QUARTERLY REVIEWS

MOLECULAR-SIEVE ACTION OF SOLIDS

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MANY important phenomena in physical and biological chemistry result from molecular-sieve action, including osmosis, dialysis, Donnan membrane equilibria (unequal ionic distributions, hydrolysis, potential differences), isotope separation, and gaseous and solution chromatography. These secondary phenomena will not be examined in detail but, instead, the causes of molecular-sieve action will be considered, together with some of the information which studies of permeability have contributed to the fundamental chemistry and physics of solids.

Molecular-sieve action may be total or partial in its effect upon the permeability. In total molecular-sieve separations the flow of one species into or through the medium is wholly prevented, while the diffusion of a second species occurs at a finite rate. In partial separations both species diffuse but at different velocities. Molecular-sieve action can, moreover, be demonstrated in two ways: the diffusion medium can be in the form of foils or of beds of powdered sorbent, through which different transmission velocities occur; alternatively, a sorbent may be exposed to a stationary molecular mixture, and different sorption velocities may be found. Elastomers and other polymers, inorganic glasses, certain metals, and also natural membranes forming the walls of plant and animal cells provide good examples of media effecting sometimes partial and sometimes total separations. Sorbent media showing ultra-porosity include porous glass, charcoals, and other xerogels, but by far the most spectacular molecular-sieve effects are shown by some dehydrated zeolite crystals, especially chabazite [$(Ca,Na_2)Al_2Si_4O_{12},6H_2O$], gmelinite [$(Na_2,Ca)Al_2Si_4O_{12},6H_2O$], mordenite [$(Ca,K_2Na_2)Al_2Si_{10}O_{24},6\frac{2}{3}H_2O$], levynite ($CaAl_2Si_3O_{10},5H_2O$), and a synthetic zeolite ($BaAl_2Si_4O_{12},nH_2O$), together with their cation-exchange modifications; and to a lesser extent by analcite ($NaAlSi_2O_6,H_2O$) and harmotome [$(Ba,K_2)Al_2Si_5O_{14},5H_2O$]. Other zeolites may show the property, but not all have yet been investigated. First, we may consider the ultra-porosity of sorbents and then that of compact membranes.

Molecular-sieve Action in Porous Sorbents

Some General Considerations.—When a gas is circulated through a porous medium, different flow rates arise in two important ways:

(1) Because greater resistance is offered to diffusion of one species than

of another ; *e.g.*, if a large and a small molecule both pass along a capillary which is of greater diameter than that of the small molecule but constricts the large molecule, then the small one diffuses more rapidly.

(2) Because of differing sorption potentials within the porous medium through which both species are flowing. If the medium has a large internal surface, considerable amounts of the diffusing species may be sorbed and so become largely immobilised. If the amount of sorbed material and thus the lifetimes of each sorbate in the sorption layer differ, then chromatographic bands may develop, or a major difference in the rates of transmission through a column of the porous medium may occur.

These two effects can act in opposition at one and the same time. For example, in powdered dehydrated chabazite crystals exposed to a mixture of ethane and propane the ethane is very speedily occluded at room temperatures and the propane is only slowly occluded [1] because the very narrow intracrystalline diffusion paths greatly restrict the mobility of the larger propane molecule while allowing the ethane to diffuse rapidly. Therefore the crystals first become charged with ethane * which is thus quickly removed from the gas stream. However, the affinity of propane for the crystals is greater than that of ethane, and therefore for comparable partial pressures of the gases at or near equilibrium there would be a larger interstitial concentration of propane. By suitably adjusting the time of transit of the ethane–propane mixture through a column of chabazite so that factor (1) was dominant, the effluent gas was wholly freed from ethane ; for very slow rates of transmission, however, the effluent gas should be enriched in ethane.

In the absence of appreciable sorption, transmission through a porous bed at high pressure follows Poiseuille's law, and there is no separation of the constituents of a gas mixture. At low pressure when the capillary radii are small compared with the mean free path of the gas the flow follows Knudsen's law, and the separation of the constituent gases is inversely proportional to the square roots of their molecular weights. As the capillary radii become still smaller and the surface to volume ratio increases, adsorption effects begin to become important. The adsorbed molecules may be immobilised but also may contribute to flow by surface diffusion. Molecular streaming in a capillary may be described in terms of the diffusion equation $\partial c/\partial t = D(\partial^2 c/\partial x^2)$, where c denotes the concentration of gas in the gas phase. The values which the diffusion coefficient, D, may then have in a given cylindrical capillary, are : [2]

$$D_1 = (4r/3)\sqrt{2kT/\pi m} \text{ (molecular streaming only) .} \qquad (1)$$

$$D_2 = \frac{4r^2}{3r\sqrt{\pi m/2kT} + \tau} \begin{array}{l}\text{(molecular streaming with adsorption to give}\\ \text{an immobile film)}\end{array} \qquad (2)$$

[1] R. M. Barrer and L. Belchetz, *J. Soc. Chem. Ind.*, 1945, **64**, 131.

[2] R. M. Barrer, *Trans. Faraday Soc.*, 1948, No. 3, 61.

* Both ethane and propane are taken up interstitially throughout each crystallite, giving a zeolitic or interstitial solid solution.

$$D_3 = \frac{4r^2}{3r\sqrt{\pi m/2kT} + \tau} + \frac{2\tau D_0}{r}\sqrt{\frac{kT}{2\pi m}}\mathrm{e}^{-E/RT} \quad \begin{array}{l}\text{(molecular \quad streaming} \\ \text{with adsorption to give} \\ \text{a mobile film) } . \quad . \quad (3)\end{array}$$

In these equations τ denotes the lifetime of a molecule in the adsorbed state ($\tau = \tau_0\mathrm{e}^{\Delta H/RT}$ where $\tau_0 = 1/\nu$, ν is the vibration frequency in the adsorbed state, and ΔH the heat of adsorption) ; m is the molecular mass, r the radius of the capillary, k the Boltzmann constant, and T the temperature. $D_s = D_0\mathrm{e}^{-E/RT}$ is the *surface* diffusion coefficient, and E is the energy of activation for surface diffusion. In deriving equation (3) it was further assumed that

$$\frac{\text{concentration on surface}}{\text{concentration in gas phase}} = \text{constant} = \tau\sqrt{kT/2\pi m}$$

This condition is probable for many systems at the low pressures where molecular streaming is the principal mechanism of transmission.

A still further diminution in capillary diameter results in " surface " diffusion becoming dominant, because in capillaries with diameters of molecular magnitudes only, the diffusing species do not leave the range of surface forces. The diffusion process now occurs by a succession of jumps in a periodically varying potential energy field due to the solid. Such periodicity arises from the discontinuous atomic structure of the medium and gives rise to the energy of activation, E.* The diffusion of many gases into gas-sorbing zeolites (see p. 303) takes place according to this mechanism.

Capillary size distributions have been estimated [3] by means of the Kelvin equation $RT \ln p/p_s = -2\sigma V \cos\theta/r$, where r is the radius of a capillary in which liquid is in equilibrium with its vapour at vapour pressure p ; p_s is the saturation pressure of the liquid, which has molecular volume V and surface tension σ. The contact angle of the liquid with the wall of the capillary is θ, and if the liquid wets the capillary θ is zero and $\cos\theta = 1$. From the sorption isotherm one can determine V, the amount sorbed. One may subtract from V the amount V_m required to form a monolayer and attribute the remainder, $(V - V_m)$, to capillary condensation. V_m can be estimated by several methods,[4] and is perhaps most easily derived from B E T plots of $p/V(p_s - p)$ against p/p_s when the intercept on the axis of V is $1/V_m c$, and the slope is $(c - 1)/V_m c$, where c is a constant. Typical structure differentiated curves of dV/dr against r derived from isotherms by the use of the Kelvin equation are given in Fig. 1.

There are limitations to the Kelvin method. Capillary condensation in the usual sense cannot occur when the capillary radius is of the order of

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[3] A. G. Foster, *Trans. Faraday Soc.*, 1948, No. 3, 41 ; 1932, **28**, 245 ; P. H. Emmett and T. de Witt, *J. Amer. Chem. Soc.*, 1943, **65**, 1253 ; P. H. Emmett and M. R. Cines, *J. Physical Chem.*, 1947, **51**, 1248 ; S. Brunauer, " The Adsorption of Gases and Vapours ", O.U.P., 1944, Chap. XI, where a summary of much earlier work will be found.

[4] " Advances in Catalysis ", Vol. 1, Academic Press Inc., N.Y., 1948, p. 65.

* Relative movements of atoms or groups in close contact, whether in chemical reaction, intramolecular rotations, diffusion, or viscous flow, all tend in this way to be jumps from one stable configuration to another, *via* a less stable transition state.

one or two molecular diameters, and the Kelvin equation may no longer
describe the phenomena occurring. Secondly, a correction to r is applied
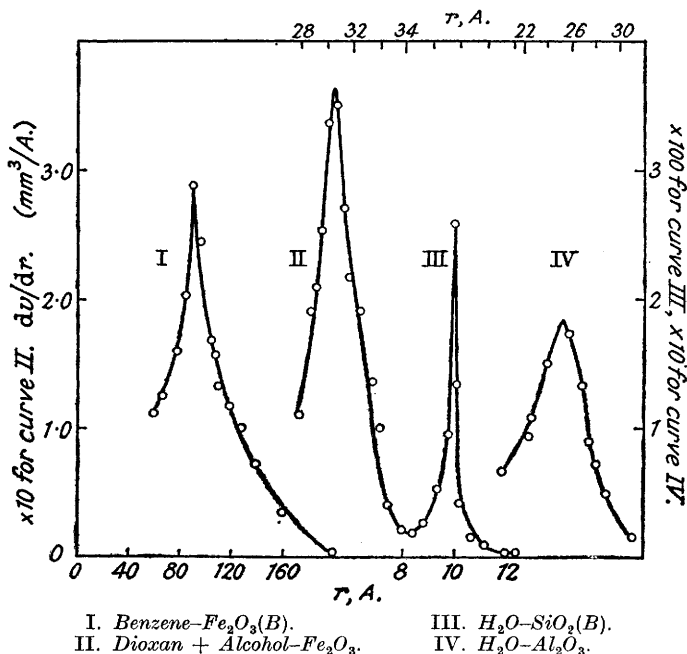

I. *Benzene–Fe$_2$O$_3$(B).*   III. *H$_2$O–SiO$_2$(B).*
II. *Dioxan + Alcohol–Fe$_2$O$_3$.*   IV. *H$_2$O–Al$_2$O$_3$.*

Fig. 1

Typical structure differentiated curves for some gel sorbents, showing range and distribution of pore sizes (Foster).

