl, HBr NO, NH_3 CH_3OH, CH_3NH_2 CH_3CN, HCN $Cl_2, CH_3Cl, CH_3Br, CH_3F,$ CH_2Cl_2, CH_2F_2 CH_4, C_2H_6, C_2H_5OH HS, CH_3SH	$CH_3CH_2CH_3$ and higher n-paraffins $C_2H_5OH, C_2H_5NH_2$ $C_2H_5F, C_2H_5Cl, C_2H_5I$ I_2, HI C_2H_5SH $HCOOCH_3, HCOOC_2H_5$ C_2H_5CN, CH_3COCH_3 CH_2Br_2 CH_3COOCH_3 $NH(CH_3)_2, NH(C_2H_5)_2$	Aromatic, cyclo-, and iso-paraffinic hydrocarbons and their derivatives Heterocyclic compounds such as thiophene, and pyridine CCl_4, $CHCl_3$, $CHCl{=}CCl_2$, CH_3CHCl_2, $CHCl_2CCl_3$, C_2Cl_6 and analogous bromo- and iodo-compounds Secondary alcohols, mercaptans, nitriles, and halides Primary amines with one NH_2 group at a secondary C atom Secondary and tertiary amines Ethers with branched chains and thioethers
C	He, Ne, A H_2, O_2, N_2 CO, NH_3, H_2O	CH_4, C_2H_6, CH_3Cl CH_3OH, CH_3NH_2 HCN, Cl_2, CH_3F, CH_3CN	All molecules in columns 3 and 4 for zeolites of class B
D	He, Ne, A $H_2, O_2, N_2,$ H_2O	A HCl NH_3	All molecules in column 4 for zeolites of class C, and also CH_4, C_2H_6, CH_3OH, CH_3NH_2, CH_3SH, CH_3CN, CH_3Cl, CH_3F

TABLE 8. Adsorption of linear, branched and cyclic hydrocarbons on molecular sieve 5A, silica gel, and activated carbon.

Adsorbate	Temp., °C	P, mm Hg	Wt.% of substance adsorbed		
			mol. sieve 5A	silica gel	activated carbon
n-Butane	25	47	9.8	3.4	24
Isobutane	25	98	0.5	4.8	26
Benzene	25	50	0.5	9.5	44

Molecular sieves have a high affinity for water vapour. At low moisture concentrations the adsorptive capacity of a molecular sieve is 6–10 times greater than that of silica gel or activated alumina. Fig. 5 gives isotherms for the sorption of water vapour on a molecular sieve, silica gel, and alumina gel[2]. Thus 1 g of zeolite type A adsorbs 20–22% of water at a relative humidity of 10%, and 10% water at a water-vapour pressure of 0.005 mm Hg[51].

that sorbent. If, for example, in the series $CHCl_3$, $(CH_3)_3CH$, $(CH_3)_2{=}CHCl$ and $CHBr_3$, the standard molecule $(CH_3)_3CH$ is not adsorbed by a zeolite of class B, then the other molecules in this series, which are similar in size and shape, will not be occluded.

The selective behaviour of small molecules compared with larger molecules is illustrated quantitatively by the data in Table 8 [71]. Activated charcoal and silica gel adsorb all three substances. The 5A molecular sieve readily adsorbs the straight-chain compound n-butane but hardly adsorbs isobutane or benzene at all.

Milton and Breck's patent[72] on the use of faujasite as adsorbent for molecules whose maximum cross-sectional area is less than that of the $(C_4F_9)_3N$ molecule gives the composition of typical faujasite specimens as 0.43–0.58 Na_2O, 0.41–0.54 CaO, and 4.54–5.00 SiO_2, per g of Al_2O_3. The same patent also gives the data for adsorption by faujasite reproduced in Table 9 (as wt.% of adsorbent).

Thermodynamic aspects of intracrystalline sorption by faujasite have been discussed by Barrer and Stuart[73].

The chief advantage of molecular sieves is their ability to adsorb relatively large quantities of substances present in low concentrations in mixtures. Fig. 4 gives isotherms for the sorption of oxygen, nitrogen, and straight- and branched-chain hydrocarbons by molecular sieves of types 5A and 4A, chabazite, and silica gel[51]. In all cases the isotherms for the zeolites rise sharply at very low concentrations and the quantity of substance adsorbed changes little with further increase in the sorbate concentration.

The high adsorptive capacity at low concentrations makes it possible to use molecular sieves for drying and purifying gases and non-polar liquids, and also for trapping valuable impurities present in small quantities in effluent gases from the chemical and petroleum industries.

TABLE 9. Adsorptive properties of faujasite.

Adsorbate	Temp., °C	Partial press., mm Hg	% of wt. of adsorbent	Adsorbate	Temp., °C	Partial press., mm Hg	% of wt. of adsorbent
Propane	25	10	2.9	p-Xylene	25	0.06	10.6
		168	9.3			6.7	19.7
1-Butene	25	0.45	7.7	Krypton	—183	0.005	11.1
		156	17.0			0.14	50.0
Argon	—196	0.092	20.0	Carbon monoxide	25	43	3.5
		9.0	31.9			708	14.6
Isobutane	25	10	8.7	Water	25	0.007	10.1
		743	12.9			23	33.4
Cyclohexane	25	0.06	10.6	Oxygen	—196	0.033	13.9
		92	17.0			121	29.3
Benzene	25	0.045	7.2	Nitrogen	—196	0.010	13.7
		0.85	23.0			310	23.6
				Neopentane	25	0.3	8.9
						404	14.9

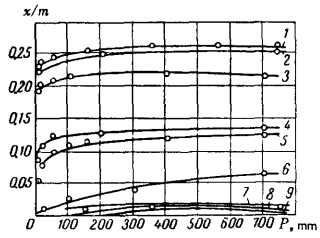


Fig. 4. Isotherms for sorption on a zeolite of type A, chabazite, and silica gel: 1) O_2 on zeolite at -183°; 2) N_2 on calcium zeolite at -196°; 3) N_2 on chabazite at -196°; 4) propene on calcium zeolite at 25°; 5) propane on calcium zeolite at 25°; 6) propane on silica gel at 25°; 7) propane on zeolite A at 25°; 8) N_2 on zeolite at -196°; 9) isobutane on chabazite or calcium zeolite at 25°.

