It has also been shown that the results of Whetham on the conductivity of potassium dichromate and those of Spitalsky on the catalysis of diazoacetic ester by chromate solutions are in substantial accord with the results from this investigation, and that the conclusion drawn by Spitalsky that his experiments indicated that the hydrochromate ion is not present in any considerable quantity in dilute solutions of chromic acid and potassium dichromate is an erroneous one.

In conclusion, I wish to thank Prof. A. A. Noyes for suggesting this investigation and for his ever-willing advice throughout its execution.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
Boston, September, 1907.

THE PERMEABILITIES OF COLLODION, GOLD BEATER'S SKIN, PARCHMENT PAPER AND PORCELAIN MEMBRANES.

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Received September 10, 1907.

Contents.

The object and scope of the investigation. Previous investigations. Apparatus. Method of measurement. The unit of permeability. The effect of changing the pressure upon the permeability of collodion, of gold beater's skin, of parchment paper, of porcelain. The results of the pressure experiment's and Poiseuille's formula. Permeability of collodion at different temperatures. Calculation to test the applicability of Poiseuille's fórmula. The effect of changing the temperature upon the permeability of parchment paper, of porcelain. Discussion of results and theory. Summary.

The Object and Scope of the Investigation.

Probably it will be conceded, without the presentation here of a summary, which, even if abbreviated until inadequate, would require too much space, that there are numerous theories, each accounting ingeniously for some of the facts included under the comprehensive title of osmotic phenomena and conflicting with others. One cause for the lack of unanimity of opinion on even the most fundamental propositions, such as the function of the membrane in an osmotic cell, is the number of unknown quantities in each single experiment. Unless we have a solvent, a solute, and a membrane, there is no osmosis in the ordinary sense of the term, but with all three present the number of possible interactions is large. It has seemed to the writer that results could be obtained, which might have an interesting bearing upon the problems of osmosis, by omitting the solute. The attention is thereby fixed on the function of the membrane.

My intention is to force a pure liquid (solvent) through several different membranes at different pressures and at different temperatures, and to force different pure liquids through one and the same membrane at different pressures and temperatures. After numerical values for these processes have been established, solutions may be put through the same treatment with some hope of elucidating valuable facts. It may be objected that the results obtained by "filtration under pressure" are different from those obtained by "dialysis", in fact Bechhold[1] in a recent article has shown to what extent this may be the case. But it by no means follows that results by "filtration" methods will be valueless in the interpretation of osmotic phenomena. The present article deals with the first division of the above program and contains an account of experiments upon the passage of water through collodion, gold beater's skin, parchment paper and porcelain at different pressures and temperatures.

Previous Investigations.—The literature bearing directly upon the specific problem, the passage of pure liquids through membranes at different pressures and temperatures, is not extensive. W. Schmidt[2] determined the rates at which water and several salt solutions passed through different animal membranes, at different pressures and temperatures. He made some interesting observations which at the same time illustrate the difficulty of securing concordant results in such work. For instance, he found that of two pieces cut from the same pig's bladder or pericardium of a cow, one would permit the passage of water three times as rapidly as the other. He found a marked difference resulted when he reversed a membrane and forced the water through in the opposite direction. In some cases the volume of water which passed in a given time was increased ten-fold by such reversal. He says this is not due to the internal structure but to differences in the tension upon the membrane, as put on its holder. Matteucci and Cima[3] in 1845 found similar differences in osmotic effects dependent on which surface of the skin of a frog, of an eel, and of other animals, was presented to the solution and which to the pure solvent. Schmidt found that a membrane allowed to dry out showed a lessened permeability in consequence. He varied his pressures only within narrow limits, in one series between 0.613 and 1.721 meters of water, and found that the amount of water driven through was almost but not quite, proportional to the pressure. He also varied the temperature within narrow limits, in one series between 11.8° and 24.8°. He inserted his values in Poiseuille's formula for the passage of liquids through capillary tubes, and having calculated new constants for the formula, decided that it applied. It would be rash to conclude from Schmidt's results alone, that the passage of liquids through animal membranes followed Poiseuille's law, as his apparatus was crude, his temperatures were calculated through a complicated series of corrections, his pressure and temperature ranges were small and his experiments few. A

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[1] Kolloidstudien mit der Filtrations methode. Z. physik. Chem., **60**, 257-318 (1907).

[2] Versuche über Filtrationsgeschwindigkeit verschiedener Flüssigkeiten durch thierische Membranen. Pogg. Ann., **99**, 337-88 (1856).

[3] Mémoire sur l'endosmose. Ann. chim. phys. **13**, [3], 63-86 (1845).

large part of Schmidt's work was upon solutions, the consideration of which does not come within the scope of this article.

Guerout[1] forced water through bladder, gold beater's skin and parchment paper membranes. Details as to his experimental methods are almost entirely lacking. He says that while the structure is doubtless something different, it is nevertheless possible to imagine all the capillaries in a membrane as prismatic tubes, perpendicular to the faces of the membrane. Making this assumption, and applying Poiseuille's formula, he calculated the average diameter of the pores in bladder as between 0.000014 and 0.000020 mm; in gold beater's skin as between 0.000008 and 0.0000175 mm, and in parchment paper as between 0.000021 and 0.000026 mm. He confirmed his results by forcing water through a bundle of fine steel wires, the open spaces in which he calculated, from microscopic measurements, to have an average cross section, between 0.0016 and 0.0033 sq. mm., while the cross section, calculated from results obtained by forcing water through, was 0.0025 sq. mm. Again, using a layer of sand, microscopic measurement gave an average cross section of 0.0004 for the interstices while the rate for passage of water gave 0.0002 sq. mm.

