[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

A Copper Membrane Gas-Molecule Sieve. Callendar's Theory of Osmosis

BY D. L. WARRICK AND EDWARD MACK, JR.

For many years large numbers of investigators have been interested in experimentation and speculation not only on the general subject of the passage of liquids[1] through septa but also, ever since the time of Thomas Graham, on the retention of gases by porous solids, and the transpiration of gases and vapors through porous membranes. Without attempting to give an adequate picture of the present state of the literature in this extensive field, we may merely refer to McBain's monograph, "Sorption of Gases and Vapours by Solids," which includes a bibliography of about six thousand experimental and theoretical papers,[2] and to the recent work of McBain[3] and his students on cellulose and other substances, and to the work of Paneth and Peters[4] and Urry[5] on the permeability of glasses to helium and neon. The idea of attempting to find in nature, or to prepare in the laboratory, membranes of the proper porous structure to act as sieves for gas molecules, would appear to be feasible. For example, if the structure proposed by Astbury for *d*-tartaric acid is correct to the extent that tunnels actually run perpendicular to the 100 face into the crystal,[6] one might expect to find sieve properties in this crystal. Pauling has also suggested the probability of sieve characteristics in the zeolites,[7] and the presence of wandering "vagabond" atoms and molecules in the lattice of the ultramarines, demonstrated by Jaeger[8] and his collaborators, suggests further available porous working substances.

It is well known that zinc[9] can be selectively distilled from brass, and it occurred to the authors that a copper membrane possessing interesting sieve properties might thus be prepared. The present paper gives a

(1) For example, see Zsigmondy, "Colloid Chemistry (Alexander)," Vol. I, Chemical Catalog Co., New York, 1926, p. 944; Manegold and collaborators, *Kolloid-Z.*, **55**, 273 (1931), etc.; Bartell and collaborators, *J. Phys. Chem.*, **32**, 1553 (1928), and other papers; Michaelis, "Molecular Sieve Membranes," "Fifth Colloid Symposium Monograph," 1927, p. 135; *Natl. Research Council Bulletin*, **69**, 119 (1929); Manning, "The Preparation of Nickel Membranes for Ultrafiltration," *J. Chem. Soc.*, 1127 (1926); and many other papers by many other authors.

(2) J. W. McBain, "Sorption of Gases and Vapours by Solids," G. Routledge and Sons, Ltd., London, 1932.

(3) McBain, *Kolloid.-Z.*, **40**, 4 (1926); "Fourth Colloid Symposium Monograph," 1926, p. 11; "Persorption and Monomolecular Sieves," *Trans. Faraday Soc.*, **28**, 408 (1932); McBain and Kistler, *J. Phys. Chem.*, **33**, 1806 (1929); **35**, 130 (1931). See also Schmidt, *Z. physik. Chem.*, **133**, 263 (1928); Weigel and Steinhoff, *Z. Krist.*, **61**, 125 (1924); Tammann, *Z. physik. Chem.*, **27**, 323 (1898).

(4) Paneth and Peters, *Z. physik. Chem.*, **B1**, 253 (1928).

(5) Urry, THIS JOURNAL, **54**, 3887 (1932). See also, for example, in connection with organic membranes, Wertheimer, *Arch. ges. Physiol.* (Pflüger's), **209**, 493 (1925); Bauer, *ibid.*, 301 (1925); Hill, *Science*, **67**, 374 (1927); Alexejev and Matalskii, *J. chim. phys.*, **24**, 737 (1927); and many others.

(6) Astbury, *Proc. Roy. Soc.* (London), **A102**, 506 (1923).

(7) Pauling, *Proc. Nat. Acad. Sci.*, **16**, 453 (1930).

(8) Jaeger, *Trans. Faraday Soc.*, **25**, 320 (1929); and other papers.

(9) For example, the papers of Graves and Turner, *J. Chem. Soc.*, **101**, 585 (1912); Turner, *J. Inst. Metals*, **7**, 105 (1912).

description of the method of preparation of the porous copper membrane and of some of the results secured by testing its porosity to various gases and vapors.