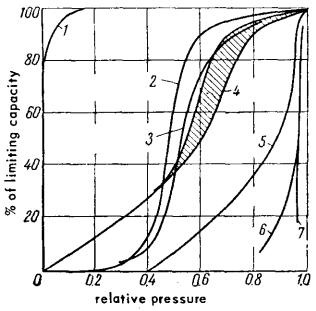


Fig. 5. Sorption of water vapour on different materials, expressed as % of the limiting sorption volume: 1) chabazite; 2) sugar charcoal; 3) pure coke carbon; 4) silica gel; 5) birch charcoal; 6) platinum; 7) glass.

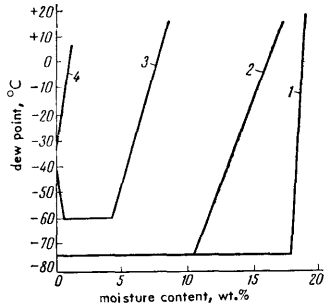


Fig. 6. Dependence of the dew point on the quantity of adsorbed moisture for a molecular sieve (1, 2, and 3) and silica gel (4): 1) at 24°, $V = 19.81$ mm sec^{-1}; 2) at 100°, $V = 19.81$ mm sec^{-1}; 3) at 95°–114°, $V = 19.81$ mm sec^{-1}; 4) at $V = 1.58$ mm sec^{-1}.

Molecular sieves also have a high adsorptive capacity under dynamic conditions. Fig. 6 shows the dependence of the dew point on the quantity of adsorbed moisture, before break-through, on a molecular sieve and on silica gel at a 6–10% relative humidity of the incoming air and a column length of 75 cm.[71] The lowest dew point is given by the molecular sieve. Break-through is observed when 17–18% of water has been adsorbed by the zeolite, whereas the figure for silica gel and alumina gel is much smaller. A molecular sieve can thus be used to dry gases more efficiently. It is possible to use smaller absorbers to achieve the same efficiency, and regeneration of the sorbent requires less heat than the removal of the moisture adsorbed by silica gel or alumina gel.

Since the zeolites hold the adsorbed molecules firmly, they retain their adsorptive power at low and high temperatures. Fig. 7 shows isotherms for the sorption of water vapour on a molecular sieve of type A, silica gel, and alumina gel at different temperatures[60]. Isotherms for sorption at different temperatures on silica gel, alumina gel, etc. have been compared by Breck et al.[51]

Zeolites adsorb water intensively at 75°–100°, while silica gel and alumina gel lose their adsorptive power at these temperatures.

Another distinctive feature of molecular sieves is their high affinity for polar molecules, which is apparently due to the electrostatic nature of the adsorptive forces[74]. This is illustrated by the isotherms for the sorption of the polar gas carbon monoxide and the non-polar gas argon (Fig. 8)[71]. Although these two substances are equally volatile and have sufficiently small critical molecular diameters to be adsorbed by a 5A molecular sieve, the sorption isotherm for carbon monoxide lies considerably higher than that for argon.

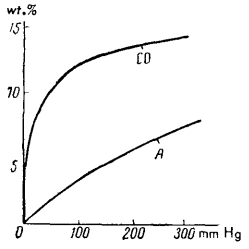


Fig. 8. Isotherms for the sorption of CO and A on molecular sieve 5A.

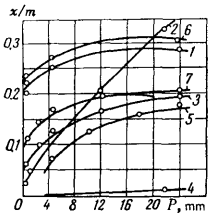


Fig. 7. Isotherms for sorption of water vapour on a molecular sieve of type A, silica gel, and alumina gel at different temperatures: 1) zeolite A, 25°; 2) silica gel, 25°; 3) zeolite A, 100°; 4) silica gel, 100°; 5) alumina gel, 25°; 6) calcium zeolite, 25°; 7) calcium zeolite, 100°.

Molecular sieves also show a marked affinity for unsaturated molecules. For example, at a pressure of 1 mm Hg a molecular sieve adsorbs 3.8% C_2H_2 and only 0.3% C_2H_6.[75] This property of molecular sieves is widely used in industry to separate acetylene, ethylene, butylene, etc. from saturated molecules of approximately the same size[60]. The separation coefficient for an ethane–ethylene mixture is 1.5 on activated charcoal, 3.0 on silica gel, and 20 on a molecular sieve[75].

The thermodynamic and energetic aspects of adsorption on zeolites have been examined by several workers[12,68,76–80].

THE SEPARATION OF MIXTURES BY MOLECULAR SIEVES

The successful separation of gas mixtures on molecular sieves depends on two main factors: (1) the difference in the rates of occlusion of the gases, which depends on the differences in the shape and size of the molecules, and (2) the relative affinity of the crystal for the substances being sorbed.