[*Reproduced by permission from* Trans. Faraday Soc., *Discussion on Interaction of Water and Porous materials, p.* 44.]

to allow for the space taken up by the monolayer film the formation of
which precedes multi-layer formation and capillary condensation.[5] Also,
the capillaries may not be shaped, as for the Kelvin equation, like test-
tubes. In charcoal, for example, many capillaries will be the space between
pairs of plate-like crystallites.* Finally, because many capillaries are open
at both ends, the condition for forming the meniscus may differ from the
condition for its equilibrium once formed. L. H. Cohan[6] considers the
condition for forming liquid in a cylindrical tube open at both ends to be
$RT \ln p/p_s = -\sigma V \cos \theta/r$, which may be compared with Kelvin's equa-
tion. Therefore capillary sizes and size distributions are best determined
on the desorption cycle of the isotherm.

   In spite of these limitations, the distribution curve of capillary radii
in terms of Kelvin's equation may have a qualitative significance. These

[5] A. G. Foster, *Trans. Faraday Soc.*, 1948, No. 3, 44.

[6] *J. Amer. Chem. Soc.*, 1938, **60**, 433.

[7] H. L. Riley, *Quart. Reviews*, 1947, **1**, 65.

* These laminæ may have diameters no more than 20–100 A. in many gas-sorbing
charcoals.[7]

curves normally show maxima, and molecular-sieve effects may become clearly defined if there is a sharp upper limit to the capillary radii, or where all the capillaries are of the same dimensions (Fig. 2, curves 2 and 1). Curve 2 may be approximated to by some gel sorbents, for which the isotherms have the form given in Fig. 3, curve 2. The comparatively flat upper part of the isotherms probably corresponds to condensation in a group of capillaries all of nearly the same radius followed by cessation of sorption
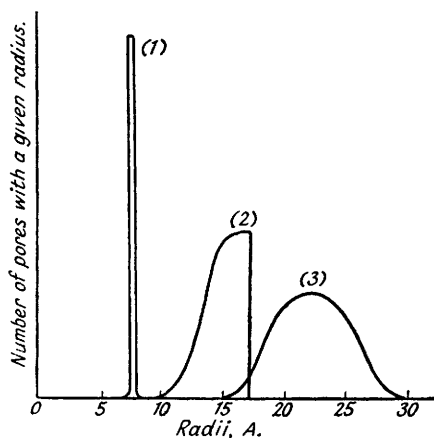

FIG. 2

Three possible distributions of pore sizes. Curves (1) *and* (2) *will give sharp molecular-sieve effects, but Curve* (3) *will not.*
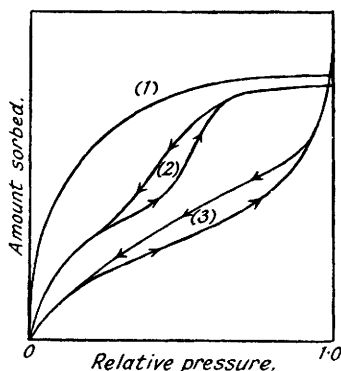
FIG. 3

Isotherms in porous solids. Isotherm (2) *corresponds with pore distributions such as those in Curve 2, Fig. 2. Isotherm* (3) *corresponds similarly with Curve 3, Fig. 2. With pore distributions like those in Curve 1, Fig. 2, but with pore radius too small for capillary condensation, Langmuir-type isotherms as in Curve 1 are observed (cf. isotherms in zeolites).*

because no larger capillaries exist in the porous gel, and because all capillaries of smaller diameters have already been filled. Curve 1 is characteristic of the crystalline zeolites, in which, however, the pore diameters are only a few A., so that capillary condensation cannot occur.

Evidence of molecular-sieve effects in charcoals has been presented *inter alia* by Miss M. Franklin,[8] who reported that apparent densities of charcoals during graphitisation depended on the dimensions of the molecules of the immersion medium (helium, water, carbon disulphide, methanol, and benzene); the larger the molecule the smaller was the apparent density, owing to incomplete penetration of the pore structure. At higher temperatures of graphitisation all the immersion media gave the same apparent density; but this density was ~ 1.7, which is lower than that of graphite, suggesting sealed pores inaccessible to molecules of any medium.

Silica gels may also show analogous effects. According to L. G. Gur-

[8] International Colloquium on Reactions in the Solid State, Paris, Oct. 1948; *Bull. Soc. chim.*, 1949, Nos. 1 and 2, D.53.

witsch's rule,[9] the volumes (reckoned as liquid) of all sorbates taken up in a porous gel sorbent should be the same when the sorbent is saturated. A. G. Foster,[10] however, found that this was not the case in some samples of silica gel ; the larger the molecule the less the volume occluded at saturation. In one case the number of moles sorbed at saturation increased linearly with the *reciprocal* of the molecular volume.

Intracrystalline Sorption.—Some crystalline zeolites, such as those noted on p. 293, can be dehydrated by heat and evacuation without appreciable lattice shrinkage, to give crystals permeated by very narrow diffusion paths, no more than a molecular diameter across. Following dehydration, therefore, a great internal " surface " is developed, and the crystals are capable of sorbing some other molecules in place of their original crystal water. The sorptive capacity in certain cases rivals that of activated charcoals, and in addition the most remarkable molecular-sieve properties are developed.[11]

Evidence as to the dimensions of the intracrystalline channels has been obtained both by X-ray methods and by the study of sorptive behaviour of the crystals. Structures have been obtained for the zeolites analcite,[12] natrolite,[13] scolecite,[13] thomsonite,[13] and edingtonite.[14] X-Ray studies have been made of chabazite,[15] harmotome,[16] phillipsite,[17] and heulandite,[12] but detailed structures are not known. However, the minerals sodalite [18] and ultramarine [19] have been successfully examined, and it is believed that the aluminosilicate framework in chabazite resembles the basket-like anionic structure recurring in a modified form in these minerals. Fig. 4 shows the channels in sodalite, which cross other channels at intervals throughout the lattice. In analcite four channels diverge from each crossing point ; in chabazite, ultramarine, or sodalite eight channels diverge from each such point. These junction points occur regularly throughout the crystal, and the channels themselves are continuous, although their diameter may vary periodically along their length.

Zeolite crystals have been subjected progressively to more and more drastic conditions of heat and evacuation, and were at the same time examined by X-ray or sorption methods.[20] Taking these data together with

[9] *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 805.

[10] *Nature*, 1946, **157**, 340.

[11] J. W. McBain, " Sorption of Gases by Solids ", Routledge & Sons, 1932, Chap. V, and R. M. Barrer, *Ann. Reports*, 1944, **41**, 31, give general summaries of the sorptive behaviour of some zeolites.

[12] W. H. Taylor, *Z. Krist.*, 1930, **74**, 1.

[13] W. H. Taylor, C. A. Meek, and W. W. Jackson, *ibid.*, 1933, **84**, 373.

[14] W. H. Taylor and R. Jackson, *ibid.*, 1933, **86**, 53.

[15] J. Wyart, *Bull. Soc. franç. Min.*, 1933, **56**, 81.

[16] J. Sekawina and J. Wyart, *ibid.*, 1937, **60**, 139.

[17] J. Wyart and P. Chatelain, *ibid.*, 1938, **61**, 121.

[18] L. Pauling, *Proc. Nat. Acad. Sci.*, 1930, **16**, 453 ; *Z. Krist.*, 1930, **74**, 213.

[19] F. M. Jaeger, Baker Lectures, Cornell University, McGraw-Hill, N.Y., 1930, Part III ; F. M. Jaeger, H. G. Westenbrink, and F. A. van Melle, *Proc. Acad. Amsterdam*, 1927, **30**, 249.

[20] W. Milligan and H. Weiser, *J. Physical Chem.*, 1937, **41**, 1029 ; R. M. Barrer, *Proc. Roy. Soc.*, 1938, *A*, **167**, 392, 406.

cleavage properties, one may make a classification of some zeolite crystals in terms of the direction stability of the lattice (Table I).   Only in the robust

Sodalite, $Na_8Al_6Si_6O_{24}Cl_2$
FIG. 4

Some of the details of the sodalite structure, showing the basket-like anionic framework, and the channels running diagonally from the eight corners of the unit cell (Hendricks).
[*Reproduced by permission from* Ind. Eng. Chem., 1945, **37**, 625.]

network group of crystals is there any general tendency for other molecules to replace water within the lattice, because the channels in fibrous and laminar zeolites collapse at least partly during heating and evacuation.