Pfeffer[2] gives a too brief account of his results obtained by forcing water through one of his copper ferrocyanide cells under pressures which were varied between 37.8 and 210.2 cm. of mercury. He gives only the pressures and the quotient obtained by dividing the quantity of water which passes per unit of time by the corresponding pressure. This quotient is so nearly constant that it proves the direct proportionality between pressure and amount passing, but as he did not include the temperature, the dimensions of the cell and the volumes of water, one cannot form an idea as to the absolute values, nor institute comparisons with other work.

Sebor[3] made the usual copper ferrocyanide membrane in a Pukall porcelain cup and determined the rate at which water passed through at 18°, varying the pressure from 4 to 23.2 cm. of water. The six observations which he made show the volumes passing to be nearly directly proportional to the pressure, through this narrow range. He made another cell according to Morse's directions[4] and states that this does not permit the passage of water appreciably in 24 hours; but his pressure was low. The rest of his experiments were upon solutions.

[1] Sur les dimensions des intervalles poreux des membranes. Compt. rend., 75, 1809-12 (1872).

[2] "Osmotische Untersuchungen". Leipzig, 70-72 (1877).

[3] Ueber die Diffusionsgeschwindigkeit von Wasser, durch eine halbdurchlässige Membran. Z. Elektrochem., **1904**, 347-53.

[4] Morse and Horn. Am. Ch. J., **26**, 80-86 (1901). Morse and Frazer. Ibid., **28**, 1-23 (1902).

Bechhold[1], in an article which reached the writer just as this communication was about to be sent to the printer, gives a few measurements on the passage of water through acetic-acid-collodion and other gelatinized membranes. He touches upon this branch of the subject only long enough to call attention to the desirability of securing exactly the series of measurements, under simplest possible conditions, which are included in my program. His object is to determine what separations, as between emulsions, colloids, and crystalloids and their solvents, can be effected by filtration under pressure through membranes. The holder which he uses for his membranes is similar to mine.

Apparatus.—In a previous article[2] the results of experiments on collodion membranes with pressures between 50 and 250 mm. of mercury, and at temperatures between 1° and 35° were given. Wishing to increase both of these ranges considerably, and also to make direct comparisons between different membrane materials, under conditions as nearly identical as might be, the apparatus shown in Figure 1 was constructed. It is simple yet adequate, and is almost entirely free from a liability to errors due to unperceived leaks.

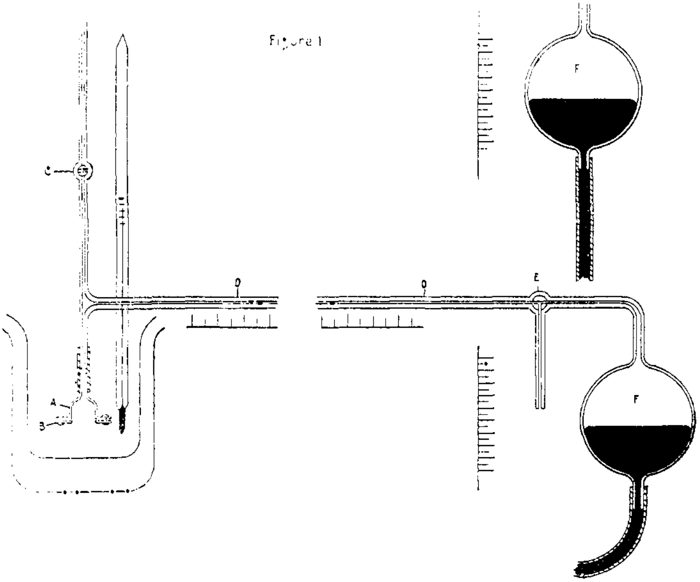
Figure 1

A flat membrane of the material to be studied closes the 15.0 mm. in diameter opening of the brass holder A and is held in place by the stout ring B, which is drawn up tightly by three screws[3]. The metal bearing on

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[1] Loc. cit.

[2] This Journal. November 1907.

[3] In principle this holder is the same as the "osmometer" described by Raoult, Z. physik. Chem., 17, 737 (1895); and Compt. rend., 121, 187.

the membrane is wide to obviate leaks sidewise. The holder is attached to the vertical glass tube by means of thick rubber tubing of the best quality, wired on and wrapped in sheet copper to prevent stretching when pressure is applied. This joint is eminently satisfactory even under the highest pressures used. D is a capillary tube in which the volumes passing through the membrane are measured. It is placed horizontally in order to avoid the necessity of correcting the pressure for different heights of water[1]. It was calibrated by weighing out with mercury; at 20° one millimeter length contained 7.68 cu. mm. plus or minus 0.08 cu. mm., that is the variations in bore involved an error of about one per cent. and other errors of the method exceeded this. The mercury pressure bulbs F, F. were chosen of good size, 10 cm. in diameter, in order that the small changes in volume, occurring in the course of an experiment, should not materially alter the pressure. The lower bulb was fixed permanently in place, the other was raised and lowered by a pulley and cord. A layer of water on the mercury in the lower bulb eliminated any possible error by evaporation from the meniscus in the capillary. Millimeter scales were placed immediately behind the capillary and between the mercury bulbs. The readings, to the tenth of a millimeter, were made by two cathetometer telescopes at a distance of 1.75 meters from the apparatus. The holder and membrane were immersed in water contained in a beaker which was wrapped in flannel and held in a larger beaker, except when heat was being applied directly. The bulb of a thermometer was in the water close to the membrane. The water was stirred frequently.