The separation is particularly efficient if the rapidly--diffusing molecule also has a high affinity for the adsorbent. If, however, the molecules with high affinity for the sorbent diffuse slowly, they may interfere with the adsorption of other molecules, and lead to "poisoning of the sorbent", making it unsuitable for the separation of the mixture [22,81].

Molecules can be "sifted out" of mixtures by zeolites either by a static method in which the immobile liquid or gas comes into contact with the vacuum-dehydrated adsorbent or by a flow method in which the mixture passes through a layer or column of the zeolite. By selecting a suitable flow rate, it is possible to separate completely the component which is adsorbed rapidly, from the component which is occluded slowly.

The adsorption is usually carried out in such a way that approximately half of the internal pore volume is saturated; the sieve is then regenerated by heating at 300°–350° under reduced pressure for several hours. In cases of slow desorption, for example in the removal of occluded long--chain hydrocarbons, the sorbate is partially extracted with superheated water [26].

The temperature chosen for the separation depends on the composition of the mixture. Since increase in temperature accelerates the adsorption of hydrocarbons, the separation of normal paraffins from iso-paraffins and aromatic hydrocarbons on chabazite has been carried out at an adsorbent temperature of 150°–220° [26]. An ethane–propane mixture is separated at room temperature, and argon is separated from nitrogen and oxygen on mordenite at -183°.

Mordenite has been used to separate the following gas mixtures: nitrogen–argon, hydrogen–nitrogen, neon–argon, and hydrogen–argon [22,82]; quantitative separation of argon from oxygen has been achieved by passing the mixture once over a small quantity of the mineral.

Barrer and Riley have compared the efficiency of activated charcoal, chabazite, and a synthetic zeolite prepared from barium salts, for the separation of the inert gases [44]. At -194.7° and an equilibrium pressure of 10 cm Hg, 1 g of the synthetic zeolite occluded (under standard conditions) 17.5 ml of neon and 0.5 ml of helium, which corresponds to a separation factor of 35; under the same conditions chabazite gave a separation factor of 12 and activated carbon a factor of only 5. Nitrogen is adsorbed much more rapidly than methane from their mixtures on to a Linde 4A molecular sieve and a separation factor of 10 has been obtained [83].

Barrer has patented methods for separating hydrocarbons with molecular sieves (1942) [84,85] and for preparing synthetic zeolites (1946) [45].

Zeolites of type A and chabazite have been used successfully to separate low-molecular-weight n-paraffins from iso--paraffins, and aromatic compounds from naphthenes (Table 10) [22]. Table 11 gives further data on the separation of various mixtures by chabazite.

Monosubstituted derivatives of methane with small substituents, for example OH, CH, CN, Cl, and Br, are occluded rapidly, but the analogous ethane derivatives are occluded slowly. Quantitative separation of these homologues (with the same substituent) can be carried out with an ordinary adsorption column filled with a molecular sieve. Molecular sieves can also be used to separate azeotropic mixtures [22,86] such as $C_2H_5OH-H_2O$, $CH_3OH-(CH_3)_2CO$, H_2O–dioxan, C_2H_5OH–iso-C_7H_{16} (Table 11), and also mixtures whose components have the same b.p., for example, n-heptane–isooctane (Tables 10 and 11).

Mixtures of certain aromatic hydrocarbons have been separated in the laboratory with molecular sieves 10X and 13X [72,87]. A very clean separation of a mixture of hydrogen, oxygen, nitrogen, methane, and carbon monoxide has been achieved on a chromatographic column of Linde 5A

TABLE 10. Separation of mixtures using chabazite (crystalline sieve type B).

Mixture	Components removed	Temperature of adsorbent, °C	Method and conditions
Ethane–propane	ethane	20	flow
Propane–isobutane	propane	150–160	static
Propane–isopentane	propane	150	"
n-Butane–isobutane	n-butane	185, 160	»
n-Butane–isopentane	n-butane	210, 160	»
Propane–n-butane–isopentane	n-butane, pentane	150	»
n-Butane–toluene–cyclohexane	n-butane	216	»
Isobutane–n-pentane	n-pentane	220	»
n-Heptane–isooctane	n-heptane	200	in liquid phase
n-Heptane–toluene	n-heptane	200	ditto
n-Butane–benzene	benzene	160	
Ethane–isobutane	ethane	20	
Ammonia–isobutane	ammonia	160	

TABLE 11. Separation of mixtures using a mineral of class B chabazite.

Mixture	Components removed	Conditions and remarks
$H_2O-C(CH_3)_2OH$	H_2O	liquid, at 20°; rapid and quantitative separation
$H_2O-CO(CH_3)_2$	H_2O	ditto
$H_2O-CH_3CO\ C_2H_5$	H_2O	»
H_2O–dioxan	H_2O	»
$CH_3OH-CO(CH_3)_2$	CH_3OH	»
$CH_3OH-C_2H_5Br$	CH_3OH	»
$CH_3OH-CS_2-CH_3CN-C_6H_6$	CH_3OH, CS_2 CH_3CN	»
$CH_3OH-H_2O-CH_3COOCH_3$	CH_3OH, H_2O	»
$CH_3OH-(COOCH_3)_2$	CH_3OH	sorption of vapour in equilibrium with liquid, complete separation
$C_2H_5OH-C_6H_5CH_3$	C_2H_5OH	liquid, at 20°; slow but complete separation
$C_2H_5OH-(CH_3)_2CHOH$	C_2H_5OH	ditto
$C_2H_5OH-n-C_7H_{16}$	C_2H_5OH	»
$C_2H_5OH-H_2O-(C_2H_5)_2O$	C_2H_5OH, H_2O	»
$C_2H_5OH-CH_3COC_2H_5$	C_2H_5OH	liquid, at 112°; rapid and quantitative separation
$CH_3O-H_2O-CH(CH_3)_2OH$	CH_3O, H_2O	liquid, at 20°; rapid and quantitative separation
$CO_2-CH(CH_3)_2OH$	CO_2	ditto, CO_2 in solution
$H_2S-C_6H_6$	H_2S	ditto, H_2S in solution
$C_2H_5SH-C_6H_6$	C_2H_5SH	liquid, at 50°; partial separation after one week
$NH_2CH_3-C_2H_5OH-N(CH_3)_3$	NH_2CH_3, C_2H_5OH	liquid, at 20°; complete removal of the two components after 16 h.
$NH_2C_2H_5-NH(C_2H_5)_2$	$NH_2-C_2H_5$	ditto; slow but complete separation
$Cl_2-C_6H_6$	Cl_2	liquid, at 20°, Cl_2 in solution; rapid and complete separation