TABLE I

Crystal chemical characters of some zeolites

Bonding characteristics.	Type of zeolite.	Examples.
Strength of bonding in the main direction of aluminosilicate chains greater than strength of cross-linking of chains	Fibrous	Natrolite Scolecite Edingtonite Thomsonite
Strength of bonding in plane of aluminosilicate sheets greater than strength of cross-linking of sheets	Laminar	Heulandite Stilbite
Strength of bonding comparable in all three dimensions	Robust network crystals	Chabazite Gmelinite Mordenite Levynite Harmotome Analcite

The interstitial volume can be determined by measuring the volume of water which can be driven off from the crystals, and is a substantial fraction of the total volume of the crystals, as the data of Table II show. The place of water can be taken by quite small molecules only, demonstrating the small cross-sectional diameter of the channels, but for these small molecules the robust network zeolites are quite exceptional sorbents. In harmotome and most analcites the only molecules sorbed are small polar molecules, but in the other zeolites in Table II and in some synthetic zeolites non-polar molecules are sorbed as well.[21]

<div align="center">

TABLE II

Interstitial volumes in some gas-sorbing zeolites

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Zeolite.	C.c. of liquid H_2O displaced from 100 c.c. of crystals (approx.).	Sorbs non-polar gases.
Chabazite . . .	50	Yes
Gmelinite . . .	50	Yes
Levynite. . . .	40	Yes
Harmotome . . .	35	No ; but sorbs H_2O, NH_3
Mordenite . . .	33	Yes
Analcite	20	As a rule, no ; but sorbs H_2O, NH_3, HCl

The kinetics of sorption can successfully be described in terms of Fick's law of diffusion, although D, the diffusion coefficient, sometimes depends upon the concentration of sorbate in the crystal.[21, 22] The channels are so narrow that the sorbates move wholly in the periodic potential-energy field of the crystal, and as already noted (p. 295) the diffusion coefficient must then obey the relation $D = D_0 e^{-E/RT}$, where D_0 is a temperature-independent factor and E is the energy of activation for a jump from one preferred sorption site to the next (cf. Table XI). The values of E depend in a complex way upon the radius and charge of the interstitial cations, and more directly upon the diameter of the diffusing molecule (Fig. 5). Thus the more closely the interstitial channel surrounds the diffusing molecule the larger E becomes, and the smaller the diffusion rate ; until, finally, large molecules do not enter the crystal at all.[21-25] Every degree of intra-crystalline mobility has been observed and so every degree of molecular-sieve effect can be expected. In an early classification of a number of molecular-sieve crystals certain sorbate molecules of known dimensions were used to compare the dimensions of the intra-crystalline channels.[23, 26]

[21] R. M. Barrer, *J.*, 1948, 127 ; R. M. Barrer and D. W. Riley, *ibid.*, p. 133.

[22] R. M. Barrer and D. Ibbitson, *Trans. Faraday Soc.*, 1944, **40,** 206.

[23] R. M. Barrer, *J. Soc. Chem. Ind.*, 1945, **44,** 130T.

[24] *Idem, Trans. Faraday Soc.*, 1944, **40,** 555.

[25] *Idem, ibid.*, 1949, **45,** 358.

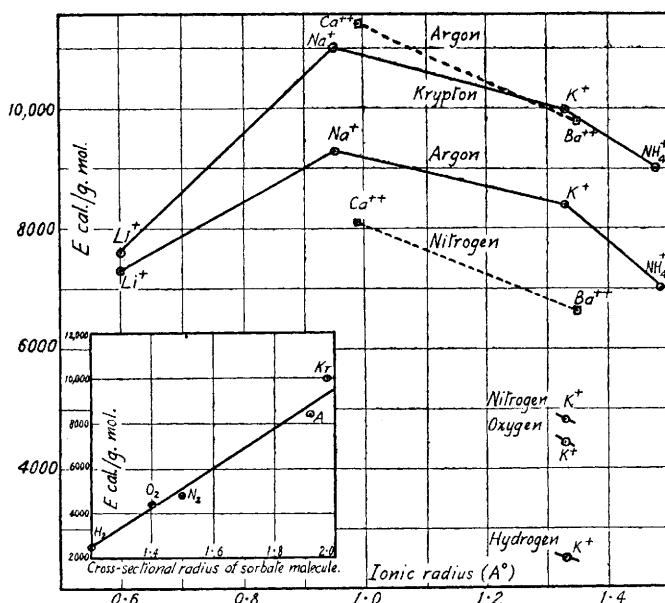[26] *Idem, Ann. Reports*, 1944, **41,** 31.

FIG. 5

Relation between the true energy of activation, E, *for diffusion and the cationic radius in a series of base exchange mordenites, for a given sorbate molecule. Inset is shown the relation between the true energy of activation,* E, *and the cross-sectional radius of a series of sorbate molecules for a given base-exchange mordenite, here K-mordenite.*

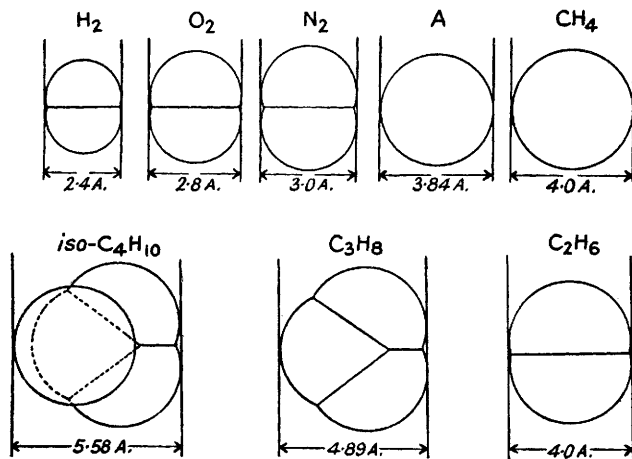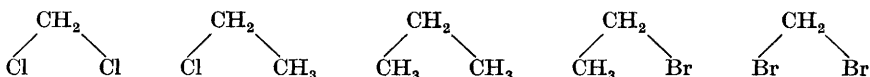[*Reproduced by permission from* Trans. Faraday Soc., 1949, **45**, 363.]

FIG. 6

Critical dimensions of some typical molecules used to classify molecular sieves.

Three categories of molecular sieve are described (Table III). The critical dimensions of these reference molecules and of some other molecular species are indicated in Fig. 6. Molecular dimensions cannot, of course, be given

with absolute certainty, but are sufficiently definite to predict the sorptive behaviour of the minerals towards other possible sorbates. Thus in the series

$$\underset{Cl}{\overset{CH_2}{\diagup}}\underset{Cl}{\diagdown} \quad \underset{Cl}{\overset{CH_2}{\diagup}}\underset{CH_3}{\diagdown} \quad \underset{CH_3}{\overset{CH_2}{\diagup}}\underset{CH_3}{\diagdown} \quad \underset{CH_3}{\overset{CH_2}{\diagup}}\underset{Br}{\diagdown} \quad \underset{Br}{\overset{CH_2}{\diagup}}\underset{Br}{\diagdown}$$
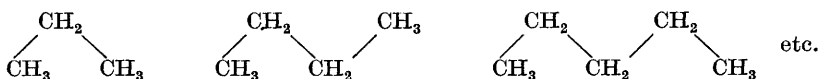
all the molecules are of similar shape and size, owing to the comparable dimensions of the Cl and Br atoms and the methyl radical. Propane is slowly occluded by chabazite, and therefore the other species should also

TABLE III

Three categories of molecular-sieve zeolite

Class 1.
  Chabazite
  Gmelinite
  Synthetic zeolite
    $(BaAl_2Si_4O_{12}, nH_2O)$
	Do not occlude *iso*-paraffins or aromatics.
	Occlude *n*-paraffins slowly.
	Occlude CH_4, C_2H_6, and molecules of smaller cross-section very rapidly.
	Diameter of narrowest cross-section of interstitial channel between 4·89 and 5·58 A.

Class 2. Mordenite (rich in Na)	Does not occlude *n*-paraffins, *iso*-paraffins, or aromatics. Occludes CH_4 and C_2H_6 slowly. Occludes N_2, O_2, and molecules of smaller cross-section rapidly. Diameter of narrowest cross-section of interstitial channel between 4·0 and 4·89 A.

Class 3.
  Ca- and Ba-rich mor-
    denites (prepared
    hydrothermally by
    cation interchange)
	Do not occlude hydrocarbons, including CH_4 and C_2H_6.
	Occlude A, N_2, and molecules of smaller cross-section.
	Diameter of narrowest cross-section of interstitial channel between 3·84 and 4·0 A.

be slowly sorbed. This prediction was confirmed. In the series $CHCl_3$, $CH(CH_3)_3$, $CHBr_3$, since chabazite cannot occlude *iso*butane, it is unable to occlude chloroform and bromoform, molecules which are once more of comparable shape and size to *iso*butane. Similarly in the *n*-paraffin series

$$\underset{CH_3}{\overset{CH_2}{\diagup}}\underset{CH_3}{\diagdown} \quad \underset{CH_3}{\overset{CH_2}{\diagup}}\underset{CH_2}{\diagdown}\underset{}{\overset{CH_3}{\diagup}} \quad \underset{CH_3}{\overset{CH_2}{\diagup}}\underset{CH_2}{\diagdown}\underset{CH_3}{\overset{CH_2}{\diagup}}\diagdown \quad \text{etc.}$$

the cross-sectional diameter of all these molecules in the fully extended configuration is the same, *viz.*, 4·89 A. Since propane is slowly occluded by chabazite, all the other paraffins should be sorbed. This sorption was followed as far as *n*-heptane, and although the sorption rate decreased as the number of carbon atoms increased, large amounts of these simple *n*-paraffins were occluded.[22, 27] It may be inferred that diffusion occurs

[27] R. M. Barrer and D. Ibbitson, *Trans. Faraday Soc.*, 1944, **40**, 195.

in a stretched-out configuration, and that the ability of the chabazite to sorb the paraffin depends on the shape and cross-sectional diameter of the molecules rather than on their molecular volume (*isobutane* has cross-sectional diameter 5·58 A. and molecular volume 96 c.c. and is not occluded ; *n*-heptane has cross-sectional diameter 4·89 A. and molecular volume 145 c.c., and is occluded). Many other examples were also found in which the observed behaviour of the zeolites as sorbents was predicted from the molecular dimensions of the sorbate molecules (Table IV).