Method of Measurement.—Having filled the membrane holder and vertical tube to above the stopcock C, and the capillary nearly to the end of the scale toward the pressure bulbs, with water, the pressure, previously adjusted by raising the movable bulb, was applied by turning the three-way stopcock E. The water was forced through the membrane and the meniscus travelled along the millimeter scale. By means of a stop watch the seconds required for the meniscus to move a given number of millimeters were determined. This interval was usually 10 mm., sometimes it was 50 or 100, occasionally only 2 or 3, depending upon the rapidity with which the water passed out. Sometimes this method was reversed and the number of millimeters traversed by the meniscus in a definite time was measured. The times and distances were selected of such lengths that the errors of observation should be about one per cent.,

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[1] Flusin, Compt. rend., **126**, 1497 (1898); Ibid., **131**, 1308 (1900), Ibid., **132**, 1110 (1901) used a horizontal tube in connection with Raoult's "osmometer" in determining rates of osmosis. It may not be superfluous to call attention to the fact that Raoult and he were measuring the rate at which one liquid passed through rubber and other membranes to a different liquid, not the rate at which a mechanical pressure drives a liquid through a membrane bathed by the same liquid on each side. This article is confined to the latter process.

certainly not more than two per cent. of the values. An interval clock materially aided in measuring the time correctly, for the eye was at the telescope and the position of the meniscus was read when the bell rang. The apparatus as thus set up has a wide range of possible applications.

The Unit for Expressing Results.—The effort was made to approximate, as nearly as possible, to an absolute measure of permeability. The volume passing, and the time, were determined directly; the area of the membrane would be known accurately from the diameter of the orifice in the holder, (15.0 mm.) only the membrane stretches under the influence of the pressure and becomes convex. By lowering the mercury bulb until the pressure is reversed, this convexity is reversed and the contents of this lens of water is forced into the capillary where the volume may be measured accurately. Knowing the diameter and the volume of a lens and assuming a regularity of curvature, the surface area may be calculated This correction, however, has not been applied to the results given in the following tables.

The number of cubic millimeters which pass through one square centimeter of membrane in one minute was adopted as the unit of permeability and this value is denoted by M in the tables and curves[1].

Permeability of Collodion at Different Pressures.—Table 1 contains the results of four series of experiments determining the rates at which water was forced through a collodion membrane by different pressures, the temperatures being maintained nearly constant. The first column contains the pressures in millimeters of mercury, the second the distance through which the meniscus in the horizontal capillary tube travelled in one minute. Three or more separate observations were made and if they agreed fairly well together the average was taken as the final result[2].

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[1] The thickness of the membranes, both dry and wet, was measured with a micrometer caliper, before and after experiments, as described in a previous article. The method gives a general idea of relative thicknesses but is not satisfactory, for it does not furnish data to reduce the experimental values to a common unit. Therefore the permeabilities are not "absolute", desirable as it would be to have them so.

[2] As an illustration take the second value in Experiment 6. The following are the laboratory notes from which this was calculated:

Temp.	Level of mercury in upper bulb	Level of mercury in lower bulb	Pressure	Average	Position of meniscus at start	Position of meniscus at end	Time	Seconds for 1 mm.
17°.6	162.3	70.7	91.6		299.0	279.0	7′55″	23.8
	160.7	70.8	89.9	90.6	265.0	255.0	3′44″	22.4
17°.8	160.3	70.6	89.7		252.0	242.0	3′56″	23.6

This was considered a satisfactory agreement and the average value of 2.567 mm per minute was calculated and inserted in the table. Multiplying this by the factor, obtained by calibrating the capillary, to convert distance into cubic millimeters, and by the factor to reduce the area of the membrane to one square centimeter, gave 11.39 as the value for M, the number of cubic millimeters which passed through one square centimeter in one minute.

TABLE 1.

COLLODION MEMBRANE NO. 6. PRESSURE VARIED.

Pressure	Mm. per minute	Temperature	M.
Exp. 3[1].			
197.5	5.971	18°.3	26.49
605.8	20.34	18°.3	90.22
Exp. 4.			
204.9	6.717	17°.2	29.80
612.4	19.78	17°.8	87.72
324.0	10.72	18°.0	47.52
Exp. 6.			
60.8	1.793	17°.	7.95
90.6	2.567	17°.7	11.39
132.8	3.637	18°.0	16.14
181.4	4.991	18°.1	22.14
228.2	6.266	18°.4	27.79
320.6	8.956	18°.6	39.72
415.9	11.43	18°.7	50.70
Exp. 7.			
323.6	9.378	19°.9	41.59
415.7	11.94	19°.7	52.97
517.9	14.76	19°.6	65.45

After experiment No. 7 the thickness of the wet membrane was measured. The thinnest portion was in the center, the smallest micrometer reading being 0.065 mm; the thickest portion was at the circumference, close to the holder, the largest reading being 0.105 mm. Five days elapsed between Experiments 3 and 7. The reasonably good agreement shows that subjecting the membrane to considerable changes in pressure produced no material alteration in it. Comparisons between experiments are best made by reference to Figure 2, page 1686, where the results have been plotted, pressures on the abscissa and permeabilities, values for M, on the ordinate. The curves are numbered to correspond with the experiments.