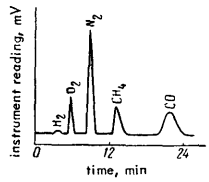


Fig. 9. Chromatogram of the separation of a gas mixture by molecular sieve 5A.

molecular sieve (Fig. 9)[88]. Normal paraffins in petroleum distillates have been separated on a 5A zeolite[89-93]. A method for separating normal paraffins from petroleum by means of molecular sieves (type 5A in particular) has been patented[94,95]. A study has been made of the selective adsorption of boron hydrides (B_2H_6, B_5H_9, $B_{10}H_{14}$) on chabazite, mordenite, and Linde synthetic zeolites 4A, 5A, and 13X[96], and of the adsorption of fluoro-substituted methanes by 4A and 5A sieves[97,98].

The adsorptive efficiency of molecular sieves is directly related to the efficiency of regeneration of the adsorbent. Water in zeolite pores may be removed by heating, and other adsorbed substances present after the zeolites have been used as adsorbents can be removed similarly. If these substances are less strongly held than water, regeneration is possible at lower temperatures. In the case of repeated regeneration, it is recommended that the heating temperatures do not exceed 300°.

Regeneration can be carried out either by heating externally or by passing a hot dry gas through the adsorbent layer. The purifying gas should not form an explosive mixture with the desorption products. After regeneration, the adsorbent is cooled in a current of a dry gas which is weakly held by the zeolite. The adsorbent can also be regenerated by heating at reduced pressure instead of using a stream of gas.

METHODS OF ALTERING THE SELECTIVITY OF ZEOLITES

Both the rate of occlusion of different molecules, and the sorptive capacity of molecular sieves, can be altered in a variety of ways. A definite quantity of a readily-adsorbed substance (usually small polar molecules such as water, ammonia, or methylamine) can be introduced into the crystal[22,99,100]. These modifying molecules enter the channels through which the molecules to be adsorbed must diffuse, and the movement of the latter is restricted. The adsorption is carried out at low temperatures to make the modifying molecules immobile.

For example, the critical size of the oxygen molecule is 2.8 Å, and that of the argon molecule 3.8 Å; under ordinary conditions both are intensively adsorbed by a class C sieve of the mordenite type. When a very small quantity of water (0.05 wt.%) is added to the degassed mordenite, its adsorptive activity towards argon is halved, but the occlusion of oxygen is little affected, so that separation of the mixture is greatly improved. Thus the modifying action of polar molecules involves a decrease in the rate of adsorption of all non-polar gases, but, other conditions being the same, large molecules are retarded to a greater extent than smaller molecules. The modifying molecules create, as it were, a semipermeable membrane between the gas phase and the inner region of the crystal. Optimum conditions for the separation of a mixture are achieved by addition of an appropriate quantity of modifying agent.

A second method of altering the selectivity of molecular sieves is by ion exchange. Since the cations which neutralise the ionic charge of the lattice lie in the channels through which the sorbate molecules move, the rate of occlusion should depend on the size and charge of these cations. Ions of different radii

	Li^+	Na^+	K^+	NH_4^+	Rb^+	Cs^+	Ca^{2+}	Ba^{2+}
r (Å)	0.78	0.98	1.33	1.43	1.49	1.69	1.06	1.33

can reduce the cross-sectional area of the channels to different extents. Additional factors include the mobility of the cations, their tendency to undergo deformation, their charge, their number, and the proportion of hydrate water that they retain on evacuation[101].

In a study of chabazites Rabinowitch and Wood[102] showed that crystals rich in potassium occlude gases weakly, whereas sodium chabazites have greater sorptive power and calcium-rich chabazites adsorb even such large molecules as n-heptane.

Barrer and Baynham[25] prepared an isomorphous series of chabazites of gradually varying composition, from the pure sodium compound to the pure calcium compound, by hydrothermal treatment of natural chabazite with concentrated Ca and Na salt solutions. As the sodium ion was replaced by calcium, the adsorptive power of the chabazite increased sharply, and when the calcium content fell below 35% of the total cation content, the sorptive power decreased sharply, particularly for large molecules.

The experiments showed that a variety of sorbents can be produced from chabazite by the ion exchange $2Na \rightleftharpoons Ca$, combined with other modification processes. Treatment of natural mordenite with concentrated $Ba(NO_3)_2$ and $Ca(NO_3)_2$ solutions, which leads to exchange of the cations and a slight lattice contraction, also changes the sorptive properties of the mineral considerably[76]. X-Ray diffraction patterns show no breakdown of the crystal structure after ion exchange[103]. The thermal stability of minerals modified by ion exchange increases with increase in cation size[104].