The grouping of some zeolites into the three classes of molecular sieve is dependent to a marked degree upon the thoroughness of removal of water and other interstitial molecules which reduce the mobility of the sorbate. By leaving known amounts of water in chabazite crystals it was possible to transform this zeolite from a Class 1 molecular sieve into one with sorptive properties towards hydrogen, oxygen, and nitrogen more nearly recalling a Class 3 sorbent.[28] The water molecules immobilised in the interstitial channels substantially impede the diffusion of other species freely mobile in the absence of the water. The rates of sorption are also reduced if the heat treatment during outgassing is so severe that a measure of lattice collapse occurs. In this connection, chabazite has been heated to 470° while still preserving its sorptive powers.[1] Analcite, harmotome, gmelinite, and mordenite and many of their cation-interchanged forms have been heated for indefinitely long periods at 350° without observable lattice collapse.[22, 24, 25] The velocity of sorption is also influenced by the dimensions of the sorbent particles, in accordance with the theory of diffusion in such crystallites.[22]

Apart from the considerations of the previous paragraph it has recently been shown that the grouping of certain zeolites into three categories of molecular sieve as in Table III is capable of considerable refinement and extension. This can be done in either of two ways : (i) by working at low temperatures,[29] or (ii) by altering the intracrystalline channel dimensions by cation interchange or other chemical processes.[25, 30]

We may first consider (i), and assign to each diffusing species a characteristic E and D_0 in the relationship $D = D_0 e^{-E/RT}$. Temperature influences the diffusion velocity differently in each individual case and, other things being equal, the relative sorption velocities should diverge exponentially as the temperature is lowered. This position is, however, modified when the varying affinities of the sorbates for the sorbents are taken into account. It has been demonstrated that in constant-volume sorption systems the interstitial concentration and concentration gradient may sometimes increase with falling temperature more rapidly than the mobilities of individual molecules decrease, giving negative instead of the more usual positive temperature coefficients to the rates of sorption (Fig. 7).[25] However, in those systems with positive temperature coefficients the relative sorption rates

[28] P. Emmett and T. De Witt, *J. Amer. Chem. Soc.*, 1943, **65,** 1253.
[29] R. M. Barrer, *Nature*, 1947, **159,** 508.
[30] *Idem, ibid.*, 1949, **164,** 12.

TABLE IV

Molecules occluded or excluded by three classes of molecular sieve

Typical molecules rapidly occluded at room temperature or below.	Typical molecules moderately rapidly or slowly occluded at room temperature or above.	Typical molecules which are not appreciably occluded at room temperature or above.
	(i) *Class* 1 *minerals.*	
He, Ne, A H_2, N_2, O_2 CO, CO_2 COS, CS_2 H_2O HCl, HBr NO NH_3 $CH_3 \cdot NH_2$ $CH_3 \cdot OH$ $CH_3 \cdot CN$ HCN Cl_2 CH_3Cl, CH_3Br, CH_3F CH_2Cl_2, CH_2F_2 CH_4, C_2H_6 C_2H_2 CH_2O H_2S $CH_3 \cdot SH$	C_3H_8 and simple higher n-paraffins $C_2H_5 \cdot OH$ $C_2H_5 \cdot NH_2$ C_2H_5F, C_2H_5Cl, C_2H_5Br I_2, HI CH_2Br_2 CH_3I $C_2H_5 \cdot CN$ $C_2H_5 \cdot SH$ $H \cdot CO_2Me$, $H \cdot CO_2Et$ $COMe_2$ $CH_3 \cdot CO_2Me$ $NHMe_2$, $NHEt_2$	Aromatic hydrocarbons, *cyclo-* and *iso-*paraffins. Derivatives of these hydrocarbons. Heterocyclic compounds (*e.g.*, thiophen, pyrrole, pyridine). $CHCl_3$, CCl_4, $CHCl:CCl_2$, $CH_3 \cdot CHCl_2$, $CHCl_2 \cdot CCl_3$, C_2Cl_6 and analogous bromo- and iodo-compounds. Secondary straight-chain alcohols, thiols, nitriles, and halides. Primary amines with NH_2 group attached to a secondary carbon atom. Tertiary amines. Branched-chain ethers, thioethers, and secondary amines.
	(ii) *Class* 2 *minerals.*	
He, Ne, A H_2, O_2, N_2 CO NH_3 H_2O	CH_4, C_2H_6 $CH_3 \cdot OH$ $CH_3 \cdot NH_2$ $CH_3 \cdot CN$ CH_3Cl, CH_3F HCN Cl_2	All classes of molecules in cols. 2 and 3, section (i).
	(iii) *Class* 3 *minerals.*	
He, Ne H_2, O_2, N_2 H_2O	A HCl NH_3	All molecules referred to in col. 3, section (ii).

usually diverge more and more as the temperature falls. Two species, both rapidly sorbed at room temperature, may then be sorbed at low temperatures at such different velocities that molecular-sieve separation should be easily possible. Fig. 8 illustrates this low-temperature differentiation between sorption velocities of oxygen, nitrogen, and argon in levynite.* Numerous examples of this method of magnifying the molecular-sieve effect have been observed.[25]

In the modification of the zeolites by cation interchange, the exchange

---

* The " foot " in the argon curve is due to a small nearly instantaneous van der Waals adsorption upon the external surfaces of the crystal powder. Intra-crystalline sorption is almost absent for argon on the time scale of the experiment.

reaction is normally effected hydrothermally in presence of excess of the exchanging salt at temperatures which may conveniently range from 150° to 250°.   Simple stainless-steel autoclaves can be used as reaction vessels
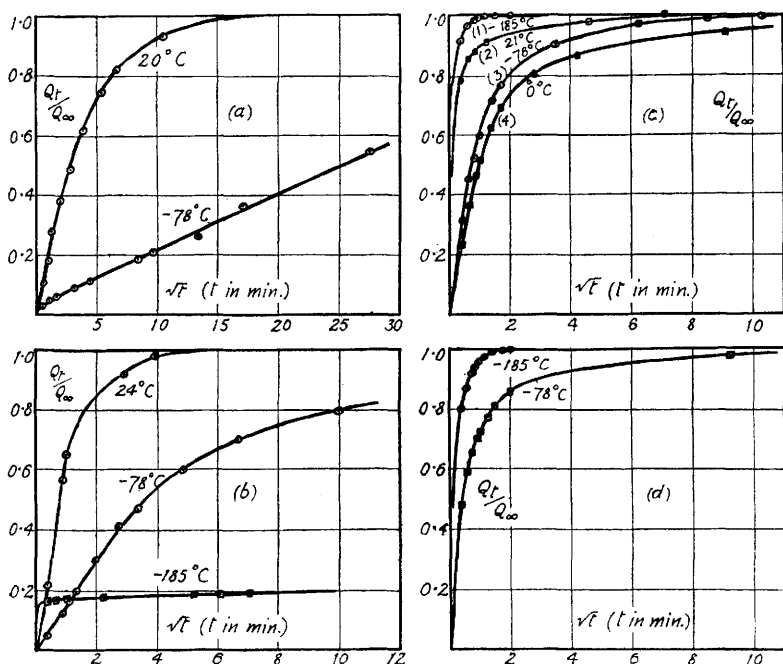

FIG. 7

Examples of positive and negative temperature coefficients in transient flow of gases in zeolitic sorbents.
(a) *Kr in synthetic Na-mordenite.*   (b) *A in Ba-mordenite.*
(c) *Curves 1 and 2 refer to N_2 in NH_4-mordenite, and curves 3 and 4 to Kr in the same sorbent.*   (d) *A in NH_4-mordenite.*

[*Reproduced by permission from* Trans. Faraday Soc., 1949, **45**, 363.]

except in the case of ammonium salts, for which the exchange is better done in glass vessels and with ammonium chloride vapour.   A range of differing molecular sieves may be prepared within limits set by a given aluminosilicate framework.   In Table V are given values of D/a^2 for argon at $-78°$ in a series of the crystals, a being the mean particle radius.[25]

TABLE V

Diffusion of argon at $-78°$ in cation-exchanged mordenites

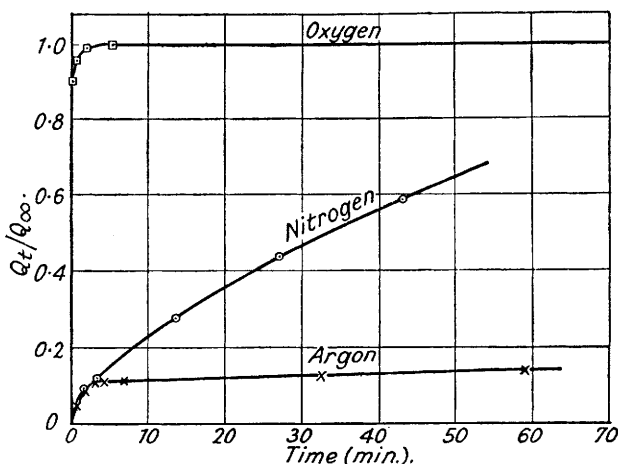| Crystal.	D/a^2 (min.$^{-1}$).	Crystal.	D/a^2 (min.$^{-1}$).
Ca-mordenite . .	$1·51 \times 10^{-8}$	Na-mordenite. . .	$3·8 \times 10^{-5}$
Levynite . . .	$7·6 \times 10^{-7}$	Li-mordenite . . .	$4·0 \times 10^{-4}$
K-mordenite . .	$2·8 \times 10^{-6}$	NH_4-mordenite . .	$1·35 \times 10^{-3}$
Ba-mordenite . .	$5·5 \times 10^{-6}$		

FIG. 8

Widely divergent sorption rates in dehydrated levynite at − 184°, due to molecular-sieve action.

