drogen ion concentration and the rate of mutarotation in solutions of such acid strength that the influence of the hydroxyl ions upon the rate can be neglected.

2. The conclusion of Osaka that the rate of mutarotation is proportional to the square root of the hydrogen ion concentration holds fairly well between the concentrations 0.01 to 0.10 molal but does not agree at all well with measurements outside this region of concentration.

3. Using Osaka's values for the rate in alkaline solution and new values for it in acid solutions, it is found that the following formula expresses accurately the rate of mutarotation of glucose at 25° in pure water and in acid and alkaline solutions. Rate = $0.0096 + 0.258(H^{\cdot}) + 9750(OH')$.

4. Hydroxyl ions are nearly forty thousand times stronger catalyzing agents of the mutarotation of glucose than hydrogen ions.

5. This stronger catalyzing action of the hydroxyl ions causes a lower rate of mutarotation in weakly acid solutions than is observed for pure water. This depression of the rate, or "negative catalysis", has been measured in a 0.001 molal hydrochloric acid solution and found to be in close agreement with the predictions of the above formula.

The measurements recorded in this article were made possible by the kindness of Professor Geo. A. Hulett, who allowed the author the use of of his well equipped laboratory at Princeton University.

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COLLODION MEMBRANES.

By S. Lawrence Bigelow and Adelaide Gemberling.

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Contents.

The convenience and usefulness of collodion membranes are not, at the present time, fully appreciated by chemists and physicists. This article contains a brief bibliography, methods for making these membranes and an account of our experiments.

Bibliographical.

The first mention of collodion membranes as applied to diffusion phenomena, which we have found, is in an article by A. Fick[1]. He recognized their advantages but had difficulties in fastening them onto holders

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

and abandoned their use. W. Schumacher[1] had more success with them and devised a method for making small closed tubes or sacs of collodion with which he carried out a variety of experiments. But these were not numerous enough nor methodical enough to serve as the basis for any important conclusions regarding osmosis or the action of membranes.

An article by Baranetzky[2] contains more information about the chemical and physical properties of collodion membranes than any other which we have as yet found. He made collodion membranes, 5 cm. in diameter, in cells built up with filter paper on a glass plate. He observed, that, in order to make these membranes permeable to water, they must be put in water before the solvents have completely evaporated. The ether of the solvent evaporates quickly, and soon the membrane contains almost exclusively alcohol, this alcohol is replaced by water, and the resulting membrane is permeable to the latter. But if the membrane dries, it becomes hard and brittle, and when put in water absorbs only an insignificant quantity and remains impervious to that solvent. We have thus, with collodion, a method for obtaining membranes, otherwise alike, but differing in permeability. The way in which the gradual diminution in the size of the interstices in collodion may be stopped by plunging it into water, may be likened to the arresting of the development of a photographic plate by washing and dipping into a fixing bath. A collodion membrane, under water, retains for a good while the particular density or structure which it happens to have reached through evaporation of the solvents before immersion; after several weeks, however, it contracts somewhat.

Like Schumacher, Baranetzky worked exclusively with solutions and was particularly interested in showing that Jolly's "endosmotic equivalent"[3] was of no great significance, and in substantiating Brücke's theory[4] regarding the passage of substances through membranes. His results show that pyroxylin membranes are distinguished from others, such as animal membranes, parchment paper, and cellulose, by a less permeability for dissolved salts.

Neither Graham[5] nor Pfeffer[6] made use of collodion membranes; they have been overlooked or neglected by chemists and physicists since 1872. References to them are more numerous in medical literature. Interest-

[1] Ueber Membrandiffusion. Pogg. Annal., **110**, 337-370 (1860).

[2] Diosmotische Untersuchungen. Pogg. Annal., **147**, 195-245 (1872).

[3] Jolly. Ph. Experimental-Untersuchungen Ueber Endosmose. Pogg. Annal., **78**, 261-271 (1849).

[4] E. Brücke. Beiträge zur Lehre von der Diffusion tropbarflüssiger Körper durch poröse Schneidewände. Pogg. Annal., **53**, 77-94 (1843).

[5] On Osmotic Force. Phil. Trans., **144**, 177-228 (1854). Liquid Diffusion applied to analysis. Phil. Trans., **151**, 183-224 (1861).

[6] Osmotische Untersuchungen, Leipzig, 1877.

ing applications of collodion sacs[1] and capsules in bacteriological investigations are described by Morpurgo and Tirelli[2], Metchnikoff, Roux and Salimbeni[3], Nocard and Roux[4], Vincent[5], Nocard[6], Novy[7], Gorsline[8], Crendiroupoulis and Ruffer[9], McCrae[10], Grubbs and Francis[11], Harris[12], Rodet and Guechoff[13], and Levy[14].