It is possible to influence the sorptive behaviour of zeolites towards gases by changing the cation density. The isomorphous replacement of silicon by aluminium increases the anionic charge of the lattice and hence the number of cations per unit cell. The number of divalent cations required to neutralise the anionic charge of the lattice is half the number of univalent cations required, and the cation density of chabazites enriched with Ca^{2+} or Ba^{2+} is accordingly reduced by half. In addition, the ability to retain water between the crystals increases with increase in the polarising power of the cations in the order $K < Na < Ca$; the sorptive capacity of the zeolite is greater the more water it can hold.

The sorptive capacity of chabazites increases with increase in the relative silica content $SiO_2 : Al_2O_3$. The actual process by which the adsorbents are prepared has a modifying effect on their properties. Products of different

sorptive capacity are sometimes obtained from the same starting material under the same conditions. In the hydrothermal synthesis not all the crystals separate immediately and the $SiO_2 : Al_2O_3$ ratio in the first-formed crystals may differ slightly from that in crystals formed later. Some of the crystals may thus have a higher Na^+ ion density and lower adsorptive capacity. Moreover, in hydrothermal treatment with concentrated salt solutions the zeolites may have a tendency to occlude these salts, with deterioration in the adsorptive properties[105]; repeated extraction with hot water is used to remove the salts[19].

The zeolite lattice is more stable the higher the $SiO_2 : Al_2O_3$ ratio. Since the Al–O bond is longer than the Si–O bond, zeolites of higher alumina content should have a lower structural stability[106], and hydrothermal extraction of alumina-rich specimens with prolonged evacuation at 350° does in fact lead to partial breakdown of the crystals[25].

Increase in the number of Al^{3+} ions in the lattice also leads to an increase in the heat of dehydration of the zeolite, owing to the greater anionic charge density[107]. During hydrothermal extraction alumina-rich zeolites lose alkali, undergoing partial hydrolysis, so that some amorphous material is formed. Thus the sorptive capacity of zeolites is influenced by the rate of crystallisation, occlusion of salts, partial breakdown during washing and evacuation, and by isomorphous replacement.

One method of modifying crystalline sieves is to replace the cations by hydrogen. Direct treatment of zeolites with acid leads to decomposition, but if the dehydrated zeolite is heated for a prolonged period in ammonium chloride vapour, the ammonium zeolite is formed[22,108], and when this is heated with oxygen, an intercrystalline reaction takes place between the ammonium cations and the oxygen to form the H-zeolite:

$$4(-O^- \ldots NH_4^+) + 3O_2 = 4(-OH) + 6H_2O + 2N_2.$$

This reaction is possible only if the zeolites can occlude oxygen. Another method for preparing the hydrogen form of zeolites[109] is to replace the cation by Ag^+, which is then replaced by hydrogen by treating the mineral with aqueous pyridine hydrochloride solution.

X-Ray diffraction patterns of the hydrogen derivatives of chabazite and mordenite show the characteristic lattice of the original materials, but the channels are more open than in the usual cationic forms. For example, H-chabazite very rapidly occludes propane, which is adsorbed slowly by the ordinary zeolite: H-mordenite also adsorbs propane, albeit very slowly, whereas ordinary mordenite does not occlude propane at all.

The difference in the rates of sorption of gases is greater at low temperatures, since the effect of the difference in the rates of diffusion increases as the temperature is reduced[22,110]. The influence of temperature on the heats of adsorption of the components of the mixture, that is on the affinity constants, must also be taken into account. If one type of molecule has a higher heat of sorption and a higher diffusion coefficient than the other, decrease in temperature will facilitate separation. If one type of molecule has a higher affinity for the adsorbent but a lower diffusion rate than the other, decrease in temperature leads to less satisfactory separation, since the molecules with the high affinity for the crystal are adsorbed on its surface and diffuse inwards very slowly, preventing the entry of the other molecules.

POSSIBLE TECHNICAL APPLICATIONS OF MOLECULAR SIEVES

As a result of their high adsorptive capacity at low concentrations and high temperatures, and their high affinity for water, unsaturated organic compounds, and other polar molecules, molecular sieves are used, or may find application, in various branches of technology[71]: (1) for drying gases and liquids; (2) for purifying gases and liquids; (3) for removing unsaturated molecules from waste gases; (4) for separating hydrocarbons; (5) as ion exchangers; (6) for maintaining high vacua; (7) as carriers for vulcanising agents for rubber and plastics; (8) for adsorbing isotopes from aerosols; (9) for removing gas samples from low pressure systems, etc. Let us examine their potential applications in more detail.

Molecular sieves as drying agents give more complete removal of moisture than any other adsorbent, and many technical and laboratory applications are possible. They have been used to dry toluene, benzene, pyridine, cyclohexane, acetone, diethyl and dimethyl ethers, ethanol, methanol, transformer oil, etc., most of which can be dried to a moisture content of 0.001%.

One experimental industrial assembly for drying air to very low moisture contents at high pressure by means of zeolites has worked continuously for 18 months[111]. Molecular sieves 4A and 5A have proved 8 times more efficient for drying an inert gas than successive drying with magnesium perchlorate and phosphorus pentoxide[65]. Molecular sieves are used to dry the coolants in refrigerators and thus to prevent corrosion. The oil and the refrigerants (fluorocarbons) have large molecules and are not adsorbed by the sieves[62].

Zeolites may find many applications as highly-active drying agents: (a) as components of packing materials to prevent corrosion of machinery in storage or during transportation; (b) in systems where space is limited and other drying agents cannot be used; (c) in systems operating at high temperatures, etc.