Experimental

Preparation of Porous Copper Membrane.—Pieces (2.5 × 4 cm.) of shim brass about 0.0028 cm. thick were placed in a quartz tube (2.5 cm. diameter) inside a horizontal electric resistance furnace. The quartz tube was sealed, through a cold trap (solid carbon dioxide), to a mercury vapor pump and a McLeod gage. The usual vacuum which was maintained was about 10^{-4} mm. Different pieces of brass were heated at different temperatures ranging from 400 to 900°; and the zinc, which distilled from the brass and condensed in the quartz tube just outside of the furnace, was more or less completely removed from the brass during the course of a few hours or a few days, depending on the temperature. At intervals the furnace was moved slightly in such a way as to expose a new section of the quartz tubing to the cooling effect of the air. In this way the remaining zinc deposited out on an entirely clean surface, and the progress of the distillation could be watched very nicely. At the end of the distillation the copper membrane which was left in the furnace was removed, its loss of weight determined (in some instances a small piece of it analyzed for zinc), and then the membrane was tested for gas molecule porosity in a manner now to be described.

Determination of Membrane Porosity.—A circular piece of the copper membrane, about 15 mm. in diameter, was cut out and mounted[10] in a specially made pipe coupling. The two large-surfaced pipe ends, between which the copper membrane was interposed, were polished steel, and they could be drawn together with a heavy wrench in such a way that the copper membrane was held clamped athwart the pipe channel in an absolutely leak-proof manner. Each end of the coupling was then connected through a glass tubing spiral to a small gas reservoir of known volume, provided with a mercury manometer. Both sides of the apparatus were pumped out and always allowed to stand for an hour to prove that no leaks were present. The desired gas was then introduced into the high pressure reservoir and allowed to transpire through the membrane into the low pressure reservoir. The rate of gas transpiration was measured by reading both of the manometers, the one on the influx side of the membrane and the one on the efflux side. In this way a further convincing check on the absence of any leak in the system was available. The whole apparatus was set up in a constant temperature room. Quite satisfactory reproducibility of transpiration rates was obtained.

Results and Discussion

The following gases and vapors were employed to test the porosity of the membranes: air, hydrogen, oxygen, nitrogen, water, carbon dioxide, methane, ethane, *n*-pentane, *n*-hexane, ethyl ether, benzene. A typical transpiration run is given in Table I.

If no leakage, either in or out, occurs, the product of 26.8 cm. (the total high pressure drop) into 215.0 cc. (volume of high pressure side) should be equal to the product of 19.2 cm. (the low pressure increase) into 292.5 cc. (the volume of the low pressure side). This is approximately true, and becomes exactly true, within the limit of the experimental error, when the volumes are corrected for the shift in the position of the mercury meniscus of the two manometers.

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[10] See Schumacher and Ferguson, THIS JOURNAL, **49**, 427 (1927).

TABLE I

TRANSPIRATION OF AIR THROUGH COPPER MEMBRANE

Membrane No. 3, first piece

Volume of high pressure side, 215.0 cc.; low pressure side, 292.5 cc. Inside diameter of coupling, 7.94 mm. Temp., 25.5°.

Time, min.	High pressure, p_h, cm.	Low pressure, p_l, cm.	P, cm. $p_h - p_0$	$k = \ln (P_0/P)/t$
0	75.8	0.1	75.7	..
3	75.5	.25	75.35	(1.55×10^{-3})
5	75.2	.4	74.8	2.39
8	74.9	.6	74.3	2.33
12	74.5	1.0	73.5	2.45
15	74.2	1.2	73.0	2.42
20	73.75	1.6	72.15	2.40
28	72.85	2.25	70.60	2.33
38	71.85	3.0	68.85	2.49
50	70.7	3.8	66.9	2.46
60	69.8	4.5	65.3	2.46
73	68.6	5.3	63.3	2.45
103	61.3	10.3	51.0	2.42
192	59.4	11.9	47.5	2.43
220	58.1	12.75	45.45	2.43
242	56.15	14.2	41.95	2.44
338	51.3	17.6	33.7	2.41
394	49.00	19.3	29.7	2.48
			Av. =	2.42×10^{-3}