(Q_t denotes c.c. sorbed at N.T.P./g.
Q_∞ denotes c.c. sorbed at N.T.P./g. at equilibrium and is for O_2, 10·02 ; for N_2, 9·77 ;
for A, 10·13.)

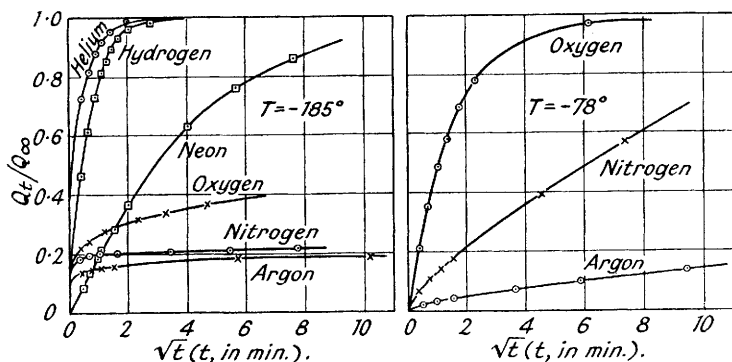[*Reproduced by permission from* Nature, 1947, **159**, 508.]

FIG. 9

Some relative sorption rates in Ca-mordenite at − 185° and − 78°. At − 185° the less easily condensed gases helium, hydrogen, and neon show no " foot " in the rate curves, but the more easily condensed gases show " feet " due to adsorption upon external surfaces of the powder. Intracrystalline diffusion for oxygen, nitrogen, and argon is, however, very slow. At − 78° the " feet " have almost disappeared, and intracrystalline diffusion rates are much increased.

[*Reproduced by permission from* Trans. Faraday Soc., 1949, **45**, 362.]

No allowance is made in the above data for variations in the value of a, but the range in the quotients exceeds anything to be expected on this count. Fig. 9 similarly shows major differences in sorption velocities for a series of gases in a given crystal (cf. also Fig. 8). For the mordenites of Table V the rate sequence $Kr < A < N_2 < O_2$, $Ne < H_2 < He$ tended,

with some exceptions, to be preserved. On the other hand, the affinities shown by the gases for the crystals were nearly in the converse order : $Kr > A$, N_2, $O_2 > H_2 > Ne > He$. The critical dimensions of some of these molecules are shown in Fig. 6.

A special method for modifying zeolites consists first in forming the ammonium zeolite and then slowly burning the ammonia away with oxygen to form the crystalline hydrogen zeolite.[30] The procedure is effective only for crystals capable of occluding oxygen. The removal in this way of some of the interstitial substance of the crystal results in a significant increase of the interstitial channel dimensions.

Separations by Total Molecular-sieve Action.—The behaviour of single species, some of which are copiously occluded while others are not sorbed (Table IV), suggests that quantitative separations might be effected merely by a single exposure of a mixture to a suitable amount of the appropriate zeolite. Such quantitative separation has been termed total molecular-sieve action (p. 293).

Chabazite-type crystals were successfully used to resolve the hydro-carbon mixtures in Table VI. Derivatives of hydrocarbons may also be separated from other such constituents in admixture.[31] Many such separations occur only very slowly but are often accelerated by a rise in temperature, within limits set by the decreasing sorption with increasing temperature, and by the thermal stability of the species.

TABLE VI

Quantitative separations of hydrocarbons using Class I sorbents [1, 28]

Mineral.	Mixture.	Temp. of removal.	Component removed by sorption.
Chabazite	C_3H_8–iso-C_4H_{10}	150°	C_3H_8
	n-C_4H_{10}–iso-C_4H_{10}	185	n-C_4H_{10}
	C_3H_8–iso-C_5H_{12}	150	C_3H_8
	n-C_4H_{10}–$iso$$C_5H_{12}$	210	n-C_4H_{10}
	C_3H_8–n-C_4H_{10}–iso-C_5H_{12}	150	C_3H_8 and n-C_4H_{10}
	n-C_4H_{10}–toluene–$cyclo$hexane	216	n-C_4H_{10}
	n-C_5H_{12}–iso-C_4H_{10}	220	n-C_5H_{12}
	n-C_7H_{16}–iso-C_8H_{18}	212	n-C_7H_{16}
	n-C_7H_{16}–toluene	200	n-C_7H_{16}
Synthetic zeolite ($BaAl_2Si_4O_{12}, nH_2O$)	n-C_4H_{10}–iso-C_4H_{10}	160	n-C_4H_{10}
	n-C_4H_{10}–iso-C_5H_{12}	160	n-C_4H_{10}
	n-C_4H_{10}–C_6H_6	160	n-C_4H_{10}
	C_3H_8–iso-C_4H_{10}	160	C_3H_8
	C_2H_6–iso-C_4H_{10}	20	C_2H_6

Some generalisations emerge from the separations effected :

(1) Monosubstituted methanes in which the substituent groups are small (Cl, CH_3, OH, CN, NH_2, and the like) are very rapidly occluded by chabazite, while monosubstituted ethanes with similar substituent groups are sorbed

[31] R. M. BARRER, *J. Soc. Chem. Ind.*, 1945, **44,** 133.

considerably more slowly. Both classes of solute can be quantitatively removed from molecules listed in col. 3, section (i), of Table IV.

(2) In mordenite monosubstituted methanes were slowly occluded but monosubstituted ethanes were excluded. Separations were then obtained of substituted methanes with substituents Cl, CH_3, OH, CN, or NH_2 from similar ethane derivatives or carbon compounds with three or more carbon atoms.

(3) Ca- and Ba-mordenites, which did not even sorb simple methane derivatives appreciably, separated only simple inorganic molecules (NH_3, H_2O, HCl) from organic species.

Separations by Partial Molecular-sieve Action.—Table IV shows in a qualitative way the great extremes in rates of intracrystalline sorption. For example sorbates in col. 1 are occluded rapidly, but those in col. 2 are only slowly occluded and with a great diversity of velocities even *inter se*. Thus in mixtures of such species it is possible to obtain separations by partial molecular-sieve action.

Separations have been carried out both by exposing the mixture to the zeolite in a static system or by gaseous or liquid chromatography.[1, 31] One sorbate is occluded and finally removed in the time interval during which the other constituent is still largely unsorbed. Partial or complete separations were found in the mixtures C_2H_6–C_3H_8 ; $CH_3 \cdot CN$–CH_2Br_2 ; $C_2H_5 \cdot OH$–CH_2Br_2 ; $C_2H_5 \cdot OH$–n-C_7H_{16} ; $CH_3 \cdot OH$–C_2H_5Br ; the molecule first mentioned being removed first. The most rapidly occluded molecules should preferably be more polar than those remaining. The more polar the sorbed molecule the greater the affinity between it and the zeolite tends to be. The affinity between sorbent and sorbate can exert a strong influence upon the intracrystalline sorption velocity,[25] as well as lessening the possibility of poisoning the sorbent by blocking of the intracrystalline diffusion paths by the bulkier and less mobile second component.

Scope of the Molecular-sieve Method.—The molecular-sieve method can be one of unusual power, which sometimes supplements other separation techniques. Mixtures may be resolved quantitatively which cannot be dealt with by distillation either because the species have practically the same boiling point (*n*-heptane and *iso*octane) or because azeotropic mixtures are formed (H_2O–$C_2H_5 \cdot OH$; $CH_3 \cdot OH$–$CH_3 \cdot CO \cdot CH_3$; H_2O–dioxan ; CS_2–$CH_3 \cdot CO \cdot CH_3$; $C_2H_5 \cdot OH$–*n*-heptane ; $C_2H_5 \cdot OH$–toluene). Many individual separations should be typical for groups of analogous compounds. For instance, mordenite removes methyl from ethyl alcohol and ought therefore to remove it from all alcohols. Ca- or Ba-mordenite, since they dry methyl and ethyl alcohol, or acetone, should dry all alcohols and ketones.

Selectivity in sorption shown by molecular-sieve zeolites is often the reverse of that normally shown in more open capillary structures such as silica gel. In gels porous on this more macro-scale the affinity between sorbate and sorbent often increases with increasing molecular dimensions for such homologous series as the paraffin hydrocarbons. In the gas-sorbing zeolites, on the other hand, the sorbate–sorbent affinity drops

sharply to zero once a certain limit in molecular size and shape is exceeded.

Possibilities already realised with mordenite of modifying the zeolites by cation interchange or in other ways, and so of altering the molecular-sieve behaviour as desired, raises the question of the availability of natural zeolites as raw materials. Except perhaps in the case of mordenite, large natural deposits are not known, so that practical developments must be limited until synthetic crystals can be made cheaply. Crystals of mordenite,[32] analcite,[33] harmotome,[34] and a chabazite substitute [21] have been successfully grown on a laboratory scale. Gmelinite, levynite, chabazite, gismondite, and other zeolites which may be valuable have not been prepared.