Many industrial gases contain, in addition to water, other undesirable impurities such as CO_2, CO, H_2S, etc., which are readily adsorbed by molecular sieves. These impurities can be removed with the water, thus eliminating the need for several adsorption assemblies[60]. The use of molecular sieves also avoids the corrosion which arises when alkali or monoethanolamine are used to remove CO_2 and H_2S.

One petroleum-chemical company in the USA has devised a scheme for removing CO_2 from ethylene used for polyethylene manufacture, by a single-stage adsorption in an immobile layer of granulated molecular sieve 5A[63]. This system requires a lower capital expenditure than alkali washing, gives efficient CO_2 removal, with simultaneous reduction of the dew point to between -60° and -75°, and does not cause corrosion of the apparatus. The adsorbent is regenerated by the passage of hot methane.

The molecular sieve 5A has been used to remove sulphur compounds and water from liquid propane and for drying transformer oils. Considerable success has been achieved in purifying benzene and toluene from traces of normal paraffins with molecular dimensions less than 5 Å. It has been shown, on the pilot plant scale, that benzene can be purified equally readily in the liquid or gaseous phase, but toluene and xylene are more effectively purified in the gaseous state[71].

The extraction of unsaturated organic compounds from the waste gases of the petroleum-chemical industry by molecular sieves should find extensive application. These compounds are not extracted at present because of the high cost of existing processes. Many gases contain considerable quantities of unsaturated hydrocarbons such as ethylene, propene, and acetylene, which can be used for the synthesis of plastics. Molecular sieves with high selectivity towards these compounds may make their extraction economical.

The use of molecular sieves in the oil-refining and gas industries to separate hydrocarbons also appears promising[67].

High vacua can be obtained by placing molecular sieves in evacuated vessels to adsorb traces of residual gases and moisture[71].

The use of molecular sieves to remove gas samples from systems at low pressure has been suggested[66]. The gas is adsorbed by a zeolite cooled in liquid air, the zeolite is sealed into an ampoule, connected to the analysing apparatus, the ampoule is broken and the gas is desorbed by heating.

The successful use of molecular sieves to adsorb I^{131} from aerosols has been reported[112,113].

Thanks to their uniform structure, molecular sieves have a greater ion-exchange capacity than most commercial resins. As with many organic resins, the sodium from the zeolites can replace cations in solution, e.g. Ag^+, Cu^{2+}, Al^{3+}, Zn^{2+}, Sr^{2+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Au^{3+}, and K^+.

The molecular sieve 4A can separate zinc from cadmium, cobalt from nickel, lithium from sodium, silver from gold, etc. The pH in these exchange reactions should be in the range 5–11.[60,71] Some cations may produce breakdown of synthetic zeolites, for example, barium, copper, and hydrogen.

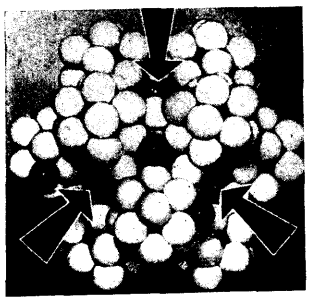


Fig. 10. Model of a molecular-sieve crystal unit[115]. Black spheres represent adsorbed molecules.

The important advantages which molecular sieves have over other ion exchangers are their high exchange capacity and the absence of swelling when wetted.

Molecular sieves have recently found a new use as carriers for certain reagents, particularly vulcanising agents for rubber and plastics, in cases where the reagents could not previously be used because of their volatility, toxicity, or instability. The pores of the zeolites are filled with the reagent, the zeolite is placed in the reaction medium, and the temperature is raised to give gradual liberation of the sorbed molecules, which then react[64,114] (see the model of a unit of a molecular-sieve crystal illustrated in Fig. 10).

The Linde company now supplies several types of chemically "loaded" molecular sieves[115,116,117], which can be used as latent vulcanising agents.

The above examples probably do not represent all the possible applications of molecular sieves, and adsorbents of this type are of interest in several industrial fields.