It will be noted, in the last column of the table, that the constancy of the transpiration constant is good. This is typical of nearly all of the tests with other membranes and other gases. The fact that the equation $-\mathrm{d}P/\mathrm{d}t = kP$, where P is the pressure difference on the two sides of the membrane $(p_h - p_l)$, holds throughout the whole course of the transpiration means that the flow is *molecular* and not *viscous*. This is indeed to be expected since the mean free paths of the gas molecules, even at atmospheric pressure, are certainly much larger than the effective diameters of the pores in the copper membrane.

Different test pieces cut from the same membrane sample sometimes showed distinctly different porosities, although they always lined up in the same order with respect to porosity to different gases. For example, in Table I, the "first piece" cut from Membrane No. 3 is tested. In Table II, the "second piece" cut from the same membrane will be observed to show a different porosity to hydrogen gas. The difference could hardly be due to variation in thickness in the shim brass, although micrometer measurement showed that this sometimes amounted to several per cent. The thickness of the copper membrane after distillation of the zinc was the same, as nearly as it could be measured, as that of the original brass foil. The differences in porosity within a given membrane sample are probably to be accounted for in terms of slightly different furnace conditions around the sample during preparation. Table II indicates the general effect of the time and temperature of furnacing on the porosity characteristics of the membrane.

TABLE II

EFFECT OF TEMPERATURE AND TIME FACTORS ON POROSITY

Sieve no.	Furnace temp., °C.	Time of heating, hr.	Loss of wt., %	Av. *k* for H_2	Av. *k* for N_2
4	400	24	3.54	Not porous	
3 (first piece)	475	$26^1/_2$	26.0	5.64×10^{-3}	......
3 (second piece)	475	$26^1/_2$	26.0	2.14×10^{-3}	6.78×10^{-4}
2	500	2	..	Not porous	
9	550	$24^3/_4$	31.43	1.00×10^{-3}	2.54×10^{-4}
8	600	19	37.7	8.17×10^{-3}	5.21×10^{-3}
12	900	7	46.0	3.08×10^{-2}	8.96×10^{-3}

The brass employed for the preparation of the membranes was found, by chemical analysis, to contain 32.3% zinc. At the lower temperatures even prolonged distillation failed to remove all of the zinc. At the higher temperatures, in the range 600–900°, not only was the zinc removed, but also some of the copper, which could be seen to condense in the cooler part of the quartz tube, a little nearer to the furnace than the zinc. The membranes prepared at 600–900° were far more porous to the small molecule gases then membranes made at lower temperatures, and they would readily pass large molecules, such as benzene and ethyl ether, which the low-temperature membranes would not allow to pass at all. In Table III are listed the relative porosities to different gases, in terms of the transpiration constant, of a low-temperature membrane.

TABLE III

POROSITY TO DIFFERENT GASES OF LOW-TEMPERATURE MEMBRANE

Membrane No. 3 (475°), Second Piece

Gas	Average *k*	Loss in porosity to N_2, %
Nitrogen	6.78×10^{-4}	
Hydrogen	21.4	0
Carbon dioxide	6.67	0
Methane	8.80	0
Ethane	7.69	2
n-Pentane	2.86	65
Benzene	0	100
Ethyl ether	0	100

After our porosity testing technique had been standardized it was found desirable to employ nitrogen as a comparison gas, and to redetermine the porosity of the membrane to nitrogen after every exposure to any other gas, in order to discover whether any change might have occurred in the porosity characteristics of the membrane. This procedure worked very satisfactorily; and indeed it was found, as shown in Column 3 of Table III, that the larger molecule gases which transpire through the membrane with difficulty, or not at all, reduce the porosity. Very likely this is due to a partial clogging of the pores, or to adsorption at the surface of the membrane, or both. At any rate it was always possible to restore the membrane to its original condition by a vacuum heat treatment (for three hours) at 400°.