Molecular-sieve Properties of Membranes

Metals.—We have now to consider selective transmission of gases and vapours through compact membranes. Some metals act as total molecular sieves, being permeable to one or two gases, but to no others. In all such cases there is a specific interaction between the diffusing gas and the metal.

Transition metals often have the power of forming interstitial solid solutions with some elements of the first short series of the Periodic Table. These elements must be small enough to enter the interstices in positions where their co-ordination number may be either 4 or 6 (so called tetrahedral or octahedral sites). Such phases occur only when the radius ratio of non-metallic to metallic elements is about 0·6 or less, and when the difference in electronegativity between non-metal and metal is not too great. For instance, though hydrogen, carbon, and nitrogen form a considerable number of these phases, oxygen forms only a few, and fluorine does not form any.[35]

The interstitial atoms often show considerable mobility within the metal, and if the metal is in the form of a membrane an atmosphere of the alloying * gas may be transmitted through it from the high- to the low-pressure side.[36] The rate of permeation is not usually large, but such membranes have been suggested as slow controlled leaks for hydrogen (using palladium) or for oxygen (using silver).[37] No other gases are trans-

[32] R. M. Barrer, *J.*, 1948, 2158.

[33] Cf. *idem*, *Trans. Faraday Soc.*, Discussion on Crystal Growth, 1949, No. 5, 326.

[34] *Idem*, unpublished data.

[35] For two discussions of properties of these phases, see R. E. Rundle, *Acta Cryst.*, 1948, **1**, 180, and R. M. Barrer, *Trans. Faraday Soc.*, Discussion on Physical Chemistry of Metallurgical Processes, 1948, No. 4, 68.

[36] A discussion of the solution and diffusion of gases in metals will be found in C. Smithells, " Gases and Metals ", Chapman & Hall, 1937 ; and in R. M. Barrer, " Diffusion in and through Solids ", C.U.P., 1941.

[37] E. L. Jossem, *Rev. Sci. Instr.*, 1940, **11**, 164.

* The term " alloy " is in many ways an appropriate description of these interstitial solid solutions, because they retain metallic conductivity, often show super-conductivity, and have a metallic lustre. Moreover, as in many alloys, the composition of the phase may vary continuously within limits. The nature of the bond has received considerable attention.[35]

mitted by these metals. Similarly, iron transmits both hydrogen and nitrogen, under conditions where the corresponding interstitial phases form.

There are two experimental procedures for studying the diffusion of gases in metals. In one, the metal is used in the form of a hollow cathode. This method has hitherto been limited to the diffusion of hydrogen.[38] In the second procedure, one side of the metal membrane is exposed to the gas at high temperature, the other side being maintained under a near-vacuum. In the electrolysis method surprisingly rapid transmission may
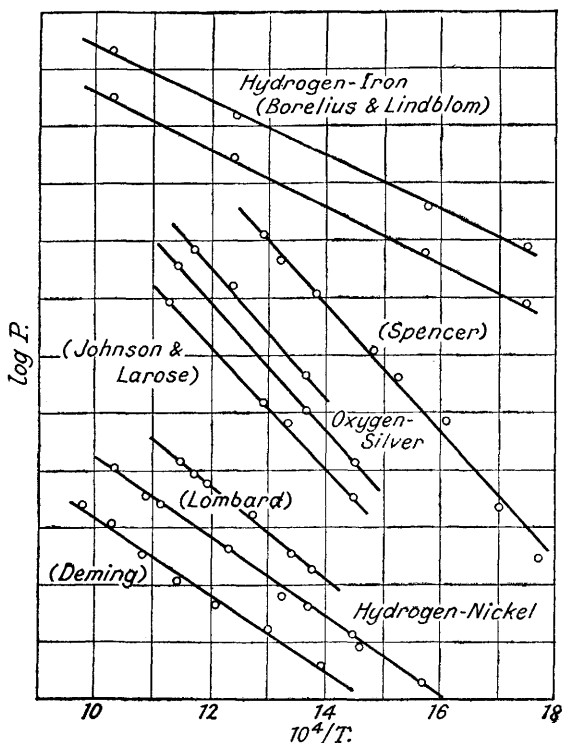

FIG. 10

Exponential increase in permeation velocity, P, with temperature $(P = P_0 e^{-E/\mathbf{R}T})$
[*Reproduced by permission from Barrer, " Diffusion in and through Solids ", C.U.P., 1941, p. 164.*]

occur even at room temperatures, but in the thermal method temperatures upwards of several hundred degrees Centigrade are necessary.[39, 36] Permeation velocities increase exponentially with temperatures (Fig. 10),[40] and some typical permeability constants are given in Table VII.[41] The non-

[38] *E.g.*, M. Bodenstein, *Z. Elektrochem.*, 1922, **28**, 517 ; G. Borelius and S. Lindblom, *Ann. Physik*, 1927, **82**, 201, and see also ref. (36).

[39] R. M. Barrer, *Trans. Faraday Soc.*, 1940, **36**, 1235.

[40] *Idem*, ref. (36).

[41] The data are taken from Barrer, ref. (36), Table 42.

metallic element always diffuses in the form of atoms, so that sorption of diatomic molecules is preceded by dissociation. The essential features of the diffusion process may be illustrated by a diagram in which characteristic periodic variations of energy are shown as a function of the positional co-ordinate of the diffusing species relative to the membrane (Fig. 11).
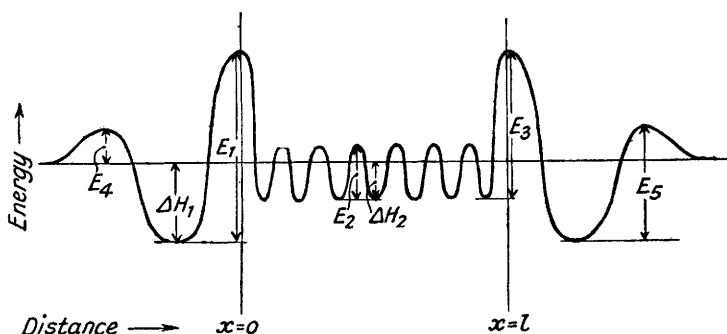

FIG. 11

A diagrammatic representation of energy relations in diffusion through a membrane bounded by the planes $x = 0$ and $x = l$.

Adsorption is an exothermal process, the heat ΔH being given by the depth of the trough in the potential-energy diagram just outside the surfaces of the membrane. E_1, E_2, and E_3 are very closely related * respectively to the energies of activation for penetration from the surface to a point just inside the metal, for " jumping " from one interstitial site to the next, and for passing from just within the surface to the surface itself. E_4 and E_5 are similarly related to the energies of activation for adsorption and desorption. The heat of occlusion is ΔH_2, and may be either positive or negative.

The phase-boundary reactions occurring with activation energies E_1 and E_3 are sensitive to modification in the nature and extent of the surface due to sintering or because of adsorbed films of foreign atoms.[36] The metal surfaces show some of the variability in activity which is shown by the same surfaces functioning as catalysts, as the data in Table VII illustrate.[41] Phase-boundary reactions may then become much slower than diffusion within the metal. Palladium shows extreme variations due to this cause.

A partial separation of isotopic species hydrogen and deuterium can be effected when these are simultaneously transmitted through palladium or platinum. On account of their different masses the isotopic atoms have in their interstitial environment different zero-point energies, that of the lighter element being the greater. For this reason energies of activation for diffusion, heats of solution and solubilities of the isotopes will differ.

* A more exact relation is : energy of activation = height of energy barrier minus the zero-point energy of the diffusing atom.

TABLE VII

Permeability constants, P, for several metallic membranes : $P = P_0 e^{-E/RT}$

System.	P_0 (c.c. per sec. per cm.² per mm. thick per atm. pressure).	E (cals./g.-atom).	System.	P_0 (c.c. per sec. per cm.² per mm. thick per atm. pressure).	E (cals./g.-atom)
H_2–Pd	$2 \cdot 3 \times 10^{-1}$ $3 \cdot 0 \times 10^{-2}$	4620 10,500	H_2–Cu	$2 \cdot 3 \times 10^{-3}$ $1 \cdot 5 \times 10^{-3}$	16,600 18,700
H_2–Ni	$1 \cdot 3 \ \ \times 10^{-2}$ $0 \cdot 85 \times 10^{-2}$ $1 \cdot 4 \ \ \times 10^{-2}$ $1 \cdot 05 \times 10^{-2}$ $1 \cdot 44 \times 10^{-2}$	15,420 13,860 13,800 13,400 13,260	H_2–Pt	$1 \cdot 41 \times 10^{-2}$ $1 \cdot 18 \times 10^{-2}$ $2 \cdot 6 \ \ \times 10^{-2}$	19,600 18,000 19,800
			O_2–Ag	$3 \cdot 75 \times 10^{-2}$ $2 \cdot 06 \times 10^{-2}$	22,600 22,600

In the steady state, and for a simple diffusion through a membrane into a vacuum in absence of slow phase boundary processes,

$$P_H/P_D = D_H C_H / D_D C_D$$

where the P's, D's, and C's are respectively permeability, diffusion coefficients, and concentrations just within the ingoing surface. Some experimental values of P_H/P_D for platinum [42] and palladium [43] are given in Table VIII.