Table 2 contains the results obtained with another collodion membrane. This was cut out of the center of a sheet membrane made by pouring the collodion onto a surface of clean mercury, a method for making them which gave membranes more uniform in thickness than when the collodion was poured onto plate glass. The membrane remained in distilled water for several days before it was used. Numerous measurements of thickness where made on the sheet from which the membrane had been cut; the smallest was 0.235 mm; the largest, 0.265 mm. After the experiments had been completed, the thinnest part of the membrane was found to be 0.065 mm., the thickest part 0.100 mm. Relatively little of the thinning was due to increase in area, for the convexity did not exceed one-tenth

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[1] The laboratory note book numbers for the experiments are retained as they give the order in which they were made. The individual values in the tables are also given in the order in which they were obtained.

the diameter. Apparently the water which it originally contained was squeezed out of it, as if it had been a sponge, and hence the thinning. That this analogy is justifiable was proved by the following simple experiment. A strip of collodion membrane was wiped dry on both sides with a pocket handkerchief and was then pulled and stretched, whereupon there immediately appeared, on both surfaces, a multitude of minute globules of water.

TABLE 2.

COLLODION MEMBRANE NO. 12. PRESSURE VARIED.

	Pressure	Mm. per min.	Temperature	M.
Exp. 9.				
	115.0	0.587	19°.0	2.602
	215.8	1.271	19°.4	5.636
	310.6	1.880	19°.4	8.341
	412.1	2.646	19°.5	11.73
	521.1	4.151	19°.5	18.41
Exp. 10.				
	519.4	3.043	19°	13.50
	621.7	3.628	19°	16.09
	722.6	4.390	19°	19.47
	834.3	5.218	19°.2	23.14
	527.0	3.273	19°.3	14.52
	327.4	2.023	19°.3	8.973
	326.3	1.969	19°.3	8.734
	113.2	0.7285	19°.3	3.230
Exp. 11.				
	117.	0.7052	18°	3.127
	306.	1.891	18°.2	8.389
	517.3	3.232	18°.2	14.35

Six days elapsed between Exp. 9 and Exp. 11.

It appears safe to conclude from these results:—First, that fairly concordant results can be obtained with this apparatus and method and one membrane; second, that thin collodion membranes immersed in water remain unaltered as regards permeability long enough for repeated experiments; third, that subjecting collodion membranes to the relatively high pressure of 840 mm. of mercury does not materially alter their permeability. This is somewhat surprising, and not in harmony with the picture one has in mind of a capillary structure. It cannot be that they stretch and then gradually come back to their original condition, for the values in Exp. 10 were obtained in the order in which they appear in the table. A slight increase in permeability is noticeable at the lower pressures immediately after the high pressures, but it is too small to show in the curves of Figure 2.

A comparison of the two tables shows that collodion No. 6 was four to six times as permeable as collodion No. 12 under like conditions. Attempts were made to determine the cause of this. It cannot be due to difference in thickness, as there was practically none. A number of experiments were carried out with pyroxylin made by nitrating for different lengths of time, ten, twenty, forty and sixty minutes, cotton kindly furnished by Professor A. B. Stevens of the School of Pharmacy. The results were inconclusive and need not be given in detail[1].

Permeability of Gold Beater's Skin under Different Pressures.—Experiments 20 and 21 of Table 3 were carried out with a membrane of gold beater's skin[2]. The maximum thickness of the membrane, dry, before the experiments, was 0.030 mm., the minimum thickness was 0.025 mm; wet, after the experiments, the maximum thickness was 0.040 mm., the minimum 0.020 mm.

TABLE 3.

GOLD BEATER'S SKIN MEMBRANE. PRESSURE VARIED.

	Pressure	Mm. per min.	Temperature	M.
Exp. 20.				
	209.5	0.535	26°.5-26°.8	2.373
	397.0	1.442	26°.9-27°	6.396
	599.2	2.670	27°.2	11.84
	806.2	4.440	27°.3-27°.5	19.69
	207.6	0.765	27°.7	
Exp. 21.				
	198.	0.88	25°.5	3.903
	102.5	0.36	25°.5	1.597
	54.4	0.19	25°.6	0.8428
	150.1	0.60	26°.0	2.662
	251.0	1.06	26°.1	4.701
	351.0	1.44	26°.3	6.387
	450.9	1.82	26°.5	8.072
	550.7	2.28	26°.5	10.11

The values show a lower permeability than for collodion membranes No. 6 and No. 12, although the latter were between two and three times as thick, and although the temperature was higher during the gold beater's skin experiments.

Permeability of Parchment Paper under Different Pressures.—Parchment paper proved to be the most irregular and vexatious material investigated. While temperature and pressure were held constant, it altered continuously in such a way as to become less and less permeable. The following values for the constant pressure 214 mm. (temperature 26.8°) are given as an illustration. Column 1 gives the time in minutes which

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[1] A few qualitative experiments showed that the more completely the solvent alcohol and ether are allowed to evaporate before the membrane is immersed in water, the less permeable is the membrane. As was said in the previous article, Baranetzky (Pogg. Ann., 147, 195-245 (1872)) made the same observation, and the observed differences here are probably due, in the main, to this cause.

[2] Surgeon's Gold Beater's Skin Plaster made by J. Ellwood Lee Co.

elapsed from the first application of the pressure before the first reading was made. Column 2 gives the seconds required for the meniscus to move one mm. in the capillary. Column 3 gives the seconds which a movement of one mm. should require, calculated on the assumption that a direct proportionality exists between the elapsed time and the diminution in permeability, taking the second value, 16″.6 as the basis for the calculation.