It is obvious from Column 2 of Table III that the smaller molecules transpire more readily then the larger ones, and that molecules above a certain size do not transpire at all.

Size of Pores

Microscopic observation (magnification 2700 diameters) fails to show the presence of any visible pore openings on the surface, even of the more highly porous copper membranes prepared at 900°. Since the transpiration, as already shown, is undoubtedly a molecular rather than a viscous flow, and since the equation for molecular flow would probably not hold as well as it is observed to hold unless the mean free path of the transpiring molecule is quite large compared with the average pore diameter, we are probably justified in assuming that the mean free path is at least *ten times* larger than the pore diameter. The mean free path for these gaseous molecules is roughly about 10^{-5} cm., and thus we may fix an upper limit to the pore diameter of approximately 10^{-6} cm., or 100 Å. Very likely the diameter is considerably smaller than this.

The fact that the gaseous benzene molecule, with a greatest distance of about 6 Å. across the ring,[11] fails to transpire through the membrane (Table III) in measurable amount might be taken as indication that the large pores have a diameter not much greater than 6 Å. Of course it is possible that the whole internal network of pores and tubes becomes lined with an adsorbed layer of benzene; and in that case, the actual diameter of the copper pores might be as large as 10–20 Å. without allowing benzene to pass through.

Dr. Herzfeld and Dr. Smallwood have given a detailed discussion of the kinetic theory of transpiration. It is interesting, in the present situation, to apply their Equation 307, which emerges from Knudsen's theory, and which gives the rate of flow in moles of gas:[12]

$$\frac{dn}{dt} = \frac{B'}{\sqrt{MRT}}(p_h - p_l)$$

Here, M is the molecular weight of the gas, and B' has the dimensions of an area and depends on the size and shape of the virtual tubes in the porous network of the membrane and not on the gas. Herzfeld and Smallwood cite the work of Graham upon the passage of gases through porous plates of gypsum and meerschaum in support of the above equa-

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[11] Mack, THIS JOURNAL, 54, 2141 (1932).

[12] Herzfeld and Smallwood, Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Co., New York. 2d. ed., 1932, p. 73.

tion. In Table IV the transpiration constants of Table III, obtained with a low-temperature copper membrane, are so treated that the rates of flow of the different gases may be compared with that of hydrogen, taken as unity; and so that the *observed* relative rates may be compared with those calculated from the above equation. It is to be noted that, in the Knudsen theory, the rate of molecular flow does not depend on the molecule cross-sectional area, and is inversely proportional to the square root of the molecular weight.

TABLE IV

OBSERVED AND CALCULATED RELATIVE RATES OF FLOW

Membrane No. 3, Second Piece

Gas	Average k	Molecular wt.	Observed rate (for H_2 set equal to 1)	Calcd. rate (for H_2 set equal to 1)
Nitrogen	6.78×10^{-4}	28	0.32	0.27
Hydrogen	21.4	2	1	1
Carbon dioxide	6.67	44	0.31	0.21
Methane	8.80	16	.41	.35
Ethane	7.69	30	.36	.26
n-Pentane	2.86	72	.14	.17

It is a little disturbing to note, in Table IV, that the observed relative rates (with the exception of pentane) are *larger* than those calculated. If it were the other way around, one might possibly find a plausible explanation in terms of the entrance of the factor of molecule cross-sectional area, in these excessively small pores. It would seem either that the rates of flow of nitrogen, carbon dioxide, methane and ethane are, for some reason, more rapid than they ought to be, or that hydrogen transpires more slowly than it should. In view of the relatively small accommodation coefficient of hydrogen, such a result is difficult to understand. On the whole, however, the agreement between calculated and observed rates is not bad, and is perhaps as good as one could reasonably expect in such a complicated structure of exceedingly small pores. The fairly satisfactory correlation between the last two columns of Table IV argues for a fairly uniform size of the gas channels. For, if there were a considerable dispersion of sizes among the pores which are actually large enough to pass hydrogen and the smaller molecules, we should expect the values for the large molecules of Column 4 to be much smaller relative to those of Column 5 (Table IV), than in the case of the small molecules; but such is not the case (with the exception of pentane).