TABLE VIII

Permeability ratios for hydrogen and deuterium

System.	P_H/P_D.	Temp.	Analytical expression for P_H/P_D.	System.	P_H/P_D.	Temp.	Analytical expression for P_H/P_D.
H_2–Pt	1·55 1·50 1·35 1·36 1·27	550° 650 750 850 950	$e^{680/RT}$	H_2–Pd	1·84 1·40 1·36 1·24	20° 106 131 186	$0 \cdot 6 e^{660/RT}$

Silica and Silicate Glasses.—Membranes of silica glass transmit helium, neon, and hydrogen and to a lesser extent oxygen, nitrogen, and argon. The diffusion process occurs without dissociation of the diffusing molecule and without specific interaction between gas and membrane, as is the case when gases diffuse in metals.[44] Selectivity is considerable, but total molecular-sieve action does not occur (Table IX). The diffusing molecules

[42] R. Jouan, *J. Phys. Radium*, 1936, **7**, 101.
[43] A. Farkas, *Trans. Faraday Soc.*, 1936, **32**, 1667.
[44] For a discussion, see R. M. Barrer, ref. (36).

TABLE IX

Relative permeabilities of silica glass at 900°

Gas	He.	H₂.	Ne.	N₂.	A.	O₂.
Relative permeability * .	100	18	3·3	2·6	1·6	—
Apparent energy of activation (cals./g.-atom or g.-mol.)	5600	10,100	9500	29,900	32,100	31,200

* There are considerable differences between permeabilities obtained when using different examples of silica glass.[44]

or atoms move in channels which sheathe them very closely.   In silicate glasses the diffusion paths become still more restricted and possibly fewer in number, as indicated by a rising energy of activation or decreasing permeability towards helium (Table X).   The apparent energies of activation in Tables IX and X are probably very nearly true energies of activation because the heats of solution of the gases, in silica glass at least, are very small.[45]

TABLE X

Relative permeabilities towards helium of some silicate glasses at 300°

Glass.	Relative permeability.	Apparent energy of activation (cals./g.-atom or g.-mol.).
Silica	100	5700
Pyrex	12·1	8700
Soda glass (283°).	0·31	—
Lead glass (283°) . . .	0·117	—
Jena 16ᴵᴵᴵ	0·114	8720
Thuringian glass	0·027	11,200

True and apparent energies of activation for intracrystalline diffusion in various zeolites are recorded in Table XI.[26, 25]   By contrast with some silicate glasses and zeolites, helium cannot under any conditions diffuse through metals, and in increasing order of openness of diffusion paths we may write the series :

Metals < silicate glasses < silica glass < levynite, mordenite < chabazite

In all these systems the diffusing species move entirely within the range of action of the interatomic forces of the solid.   The condition described by equation (3) (in which diffusion occurs in part as above and in part as a molecular streaming) requires appreciably wider channels.

[45] G. A. Williams and J. B. Ferguson, *J. Amer. Chem. Soc.*, 1924, **46**, 635 ;   H. Wüstner, *Ann. Physik*, 1915, **46**, 1095.

TABLE XI

*Some true and apparent energies of activation for
intracrystalline diffusion in zeolites*

Crystal.	Diffusing gas.	True activation energy (cals./g.-mol.).	Apparent activation energy (cals./g.-mol.).
Chabazite : Natural crystals	C_3H_8	—	4500 ; 6700
	$n\text{-}C_4H_{10}$	—	8900 ; 8600
	$n\text{-}C_5H_{12}$	—	7100 ; 6800
	$n\text{-}C_7H_{16}$	—	11,100 ; 11,400 ; 9600
	$C_2H_5 \cdot CN$	—	5900
	$H \cdot CO_2Et$	—	7300
	$CH_3 \cdot CO_2Me$	—	$\sim 40,000$
Mordenite : Ba-rich crystals	N_2	6600	3500
	A	9800	4900
Ca-rich crystals	N_2	8100	1040
	A	11,500	—
Na-rich crystals	C_2H_6	—	4300
	CH_3CN	—	8300
	A	9300	—
	Kr	11,000	—
Li-rich crystals	A	7300	—
	Kr	7600	—
NH$_4$-rich crystals	A	7000	—
	Kr	9000	—
K-rich crystals	H_2	2500	—
	O_2	4400	—
	N_2	4800	—
	A	8400	—
	Kr	10,000	—
Levynite : Natural crystals	Ne	2600	—
	A	9400	—
	Kr	12,000	—

Organic Membranes.—Pronounced molecular-sieve effects arise when gases and liquids diffuse through organic foils. Some of these membranes, such as cellulose and some proteins, are largely crystalline ; others, including natural and synthetic elastomers, are normally amorphous. The elastomers provide an interesting new feature in the diffusion process, because individual molecules of the elastomer possess considerable flexibility and (within limits) mobility, which play an important part in the diffusion of solutes within the medium. Each unit diffusion process is believed to involve not only the solute molecule but also segments of polymer chains adjacent to the solute, in a zone of activation in which

co-operative movements of polymer segments and solute result in a successful place change of the solute molecule.[46, 47]
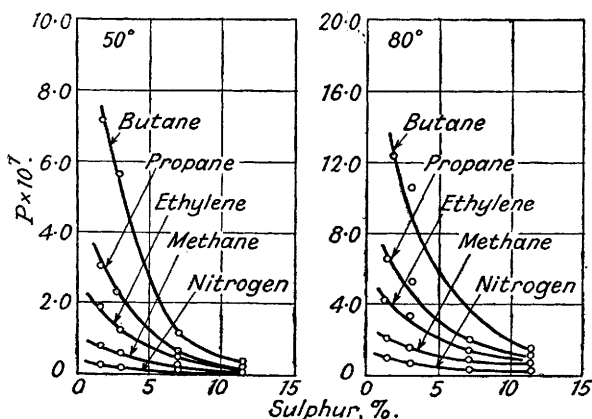

FIG. 12

Permeability constants of some hydrocarbons in natural rubber vulcanisates (P in c.c. of gas at N.T.P. passing per second through 1 cm.² of membrane 1 mm. thick under a pressure difference of 1 cm. of Hg).

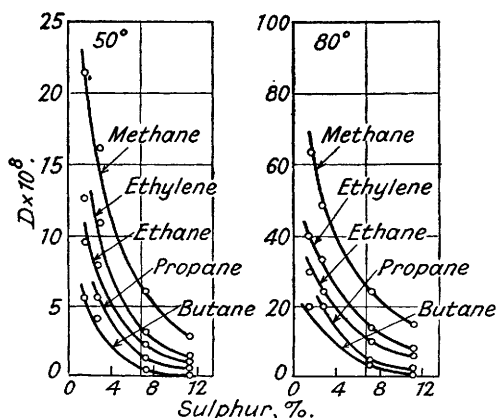[*Reproduced by permission from* J. Polymer Sci., 1948, **3**, 554.]

FIG. 13

Diffusion coefficients of some hydrocarbons in natural rubber vulcanisates (D in cm.²sec.⁻¹).

[*Reproduced by permission from* J. Polymer Sci., 1948, **3**, 554.]
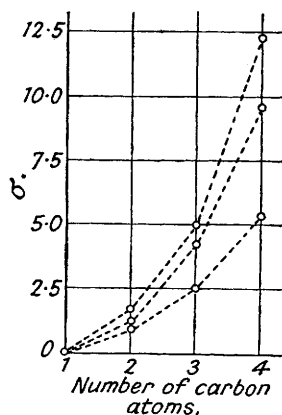

FIG. 14

Solubility constants, σ, for some hydrocarbons in a rubber vulcanisate containing 1·7% of combined sulphur. The upper curve was obtained at 40°, the middle curve at 60°, and the lowest curve at 80°. σ is measured in c.c. at N.T.P. dissolved in 1 c.c. of rubber at 1 atm. pressure.

[*Reproduced by permission from* J. Polymer Sci., 1948, **3**, 566.]

[46] R. M. Barrer, *Trans. Faraday Soc.*, 1939, **35**, 628.
[47] R. M. Barrer and G. Skirrow, *J. Polymer Sci.*, 1948, **3**, 549, 564.

It is interesting to trace the effects of systematically reducing the flexibility and mobility of elastomer chains upon the permeability of a group of solute molecules which are themselves of regularly increasing molecular volume.   Cross-linking by vulcanisation was used to reduce the mobility of elastomer chains, and the n-paraffins from methane to n-butane were used as solutes.   Several of the effects observed are illustrated in Figs. 12, 13, and 14.   There was no marked change in the *solubility* of a given hydrocarbon as the amount of combined sulphur increased, but the *diffusion* coefficients decreased steadily, and the decrease was greatest for the solute of greatest molecular volume.[47]

TABLE XII

Relative permeability (P) *and diffusion coefficients* (D) *at* 40°

Gas.	Natural rubber (1·7% combined S).		Natural rubber (11·3% combined S).	
	Relative P.	Relative D.	Relative P.	Relative D.
N_2	1·00	100	1·00	100
CH_4 . . .	2·90	73	2·17	—
C_2H_6 . . .	7·4	27	4·16	15·5
C_3H_8 . . .	13·0	17	3·46	4·95
n-C_4H_{10} . . .	31·8	17	10·2	4·41

Typical relative permeability and diffusion coefficients are shown in Table XII.   The relative value of P is proportional to the product of the diffusion coefficient, D, and the solubility constant.   The solubility constant increases rapidly with increasing molecular weight of the paraffin (Fig. 14), whereas D decreases (Fig. 13), so these two effects influence the permeability constant in opposite senses.   The net effect is, however, that P becomes larger as the molecular weight of the diffusing hydrocarbon becomes greater (Fig. 12).   However, increasing the combined sulphur in the rubber decreases D proportionately more for higher molecular-weight paraffins, while leaving the solubilities largely unaltered.   Hence the molecular-sieve action towards the paraffins, as measured by the relative value of P, becomes smaller in the vulcanisate of larger combined sulphur content.