1	2	3
13′.5	7″.9	9″.1
24′.5	16″.6	16″.6
52′.5	33″.8	35″.6
80′	50″	54″.5

What significance this close approximation to a direct proportionality has, is not evident[1].

That this diminished permeability is not due to any permanent change in the membrane, was proved as follows. A pressure of 592 mm. was applied to a membrane until the permeability had fallen to one-half its original value. The pressure was then taken off and the membrane remained for two hours under no pressure. At the end of this time the same pressure was again applied and the membrane showed its original permeability well within the limits of experimental error.

One might imagine that when subjected to a fairly high pressure the membrane would stretch, any capillary holes would increase in diameter, and it would be much more permeable thereafter at all pressures. The diminishing permeability at constant pressure flatly contradicts any such assumption. Moreover, a membrane which showed an initial permeability of 35 was subjected to a pressure of 205 mm. until the permeability had fallen to 5. The pressure was then raised and held at 814 mm. for some time and then reduced to 205 mm. again. Immediately after the reduction the membrane showed a permeability of 12, *i.e.* greater than just before the increase, but only about one-third of the original value.

A satisfactory explanation for the peculiar behavior of parchment paper has not been found. In order to institute some sort of comparison with other membranes, although for the above reasons it is almost void of quantitative significance, Table 4 is given, containing a few, out of a long series of values.

[1] The regularity with which the permeability falls off, and the fact that the falling off is far greater than anything observed with any other material, makes it highly improbable that the phenomenon is due to a mechanical stoppage of pores by solid particles. Indeed there was no indication of a clogging of any membrane by dust, which might be suspended in distilled water, and the preliminary experiments showed that the excessive precautions adopted by other investigators (Schmidt, Baranetzky, Loc. cit.) to remove such particles were superfluous.

TABLE 4.

PARCHMENT PAPER MEMBRANE. PRESSURE VARIED.

Exp. 17.

Pressure	mm. per min.	Minutes pressure had acted	Temperature	M.
213.9	1.07	92[1]	27°.2	4.745
407.2	5.00	6	27°.3	22.18
595.0	12.76	7	27°.3	56.59
814.5	21.95	5	27°.4	97.34
(205.0	2.10)			

Permeability of Unglazed Porcelain under Different Pressures—A disc was cut from an unglazed porcelain plate and it was given an even surface and thickness by rubbing on fine emery paper. Its maximum thickness was 2.70 mm., its minimum thickness 2.64 mm. It was put in the membrane holder with washers of dental rubber dam on each side[2].

Table 5 gives the values obtained. Plotted on the diagram Exp. 16 gives the rapidly ascending curve 16. In order to show the full course of the experiments within the limits of the figure, the values for M. were divided by four and curves (15) and (16) were obtained.

TABLE 5.

PORCELAIN MEMBRANE. PRESSURE VARIED.

	Pressure	Mm. per min.	Temperature	M.
Exp. 15.				
	234.0	25.86	21°.8	114.7
	126.0	15.46	21°.8	68.58
	71.5	9.50	21°.8	42.14
	313.	41.39	21°.9	183.5
	123.3	17.14	21.°9	76.03
Exp. 16.				
	412.	54.55	21°.7	241.9
	333.	42.86	21°.8	190.1
	277.5	35.30	21°.9	156.5
	227.2	28.77	22°.2	127.6
	185.2	23.69	22°.4	105.1
	145.2	18.52	22°.6	82.15
	122.5	15.79	22°.7	70.03
	85.3	10.77	21°.9	47.80
	58.8	7.68	22°.1	34.06
	38.1	5.11	22°.2	22.65
	18.7	2.90	22°.3	12.85
	9.8	1.70	22°.5	7.50

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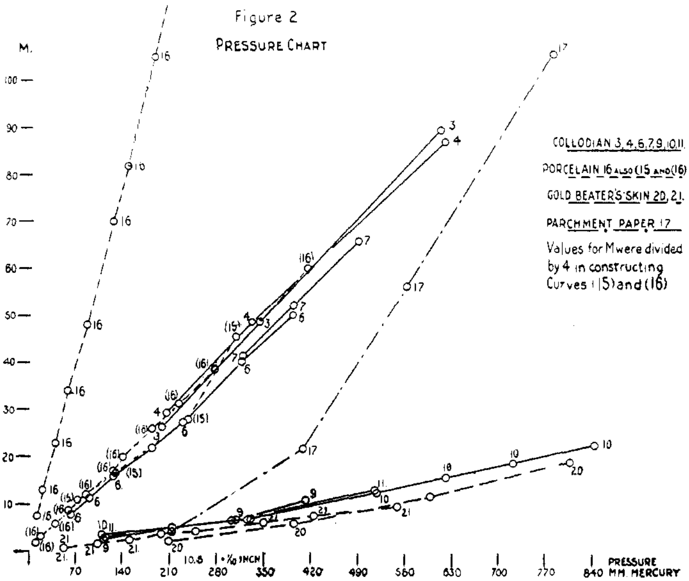
[1] These values have the following significance: The pressure of 213.9 mm. had been on the membrane for 92 minutes before the recorded observation was made; the pressure was raised to 407.2 mm. and after this new pressure had been on for 6 min. the first reading was made for that observation, and so on.