In a membrane prepared at the *higher temperatures* (600–900°) the zinc atoms undoubtedly tear their way out of the brass lattice more violently than at lower temperatures, and this effect together with the partial volatilization of the copper and the probable realignment of internal structural features due to the play of surface tension and sintering forces would naturally lead to larger channels and to a more porous membrane.

It is interesting to indulge in a little speculation in a rough attempt to estimate the population of pores per unit area. For this purpose let us imagine that the porosity is due to a system of tiny cylindrical capillary tubes running from one face of the membrane to the other. If we take d, the average capillary diameter as 10 Å., and p_{h} as a pressure of one atmosphere and p_{l} as zero pressure, we may calculate the rate of flow of hydrogen in moles per second through a single capillary by using Knudsen's equation (Herzfeld and Smallwood, Equation 304)

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \pi(d/2)^2 \frac{4d}{3L} \frac{1}{\sqrt{2\pi MR}} \frac{p_{\text{h}} - p_{\text{l}}}{\sqrt{T}}$$

where L is the length of the capillary. Because of the probable tortuosity of the capillary channels we might do well to set L equal to about twice the thickness of the membrane, namely, 2×0.0028 cm. The calculation gives about 3.3×10^{-19} mole per second, or about 2.0×10^{-17} mole per minute, which is equivalent to about 1.2×10^{7} molecules of hydrogen per minute through a single capillary, or about 4.9×10^{-13} cc. at 76 cm. and room temperature. Now with Membrane No. 3 (Table III), about 0.54 cc. of hydrogen per sq. cm. of membrane per minute passed through when p_{h} was 1 atm. and p_{l} was zero ($k = 21.4 \times 10^{-4}$). It follows therefore that the number of capillaries per sq. cm. of membrane surface would have to be about 10^{12} to explain the observed rate of flow. This would mean about 10^{6} capillaries per cm., or capillaries of diameter 10 Å. spaced about 100 Å. apart. This seems reasonable enough. The volume of 10^{12} capillaries of this sort would be about 4.5×10^{-5} cc., or about one-sixtieth of the total volume of the membrane (1×0.0028 cc.). Since the volume occupied by the zinc atoms in brass of composition 32.3% zinc would probably be about one-third of the total, this means that roughly one-twentieth of the empty space vacated by the zinc atoms is formed into main artery channels large enough to allow passage to the gas molecules, while the rest of the spaces deserted by the zinc are too small, or too much like blind alleys, to play any part in conducting the gas through the membrane.

While there is, of course, a considerable latitude for choice of the capillary diameter, this simplified but fanciful picture may resemble the actual membrane structure, and leads in effect to the same porosity characteristics actually possessed by the membrane. The same calculation which has here been made for hydrogen flow could be made for any of the other gases. The only difference involved would be the different values of M; and the different calculated absolute rates of flow would be related to one another in the same manner as the relative rates in the last column of Table IV.

Further Experiments

It would be extraordinarily interesting if one could make a porous membrane by means of which it would be possible to separate, by direct sieving, small molecules from large molecules in the gas phase. We have attempted to do this for a mixture of hydrogen and benzene, and for nitrogen and benzene. But, unfortunately, the large benzene molecules, which will not pass through the membrane themselves, also stop the flow of the smaller molecules. When the temperature of the mixture is raised to 400° to drive off the adsorbed benzene molecules, which presumably are plugging the holes, flow begins again, but the membrane almost immediately develops macroscopic lesions and begins to leak. It would not seem impossible, however, to make a membrane which would resist degeneration at 400°, and which would thus be able to perform for mixtures of gas molecules of various assorted sizes the same function that palladium performs for a mixture of hydrogen and nitrogen (although we do not wish to commit ourselves to the view that palladium conducts hydrogen by the same mechanism as the porous copper membrane).