On the other hand, for the permanent gases, where the solubility constants are all of the same order, P usually decreases with increasing molecular weight.   In this case the molecular-sieve action of the rubber towards the gases increases as combined sulphur content of the vulcanisate increases (Table XIII).[48]   Clearly, in ebonite, a highly cross-linked three-dimensional network, molecular dimensions exercise a dominant influence.   As a final example of selective transmission one may give some relative permeabilities towards polar and non-polar gases of foils of celluloid, rubber, and gelatin (Table XIV).[49]   The greater permeability towards polar gases is due to their much larger sorption in the polar media.   Natural-rubber membranes normally contain polar impurity such as protein.[50]

[48] R. M. Barrer, *Trans. Faraday Soc.*, 1940, **36**, 644.   [49] *Idem*, ref. (36).
[50] C. Boggs and J. Blake, *Ind. Eng. Chem.*, 1926, **18**, 224.

TABLE XIII

Relative permeabilities of gases in rubber and ebonite

Gas.	Molecular diameter,* A.	Relative permeability in low-sulphur rubber at 25°.	Relative permeability in high-sulphur rubber (ebonite) at 67°.
He	~ 2·2	100	100
H_2	3·0	161	30·0
N_2	4·08	25·8	0·53

* For N_2 and H_2 the distances of closest approach in the crystals are given.

TABLE XIV

Relative permeabilities towards polar and non-polar gases

Gas	O_2.	H_2.	CO_2.	SO_2.	NH_3.
Membrane { Celluloid . . .	100	247	898	—	6160
Rubber . . .	100	286	906	2500	3600
Gelatin . . .	100	100	413	3190	9520

Molecular-sieve Processes in Solution

Although it is not possible here to discuss in detail data on selective transmission of ions and dissolved species through solids, nevertheless some reference to the phenomena noted should be made.

Crystals and glasses are often highly selective in transmitting ions. Glass membranes functioning as hydrogen electrodes are normally regarded as permeable to hydrogen ions ; and other glasses may function similarly as sodium, potassium, silver, or zinc electrodes.[51] Membranes composed of clay crystallites can also function as electrodes reversible with respect to ions which they may take up by cation interchange.[52] Crystalline zeolites, ultramarines, sodalite–hauyne minerals, as well as amorphous zeolite gels such as " permutit " or " doucil ", also interchange cations comparatively freely.[53, 54, 55] Sometimes there is a high selectivity in these exchange reactions : analcite ($NaAlSi_2O_6,H_2O$) will exchange Na^+ for K^+ or NH_4^+ but not for Li^+, Cs^+, Ca^{++}, or Ba^{++} save to a minor extent ; leucite ($KAlSi_2O_6$) similarly exchanges K^+ for Na^+ or NH_4^+ but not for the other ions. Such selective exchanges indicate the possibility of preferentially

[51] See W. M. Clark, " Determination of Hydrogen Ions ", Baillière, Tindall & Cox, 1928, 3rd Edn., p. 430, for a summary of such observations.
[52] C. Marshall and C. Krinbill, *J. Amer. Chem. Soc.*, 1942, **64**, 1814 ; C. Marshall and W. E. Bergmann, *ibid.*, 1941, **63**, 1911 ; *J. Physical Chem.*, 1942, **46**, 527, 325.
[53] H. F. Walton, *J. Franklin Inst.*, 1941, **232**, 305.
[54] R. M. Barrer, International Colloquium on Reactions in the Solid State, Paris, Oct., 1948 ; *Bull. Soc. chim.*, 1949, Nos. 1 and 2, D.71.
[55] S. B. Hendricks, *Ind. Eng. Chem.*, 1945, **37**, 625.

interconverting sodium, potassium, or ammonium salts by hydrothermal chromatography.[53, 56]   Other zeolites, such as chabazite, or mordenite or zeolite gels, interchange a much greater diversity of cations.   Crystalline zeolites show cation interchange freely in the range 150—250° and less rapidly below 150° ; zeolitic gels, organic exchangers, and some clays, however, interchange ions freely even at room temperature.

Both organic and inorganic gel membranes may serve as ultra-filters for dissolved species whether ionic or non-ionic.   Membranes may therefore establish and maintain differences in potential, pH, or concentration between opposite faces.   They may bring about hydrolysis, effect dialysis, and permit also the establishment and measurement of osmotic pressures.   Reasons for the selective transmission giving rise to these effects may be considered.

Membranes which selectively transmit *cations* include : polyacrylic acid co-deposited with acetyl cellulose ; oxycellulose ; cellulose impregnated with dyes containing acid groups ; and to a lesser degree nitrocellulose and acetyl cellulose, which both contain some free carboxyl groups.   On the other hand, membranes may be prepared which contain both anionic and cationic groups, for instance, by condensation of triethanolamine and phthalic acid.   Here there are tertiary amino-groups and carboxyl groups.   In alkaline media, where the ionisation of the amino-groups is suppressed and that of the carboxyl groups promoted, the medium is cation-permeable.   However, if the tertiary amino-groups are converted into quaternary groups by reaction with methyl iodide the membrane is anion-permeable under all conditions.   Protein membranes are also amphoteric, and according to the pH of the solution they transmit anions (in acid media) or cations (in alkaline media).   Basic membranes sorb acid dyes, acid membranes sorb basic dyes.   Clearly, electrostatic forces govern in part the selective transmission in such systems.[57]   In membranes without ionisable groups and of very open character, the mobility of ions is substantially the same as in aqueous solution.   As the capillaries become more and more restricted the mobilities become increasingly different from their values in " free " transport.   In membranes which also contain ionisable groups these molecular-sieve effects may be superposed upon the further specificity due to electrostatic attractions or repulsions between charged groups in the organic network and the ions diffusing.   A quantitative interpretation of the over-all transmission is due to T. Teorell [58] and to Meyer and Sievers.[59]

The relative permeation velocity is N_c/N_a, where N_c and N_a are the numbers of cations and anions transmitted per unit time.   This ratio in the steady state depends on the product of the ratios U/V and C_c/C_a, where U and V are mobilities of cation and anion respectively, and C_c and

[56] S. Green and C. McCarthy, *Ind. Eng. Chem.*, 1944, **36**, 412.

[57] K. H. Meyer, " Natural and Synthetic High Polymers ", Interscience, 1942, p. 631.

[58] *Proc. Soc. Exp. Biol. Med.*, 1935, **33**, 282.

[59] Address to the Assoc. Chim. de Genève, 1935 ; *Helv. Chim. Acta*, 1936, **19,** 649, 665, 987 ; K. H. Meyer, H. Hauptmann, and J. F. Sievers, *ibid.*, p. 948.

C_a are the concentrations of cations and anions just inside the ingoing surface of the membrane. As an example one may consider an uni-ivalent electrolyte, which is fully dissociated. Let the concentration in the solution be C, and let X denote the concentration of non-diffusible fixed ionic groups in the membrane, expressed in g.-equivs. per litre of imbibed liquid ; X is a constant characteristic of the membrane at any one liquid content. Also, Y denotes the concentration of imbibed electro-lyte in g.-equivs. per litre of imbibed liquid. In a membrane where the fixed ionic groups are anionic, the concentration of diffusible anions is Y, and of cations $X + Y$. The Donnan membrane equilibrium condition yields *

$$C^2 = Y(Y + X)$$

which may be combined with the relation

$$N_c/N_a = U(Y + X)/VY = UC_c/VC_a$$

to give

$$\frac{N_c}{N_a} = \frac{U}{V} \frac{\sqrt{4C^2 + X^2} + X}{\sqrt{4C^2 + X^2} - X}$$

In this equation one sees separately the effect of the mobility ratio, and that of electrolyte concentration and concentration of fixed anionic groups, upon the permeability ratio.

According to the equation, as C becomes very small the network of the anionic membrane contains only diffusible cations and is permeable only to cations. At higher electrolyte concentrations both ions are transmitted.

Membranes with graded pore sizes have been prepared from cellulose nitrate or acetate. These membranes can be used in the separation and characterisation of colloidal particles, bacteria, and viruses.[60, 61, 62] The ester, dissolved in solvents such as acetone, was poured on to a suitable surface, and the solvent allowed partly to evaporate. The foil, still con-taining solvent, was further precipitated with coagulating agents such as dilute acetic acid. By varying the conditions of formation (nature of solvent, amount of solvent in partly dried film, and amount of coagulant), the texture of the porous membrane was altered and a series of graded ultra-filters obtained which transmitted particles of up to 500 mμ. in diameter. Such membranes must be stored in water to prevent the irre-versible shrinkage which would follow drying. Standard particles such as

[60] H. Bechold and K. Silbereisen, *Biochem. Z.*, 1928, **199**, 1 ; H. Bechold, *Kolloid-Z.*, 1934, **66**, 329 ; 1934, **67**, 66.
[61] F. Erbe, *ibid.*, 1932, **59**, 32 ; 1933, **63**, 277.
[62] W. J. Elford, *Trans. Faraday Soc.*, 1937, **33**, 1094.
* This equation, in terms of activities, should be written

$$C^2 = Y(Y + X)\gamma_c\gamma_a/\gamma_+\gamma_- = Y(Y + X)R$$

where γ_c and γ_a are the ionic activity coefficients of the imbibed ions, and γ_+ and γ_- are these coefficients in the surrounding electrolyte. The correction factor R may then be introduced.

hæmoglobins were employed to calibrate the membranes. It is considered
that the particles being separated should be more or less spherical and that
this molecular-sieve method is not suitable for separating chain polymers.