1. M.M.Dubinin, "Issledovanie v Oblasti Adsorptsii Gazov i Parov Uglerodnymi Adsorbentami" (Studies on the Adsorption of Gases and Vapours by Carbonaceous Adsorbents), Izd.Akad.Nauk SSSR, Moscow, 1956.
2. J.W.McBain "The Sorption of Gases and Vapours by Solids" (Translated into Russian), ONTI, Goskhimizdat, Moscow – – Leningrad, 1934.
3. R.M.Barrer, Ann.Reports, 41, 31 (1944).
4. R.M.Barrer, Quart.Rev., 2, 293 (1949).
5. R.M.Barrer, J.Chim.phys., 47, 82 (1950).
6. O.Weigel and E.Steinhoff, Z.Krist., 61, 125 (1925).
7. L.Lapidus, Chem.Eng.Progr., 53, 517 (1957).
8. L.G.Betekhtin, "Mineralogiya" (Mineralogy), Gos.Izd.Geol. Lit., Moscow, 1950.
9. W.H.Taylor, Proc.Roy.Soc., 145A, 80 (1934).
10. J.Wyart, Bull.Soc.franc.Miner., 56, 81 (1933).
11. R.M.Barrer, "Diffusion in and through Solids" (Translated into Russian), Chapter III, Moscow, 1948.
12. R.M.Barrer, Proc.Roy.Soc., 167A, 392 (1938).
13. G.Friedel, Bull.Soc.franc.Miner., 21, 5 (1898).
14. H.Strunz, Naturwiss., 485 (1955).
15. L.S.Dent and J.V.Smith, Nature, 181, 1794 (1958).
16. A.B.Lamb and J.O.Woodhouse, J.Amer.Chem.Soc., 58, 2637 (1936).
17. W.Nowacki and H.Koyama, Mladeck.Experientia, 14, 396 (1959).
18. R.M.Barrer, F.W.Bultitude, and J.W.Sutherland, Trans. Faraday Soc., 53, IIII (1957).
19. R.M.Barrer, Brit.Chem.Eng., No.5, 1 (1959).
20. W.H.Taylor, C.A.Meek, and W.W.Jackson, Z.Krist., 84, 373 (1953).
21. R.M.Barrer, "Aspects of Sorption in Porous Crystals", Proc. of the 10th Symp., Colston Res.Soc., "The Structure and Properties of Porous Materials", Bristol, 1958.
22. R.M.Barrer, Brennstoff-Chem., 35, 325 (1954).
23. R.M.Barrer, W.Buser, and W.F.Grutter, Chimia (Switz.), 9, 118 (1955).
24. R.B.Barrer and J.W.Sutherland, Proc.Roy.Soc., 237A, 439 (1956).
25. R.M.Barrer and J.W.Baynham, J.Chem.Soc., 2892 (1956).
26. R.M.Barrer, J.Soc.Chem.Ind., 64, 130 (1945).
27. A.Guyer, M.Theichen, and P.Guyer, Helv.Chim.Acta, 40, 1603 (1957).
28. German Pat. DAS 1 023 007 (16th Dec., 1954, published 23rd Jan., 1958), Chem.Zentr., 7585 (1959).
29. G.L.Kington and W.Laing, Trans.Faraday Soc., 51, 287 (1955).
30. R.M.Barrer, J.Chem.Soc., 127 (1948).
31. R.M.Barrer, Trans.Brit.Ceram.Soc., 56, 155 (1957).
32. R.M.Barrer, Proc.Intern.Symp.React.Solids, Gothenburg, Pt.1, 373 (1952).
33. R.M.Barrer, Discuss.Faraday Soc., No.5, 326 (1949).
34. J.Wyart, ibid., No.5, 172 (949).
35. R.M.Barrer and E.White, J.Chem.Soc., 1267 (1951).