[2] Water could escape out of the rim of this disc, but the shortest distance from the inner surface in contact with the water under pressure, to the rim, was more than 6 mm. This sidewise leak could not alter the general trend of the results, although it would have to be stopped to obtain accurate values for the absolute permeability.

All the results with different pressures are brought together in Figure 2. Pressures are laid off on the abscissa and values for M on the ordinate.



Poiseuille's formula[1] for the passage of liquids through capillary tubes is

$$Q = k \frac{PD^4}{L} T$$

where Q = the quantity of liquid passing in time T, P = the pressure, D = the diameter, L = the length of the capillary and k = a constant for a definite temperature. According to this formula the quantities which pass in unit time are directly proportional to the pressure. If the passage of water through the membranes investigated be a capillary phenomenon, the curves in Figure 2 should be straight lines. They are straight lines, within the limits of experimental error, therefore the passage of water through these membranes is probably a capillary phenomenon. If they had not been straight lines, that might have been accepted as conclusive proof that the phenomenon was not capillary, but the converse does not hold, and, although they are straight lines, this does not definitely prove that the phenomenon is capillary. Still, it is fairly strong evidence in favor of that view.

Permeability of Collodion at Different Temperatures.—The following tables show the change in permeability of membranes with changes of temperature, pressure being held nearly constant. Table 6 gives the values obtained with collodion membrane No. 6 the same used in experi-

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[1] See any text on physics, for instance Chwolson. Lehrbuch der Physik, Vol. 1, p. 959 (1902).

ments 3, 4, 6, and 7, and Table 7 gives the values obtained with collodion membrane No. 12, used also in experiments 9, 10 and 11.

Poiseuille's formula to express the variation of k with the temperature is: $k = k_0(1 + 0.03368t + 0.000221t^2)$[1]

In my experiments $M = Q$, P and T were held constant. If we assume that D and L remained constant, $\frac{PD^4}{L}T$ = a constant, C, and we have, $M = kC$. Substituting in the temperature equation we have $\frac{M}{1 + 0.03368t + 0.000221t^2} = k_0C$, or we can calculate the value of k_0C from the measured M and temperature. If the laws for the flow of liquids through capillary tubes apply, we should get always the same value for k_0C throughout one experiment. Of course these values will not remain the same in different experiments, if the pressure is altered, nor if different membranes are used, when doubtless D and L have different values.

These values for k_0C were calculated as described for three collodion experiments and for the porcelain plate experiment and the results of the calculations are included in the tables in the columns headed k_0C.

TABLE 6.

COLLODION MEMBRANE NO. 6. TEMPERATURE VARIED.

Exp. 5.

Pressure	Mm. per min.	Temperature	M	k_0C
324.2	25.54	72°.	113.2	24.80
323.9	22.87	68°.7	101.4	23.27
323.6	21.63	65°.5	95.92	23.09
323.3	20.87	62°.0	92.58	23.51
323.0	19.52	56°.0	86.56	24.18
322.7	18.75	54°.1	83.18	23.98
322.4	17.78	51°.2	78.86	23.88
321.4	15.39	42°.4	68.25	24.16
321.3	12.35	33°.0	54.79	23.29
321.2	10.31	24°.0	45.76	23.64

TABLE 7.

COLLODION MEMBRANE NO. 12. TEMPERATURE VARIED.

Exp. 12.				
305.	1.091	0°.9	4.840	4.697
300.8	1.120	2°.6	4.967	4.561
301.0	1.282	7°.0	5.689	4.564
299.1	1.592	14°.5	7.058	4.598
298.0	1.695	17°.9	7.518	4.492
298.2	1.783	19°.5	7.909	4.543
297.7	1.997	24°.5	8.857	4.524
297.5	2.355	30°.0	10.44	4.726
297.8	2.816	38°.5	12.48	4.755
Exp. 13.				
320.0	2.006	20°.0	8.898	5.050
319.7	2.786	32°.5	12.36	5.308
318.8	3.215	44°.0	14.26	4.901
318.7	4.146	56°.2	18.39	5.121
318.7	5.081	68°.5	22.53	5.186
319.1	6.546	85°.5	29.03	5.282
317.1	6.384	99.°2[2]	28.31	4.345

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[1] See Chwolson p. 659.

[2] The water was boiling vigorously; the barometric pressure was 738.6 mm.

At temperatures above 80° the movements of the meniscus became rather irregular and concordant results were hard to obtain. Apparently a maximum permeability is reached at about this temperature, and a slight diminution occurs upon further heating. This behavior was totally unexpected. The value of 29.03 is the average from eleven and the value 28.131 is the average from ten separate observations.

Observations made the day after Experiment 13, proved that the permeability of the membrane at low temperatures had not been altered by the boiling.

There is a fairly good agreement between Experiments 12 and 13. This is best seen by reference to Figure 3, where all the results with different temperatures are brought together in the form of curves, temperatures being laid off on the abscissa and values for M. on the ordinate.

The permeability of collodion membrane No. 6 increases much more rapidly with increase of temperature than does that of collodion membrane No. 12. But the coefficient of the increase is about the same; roughly speaking, an increase of 30° to 35° about doubles the rate at which water passes.

Permeability of Parchment Paper at Different Temperatures.—Parchment paper membranes were even more troublesome in the temperature experiments than in the pressure experiments. As the temperature was increased the permeability at first fell off, reached a minimum and then rose. The falling off of the permeability of parchment with time is not the sole cause of this erratic behavior. Observations were made at definite time intervals and it was very evident that the heating itself caused a diminution in the permeability. The numerical values which demonstrated this fact will be omitted, to save space. They were used to plot Curve 19 of Figure 3.