Essentially the same sort of porous membranes have been prepared by distillation of mercury from a dental amalgam, by the removal of water from massive $Al_2O_3 \cdot 3H_2O$,[13] and by the evaporation of various solvents from various cellulose ester[14] films. In the last case the size of the pores seems to be conditioned to a considerable extent by the size of the solvent molecules which escape from the cellulose ester film as it gradually dries out.

The authors have attempted, but so far without success, to carry out a reduction (of nitrobenzene) by generating hydrogen electrolytically at one face of the membrane, and allowing it to transpire through the membrane before coming into contact with the substance to be reduced, in contrast with the usual procedure of generating the hydrogen directly in contact with the reducible substance.

Osmosis

Callendar's Theory.—In his monograph on "Osmotic Pressure" Findlay[15] gives the essence of Callendar's theory of osmosis in the following words: "The semi-permeable membrane consists of fine capillaries which are not wetted by the liquids but which admit of the passage of vapour, or in other words the membrane is a vapour sieve. Since the pure solvent at one end of the capillaries has a higher vapour pressure than in the solution at the other end, distillation will take place from the solvent, and the vapour on passing through the capillary will condense on the surface of the solution. . . ."

We have thought that it would be intensely interesting to test out this theory with our porous copper membrane. For this purpose a membrane (No. 5, second piece) was interposed between water and a 2 *M* sucrose solution in an osmotic pressure apparatus in a constant temperature room.

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[13] Samples were very kindly supplied to us by Dr. F. C. Frary, of the Aluminum Company of America.

[14] Kindly furnished by Dr. Wm. Hale Charch, of the Dupont Cellophane Company.

[15] Findlay, "Osmotic Pressure," Longmans, London, 1913, p. 76.

The osmotic flow was rather slow, and it was found necessary to employ a glass capillary tube in which to observe conveniently the rise of the sugar solution. The *observed rise* over a period of several days was 2.36 cm. in twenty-four hours. The same membrane was then tested for porosity toward water vapor. From the transpiration constant (1.33×10^{-3}) and the known vapor pressures of the water and sugar solution (35.26 and about 32.29 mm. at 31.8°) and the area of the membrane exposed to osmotic flow (58 sq. mm.), the transpiration rate was calculated to be 1.36×10^{-3} g. of water per twenty-four hours. This is equivalent to a *predicted rise* in the capillary of 1.46 cm. in twenty-four hours. In the case of another membrane (No. 5, third piece) a porosity measurement *before* osmosis gave a predicted daily rise of 1.71 cm., that actually observed was 2.72 cm., and a porosity measurement on the same membrane *after* osmosis gave a predicted rise of 1.19 cm.

The observed and predicted rates of osmotic flow agree well enough to make it seem very likely that we have, in the case of porous copper, at least *one* semi-permeable membrane which may actually allow osmosis to occur by the mechanism suggested by Callendar.

The authors desire to express their appreciation to Dr. Saul Dushman of the General Electric Company for helpful suggestions made to us during the writing of this paper.

Summary

The preparation of a porous copper membrane by vacuum distillation of the zinc from thin sheet brass is described.

The porosity characteristics depend on the time and temperature of the preparation. It is shown that the transpiration of a gas through the membrane is a molecular rather than a viscous flow. Typical relative rates of transpiration are given for a number of gases through a membrane which will allow small molecules to pass through but is not porous to benzene and ethyl ether.

The pores, in a typical low-temperature membrane, are probably larger than 6 Å. and smaller than 20 Å. in diameter. A calculation gives the pore population as about 10^{12} per sq. cm.

Callendar's theory of osmosis is tested by interposing a copper membrane between water and a sugar solution. The agreement between the observed and predicted rate of osmotic flow is sufficiently good to make the Callendar mechanism seem plausible.

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