36. R.M.Barrer, L.Hinds, and E.A.White, ibid., 1466 (1953).
37. R.M.Barrer and N.McCallum, ibid., 4029 (1953).
38. R.M.Barrer, J.W.Baynham, and N.McCullum, ibid., 4035 (1953).
39. H.E.W.Taylor, ibid., 1253 (1949).
40. F.G.Straub, Ind.Eng.Chem., 28, 113 (1936).
41. R.M.Barrer, Chem.Soc.Special Publ. 2158 (1948).
42. R.M.Barrer and J.W.Baynham, ibid., 2882 (1956).
43. R.M.Barrer and E.A.D.White, ibid., 1561 (1952).
44. R.M.Barrer and D.W.Riley, ibid., 113 (1948).
45. R.M.Barrer, U.K. Pat.574 911 (25th Jan., 1946); Chem. Abs., 43, 1618 (1949).
46. R.M.Barrer and J.W.Baynham, German Pat. DAS 1 041 020 (27th Feb., 1957, published 16th Jan., 1958); Chem.Zentr., 10 687 (1959).
47. E.E.Sensel, U.S.Pat.2 841 471 (23rd Oct., 1956, published 1st July, 1958); Chem.Zentr., 7912 (1959); J.H.Estes, U.S.Pat.2 847 280, (23rd Oct., 1956, published 2nd Aug., 1958); Chem.Zentr., 7912 (1959).
48. J.W.McCormick and M.H.Westerland, German Pat. DAS 1 038 015 (16th June, 1959, published 4th Sept., 1958); Chem.Zentr. 10 363 (1959).
49. R.M.Milton, U.S.Pats. 2 882 243, 2 882 244, (14th April, 1959); Chem. Abs., 53, 13 454f (1959).
50. D.W.Breck, W.G.Eversole and R.M.Milton, J.Amer. Chem.Soc., 78, 2338 (1956).
51. D.W.Breck, W.G.Eversole, R.M.Milton, T.B.Reed, and T.S.Thomas, ibid., 78, 5963 (1956).
52. T.B.Reed and D.W.Breck, ibid., 78, 3972 (1956).
53. Ya.V.Mirskii, Dokl.Akad.Nauk SSSR, 130, 115 (1960).
54. I.E.Neimark, M.A.Piontkovskaya, A.E.Lukash, and R.S. Tyutyunnik, Kolloid.Zhur., 22, 251 (1960)
55. R.M.Barrer, J.W.Baynham, F.W.Bultitude, and W.M. Meier, J.Chem.Soc., 195 (1959).
56. W.I.Mitchell and W.F.Moore, German Pat. DAS 1 055 515 (12th Nov., 1957, published 23rd April, 1959); Chem.Zentr. 13 283 (1959).
57. R.E.Van Dyke and R.P.Trainer, U.S. Pat.2 865 807 (23rd Dec., 1958); Chem.Abs., 53, 6486 (1959).
58. R.E.Van Dyke and R.P.Trainer, German Pat. 1 044 782 (24th Dec., 1957, published 27th Nov., 1958); Chem.Zentr., 8671 (1959).
59. H.V.Hess and W.A.Ray, U.S.Pat.2 885 368 (1st May, 1959); Chem.Abs., 53, 15 428 (1959).
60. P.R.Scarre, Chem.Age, India, 8, 81 (1957).
61. R.M.Barrer and M.J.Hampton, Trans.Faraday Soc., 53, 1462 (1957).
62. H.Lautensack, F.M.O'Connor, and M.L.Suval, Refrig.Eng., 65, 33 (1957).
63. Petroleum Proc., 79 (1955).
64. Canadian Chem.Proc., No.7, 55 (1958).
65. C.C.Addison, E.Iberson, and J.B.Raynor, Chem.and Ind., 96 (1958).
66. B.L.Tonge and D.G.Timms, Chem.and Ind., 155 (1959).
67. R.M.Barrer and L.Belchetz, J.Soc.Chem.Ind., 64, 131 (1945).
68. R.M.Barrer and D.A.Ibbitson, Trans.Faraday Soc., 40, 195 (1944).
69. R.M.Barrer and D.A.Ibbitson, ibid., 49, 807 (1953).
70. R.M.Barrer, Disc.Faraday Soc., No.7, 135 (1949).
71. Reprinted from The British Drug Houses, Ltd.
72. R.M.Milton and D.W.Breck, U.K.Pat.776 467 (5th June, 1957); Chem.Zentr. 33, 9315 (1958).
73. R.M.Barrer and W.I.Stuart, Proc.Roy.Soc., 249A, 464 (1959).
74. H.H.de Boer and J.F.H.Custens, Z.phys.Chem., 25B, 225 (1934).
75. N.Kel'tsev, Gazov.Prom., No.9, 38 (1957).
76. R.M.Barrer, Trans.Faraday Soc., 40, 555 (1944).
77. R.M.Barrer, ibid., 40, 374 (1944).
78. R.M.Barrer, Nature, 181, 176 (1958).
79. R.M.Barrer and D.W.Brook, 49, 1049 (1954).
80. R.M.Barrer, Inst.intern.chim.Solvay, 10th Conseil Chim., 1956, 21, Brussels. 1956.
81. R.M.Barrer and A.B.Robins, Trans.Faraday Soc., 49, 807 (1953).
82. R.M.Barrer and A.B.Robins, ibid., 49, 929 (1953).
83. H.W.Habgood, Canad.J.Chem., 36, 1384 (1958).
84. R.M.Barrer, U.S.Pat.2 306 610 (29th Dec., 1942); Chem. Abs., 37, 3103 (1943).
85. R.M.Barrer, U.K.Pat.548 905 (29th Oct., 1942); Chem. Abs., 38, 374 (1944).
86. R.M.Barrer, J.Soc.Chem.Ind., 64, 133 (1945).
87. B.J.Mair and M.Shamaiengar, Analyt.Chem., 30, 276 (1958).
88. L.Kyryacos and C.E.Boord, ibid., 29, 787 (1957)
89. R.D.Schwartz and D.J.Brasseau, ibid., 29, 1022 (1957).
90. K.M.Nelson, M.D.Grimes and B.J.Heinrich, ibid., 89, 1026 (1957).
91. B.T.Witham, Nature, 182, 391 (1958).
92. N.Brenner and V.J.Coats, Nature, 182, 1401 (1958).
93. M.S.Norris and J.G.O'Connor, Analyt.Chem., 31, 275 (1959)
94. H.V.Hess and E.R.Christensen, U.S.Pat.2 886 508 (12th May, 1959); Chem.Abs., 53, 15 545 (1959).
95. E.R.Christensen and H.V.Hess, U.S.Pat.2 886 509 (12th May, 1959); Chem.Abs., 53, 15 546 (1959).
96. H.C.Beachell and J.Andrew, J.Chim.phys., 55, 280 (1958).
97. P.Cannon, J.Amer.Chem.Soc., 80, 1766 (1958).
98. P.Cannon, J.Phys.Chem., 63, 160 (1959).
99. R.M.Barrer and L.V.Rees, Trans.Faraday Soc., 50, 852 (1954).
100. R.M.Barrer and L.V.Rees, ibid., 50, 989 (1954).
101. R.M.Barrer, ibid., 45, 358 (1949).
102. E.Rabinowitch and W.C.Wood, ibid., 32, 947 (1936).
103. R.M.Barrer and D.C Sammon, J.Chem.Soc., 2838 (1955).
104. R.M.Barrer and D.A.Langley, ibid., 3804 (1958).
105. R.M.Barrer and W.M.Meier, ibid., 3811 (1958).
106. R.M.Barrer and D.A.Langley, ibid., 3811 (1958).
107. R.M.Barrer and D.A.Langley, ibid., 3817 (1958).
108. R.M.Barrer, Nature, 164, 112 (1949).
109. I.R.Beattie and A.Dyer, J.Chem.Soc., 4387 (1957).
110. R.M.Barrer, Nature, 181, 176 (1958).
111. R.M.Barrer and W.I.Stuart, Proc.Roy.Soc., 249A, 464 (1959).
112. M.A.Wahlgren and W.W.Meinke, Nucleonics, 15, 156 (1957).
113. B.Harris, Ind.Eng.Chem., 56, Nos.3–11, 424 (1958).
114. F.M.O'Connor, T.L.Thomas, and M.L.Dunham, Ind. Eng.Chem., 57, 531 (1959).
115. Plastics, 23, 466 (1958); 34-36, September (1958).
116. Rubber Age, 83, 482 (1958).
117. Rubber World, 138, 424, 426 (1958).

Institute of Physical Chemistry,
Ukrainian SSR Academy of Sciences
and Scientific Research Institute for
Fundamental Chemistry