Permeability of Gold Beater's Skin at Different Temperatures.—Owing to a series of difficulties and accidents, having little or nothing to do with the principles involved, concordant results upon the influence of temperature on the permeability of gold beater's skin membranes have not as yet been obtained.

Permeability of Porcelain at Different Temperatures.—Table 9 shows the change in permeability with temperature, of the same porcelain disc used in Experiment 15.

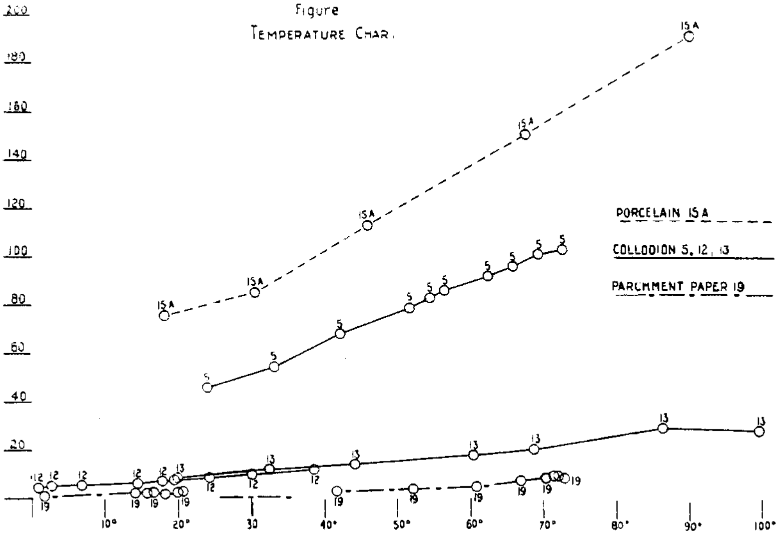
TABLE 9.

PORCELAIN MEMBRANE. TEMPERATURE VARIED.

Exp. 15 A.

Pressure	Mm. per min.	Temperature	M.	k_0 C
123.3	17.14	21°.9	76.03	41.13
123.5	20.00	30°.5	88.72	39.73
122.6	25.71	45°.5	114.0	38.13
122.4	34.01	67°.2	150.9	35.41
119.0	43.25	89°.3	191.8	33.24

The results obtained by varying the temperature are brought together in the form of curves in Figure 3. Temperatures are laid off on the abscissa and values for M on the ordinate.



The resemblance between the curves in this figure is not so striking as it was between the curves obtained for varying pressures, and yet, if we disregard the peculiarities shown by parchment paper they are enough alike to furnish further evidence that the nature of the process, whatever it may be, is the same with each of these membranes.

The values for k_0C are nearly constant in each series with collodion membranes. This constancy means that the rate of passage of water through these membranes is expressible by the capillary laws. The lack of constancy of k_0C for the porcelain plate, precisely the case in which one would expect the best agreement, is probably because some of the necessary conditions discovered by Poiseuille were not fulfilled, for instance, the "capillary tubes" in the porcelain plate may have been below the minimum length for their diameters.

Discussion of Results and Theory.[1]

All the theories regarding the function of the membrane in osmotic

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[1] Anything like a bibliography of the theories regarding osmotic phenomena would be too extensive for insertion here. Besides those to whom reference is made in the text, it would have to include such well known names as Arrhenius, Batelli and Stephanini, Lord Berkeley, Dutrochet Findlay, Fischer, Griffiths, Hamburger, van't Hoff, Hulett Jolly, Kahlenberg, Larmor, Liebig, Lowry, Ludwig, Magnus, Morse and his fellowworkers, Nernst, Nollet, Ostwald, Parrot, Pickering, Poisson, Poynting, Quincke, Ramsay, Raoult, Tammann, J. Traube, M. Traube, De Vries, Walden and many others. I have therefore reduced my citations to the lowest possible number, and desiring to recognize priority so far as my knowledge of the literature permits, have given preference to the earliest articles known to me in which the appropriate statements may be found.

cells may be ranged along a scale at one end of which is the purely physical conception of capillary pores of measurable diameters, at the other, the purely chemical conception of chemical combination between the membrane itself and the substance passing through it. Each extreme and many intermediate hypotheses, found expression much earlier than appears to be generally realized. The two extreme views were, and still are, held to be mutually exclusive. For instance, Fick[1] said that we must distinguish between "pore diffusion" occurring through capillary openings, and true endosmosis, occurring through the much smaller molecular spaces. He concludes, with regret, that since the capillary theory, as so ingeniously worked out by Brücke[2], does not agree with all the facts it must be materially modified or supplanted by something else. He says he sees no alternative but "to adopt the very vague idea that osmotic processes do not occur through so called pores but rather through the actual molecular interstices".

This is, in effect, the "solution theory", the main premise of which is that a substance will pass through a membrane only if soluble in that membrane. This theory probably has more supporters today than any other. It is by no means new, for one could hardly read Graham's or Liebig's articles, particularly the latter's in which he describes his determinations of the "imbibition" of liquids by membranes, without feeling that they had this solution idea in mind. But Lhermite[3] was the first to state the "solution theory" clearly and to support it with good experimental evidence. To him we owe the ingenious "three liquid layers" experiments which have since been repeated by numerous others with various modifications. With the express intention of demonstrating that a substance which passes through a membrane dissolves in that membrane, he superposed layers of water, castor oil and alcohol, also of water, turpentine or essence of lemon and dilute alcohol, also layers of oil of bitter almonds, water and ether, in cylinders. In each case he found the uppermost layer dissolved in the middle layer and passed through this to the bottom layer. Although references to his article are given, in some way he does not seem to have received the full credit he deserves. That his priority with the solution theory is beyond question, is conclusively proved by the following quotations from the article already cited. On page 427 he says: "Cette expérience fait parfaitement comprendre le jeu de la membrane. Quel que soit le nom qu'on donne à la faculté qu'elle a de s'impregner de certains liquides et de les partager avec d'autres liquides qui ont pour les premiers autant d'affinité qu'elle, les conséquences de cette propriété doivent être les mêmes que celles qui

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[1] Ueber Diffusion. Pogg. Ann., **94**, 59-86 (1855).

[2] Beiträge zur Lehre von der Diffusion, tropfbarflüssiger Körper durch poröse Scheidewände. Pogg. Ann., **58**, 77-94 (1843).

[3] Recherches sur l'Endosmose. Ann. chim. phys., [3], **43**, 420-431 (1855).

résultent de la faculté dissolvante''. Again on page 431 he says: ''En résumé, les phénomènes d'endosmose ne sont qu'un cas particulier de la force dissolvante. La propriété des tissus de s'imbiber de liquide est le contre-pied de la solubilité d'un solide dans l'eau. La cloison membraneuse peut être considérée comme un troisième liquide''. Nothing could be clearer than that fifty-two years ago Lhermite said a substance passing through a membrane dissolved in that membrane.

One more instance may be given to establish the fact that these views were at the basis of much work and that they were considered as contradictory. Eckhard[1], as a result of extensive investigations reached the conclusion that there was not experimental evidence enough to prove the necessity of distinguishing between two kinds of permeabilities, one through capillaries and the other through molecular interstices, and that the capillary theory is capable of covering all cases. Eckhard's conclusion is also open to an interpretation the converse of his own, namely, that the ''molecular interstice theory'' is capable of covering all cases, even those undoubtedly capillary.

As a matter of fact the different views, even the two extremes are not mutually contradictory but may be entertained simultaneously. They may be unified as follows. The experimental results given in this article demonstrate that the laws which have been found for the passage of liquids through capillary tubes apply to the passage of water through the membranes studied. These membranes may be considered as typical of certain classes, parchment paper and collodion of vegetable membranes, gold beater's skin of animal, and a porcelain plate of inorganic membranes. Capillary pores are without doubt present in a porcelain plate; good authority has been cited in favor of the view that water passing through a collodion membrane dissolves in that membrane, *i. e.*, occupies intermolecular spaces; but the continuity in the nature of the phenomenon through all these membranes is unmistakable. Pfeffer's[2] results also indicate that the capillary laws apply to the passage of water through copper ferrocyanide membranes and Schmidt's[3] results indicate the same for animal membranes, therefore we are justified in saying that *the rate of passage of liquids through molecular interstices is expressible by the same laws which formulate the rate of passage of liquids through capillary tubes.*

This statement not only harmonizes theories at present in conflict but has some interesting corollaries, for it furnishes a link connecting capillary with chemical processes. We have no alternative but to assume that a solute occupies molecular interstices of the solvent, then the phenomena

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[1] Der gegenwärtige experimentelle Thatbestand der Lehre von der Hydrodiffusion durch thierische Membranen. Pogg. Ann., **128**, 61-100 (1866).

[2] Loc. cit.

[3] Ibid.

of solution and diffusion must be in the same general class with capillary phenomena. The interesting work now being done upon the theory of of "hydrates in solution" makes it increasingly probable that there is no sharp demarkation between the process of solution and chemical combination. Such continuity and lack of boundary lines is a well recognized universal principle in natural phenomena. Thus the phenomena of chemical affinity seem to merge, without any abrupt change, into capillary phenomena. It is then probable that facts obtained by the study of the diffusion of liquids through membranes will increase our knowledge of chemical processes.

This idea that capillary phenomena are different in degree but not in kind from chemical phenomena has been neglected, or forgotten perhaps, but is not new. To refer once more to that brief but extraordinary article by Lhermite,—on page 421 he says: "I hope to demonstrate by my own experiments and by a discussion of those of my predecessors, that osmosis, or endosmosis, is not the result of a special force, but of affinity itself, extending the acceptation of this word to include capillary attraction, which is the first manifestation of affinity and which we might call tendency toward affinity". In order that there may be no possibility of misunderstanding his meaning, on page 424, he says: "I said above that we might consider capillary force as the first degree of chemical affinity".

Summary

1. An apparatus is described to determine the permeabilities of equal areas of membranes through wide ranges of pressure and temperature both accurately and quickly.

2. The permeabilities for water of collodion, parchment paper, gold beater's skin, and unglazed porcelain membranes were determined in terms which, while not quite deserving the name of specific or absolute permeabilities, approximate this desideratum.

3. These results made possible comparisons between the relative permeabilites of the substances studied.

4. The change in permeabilities with change in pressure and with change in temperature was determined through a rather wide range.

5. The fact that Poiseuille's laws for the passage of liquids through capillary tubes apply to the passage of water through the four membranes, was demonstrated graphically and by calculation.

6. The conclusion was reached that the rate of passage of liquids through molecular interstices is expressible by the same laws which formulate the rate of passage of liquids through capillary tubes.

UNIVERSITY OF MICHIGAN,
September, 1907.