[1] The most convenient method yet devised for making collodion sacs large enough for carrying out separations by dialysis in the chemical laboratory is that of Novy. As these sacs are admirably adapted for lecture demonstrations and other purposes and as the references given may not be convenient, a description of the method follows:—A small orifice one or two mm. in diameter, is blown in the bottom of a tube of the diameter of the sac which it is desired to make. This hole is first closed with a layer or two of collodion, care being taken not to allow any collodion to go through the opening to the interior of the tube. This closing is conveniently accomplished by touching the bottom of the perforated tube with a cork carrying some collodion solution, allowing time for a portion of the solvent to evaporate, touching again, and so on until the closure is of the desired thickness. A flask, or cylinder, containing the collodion solution is tipped so that the tube mold, or "roll-tube", may be inserted and may be rotated just touching the surface of the collodion for a length somewhat in excess of that of the sac to be made. The tube thus coated with collodion, is taken out of the flask and a short time is allowed for some of the solvent to evaporate. It may then be inserted in the flask and rotated once more to give it another coat, and these operations may be repeated until the collodion membrane has acquired almost any desired thickness. But it is desirable to use a collodion of such consistency that one insertion and rotation suffices. When the coating has "set" and does not stick to the finger, the tube is plunged into water and water is poured into the interior. If the collodion is immersed in water too soon it becomes white and opaque, somewhat brittle and not durable. If the immersion is too long delayed, the collodion is apt to adhere to the tube so firmly that it is difficult to remove it without tearing. The proper interval, varying between two and 15 minutes, according to the consistency of the original collodion, is easily learned in two or three trials. By blowing into the tube and simultaneously pulling and twisting the membrane gently, the water is forced through the perforation and between the collodion membrane and the tube. With moderate care it is not at all difficult to detach the very transparent and tough collodion sac. There appears to be almost no limit to the size of the sacs which may thus be made. Novy and Gorsline's sacs for their striking demonstrations of the phenomena of dialysis were frequently 40 cm. long by 2-3 cm. in diameter.

Dialysis occurs with great rapidity through such sacs and the whole process can be watched without the least difficulty because of their transparence.

[2] Arch. ital. biol., **18**, 187-192 (1893).

[3] Ann. inst. Pasteur, **10**, 261 (1896).

[4] Ibid., **12**, 240 (1898).

[5] Ibid., **12**, 787 (1898).

[6] Ibid., **12**, 564 (1898).

[7] Laboratory work for Bacteriology by F. G. Novy, **1899**, 499.

[8] C. S. Gorsline "On the Preparation and Use of Collodion Sacs," "Contributions to Medical Research" dedicated to Dr. V. C. Vaughan, **1903**, 390-394.

[9] Compt. rend. soc. Biol., **52**, 1109-1110 (1900).

[10] J. Exp. Med., **6**, 635 (1901).

[11] Bulletin No. 7 of the Hygienic Laboratory of the U. S. Marine Hospital Service, **1902**.

[12] Muir and Ritchie's Manual of Bacteriology, American edition, **1903**, 67.

[13] Compt. rend. soc. Biol., **52**, 965-67 (1900).

[14] J. Infectious Diseases, **2**, 1-48 (1905).

Gorsline found that pepton, albumose, starch, dextrin, albumin and enzymes, employed in from one-half to one per cent. solutions all passed through his collodion sacs in less than twenty-four hours at a temperature of 35° in sufficient quantities to give positive tests. Because they permit the passage of colloidal substances in small quantities, it should not be inferred that these membranes are inferior to others for the purpose of dialysis. The process of dialysis does not furnish us with positive means of separation, but just as we may accomplish much by fractional distillation and crystallization, so may we by fractional dialysis. Graham recognized this clearly enough and recorded the facts that albumin, starch, etc., passed through his parchment paper and animal mucous membranes, though in much smaller quantities, relatively, than crystalloids. That the permeability of a membrane for different substances is relative, that there is no such thing known as a strictly semi-permeable membrane, but only membranes through which one substance passes much more slowly than do other substances, has always been understood and recognized. That one substance passes in and another out, and that what we observe in every case is the resultant of oppositely directed streams, is not a discovery of the last few years. This is clear enough from the old terms, endosmosis for the passage inward, and exosmosis for the passage outward, terms first suggested and defined by Dutrochet[1] in 1827.

Malfitano[2] filtered a solution containing a colloid to which he ascribed the formula $HN(Fe_2O_6H_6)Cl$ through collodion and found that the greater part of the colloid was held back by the filter. Bierry and Giaja[3] made the interesting observation that pancreatic secretion having passed through a collodion membrane, no longer acted on starch or maltose, but that adding an electrolyte, preferably one containing a chlorine or bromine ion to this inactive material restored its lost activity and ability to act on starch.

This bibliography might be extended, and such extension would probably not be without interest to chemists. But enough has been given to show that collodion membranes in one form or another are frequently employed by bacteriologists, seldom by chemists and physicists, and that they are attractive and promising objects of study.

Experiments.

Dialysis Through Collodion, Parchment Paper and Gold Beater' Skin.—We wished to ascertain, by direct experimental comparison, the relative efficiencies of collodion, parchment paper and gold beater's skin, for separations by dialysis as ordinarily carried out in the laboratory. A collodion solution was made according to the directions in the U. S.

[1] Dutrochet. Nouvelles observations sur l'Endosmose et l'Exosmose, et sur la cause de ce double phénomène. Ann. chim. phys., **35**, 393-400, (1827).

[2] Compt. rend., **141**, 660-62, (1905).

[3] Compt. rend. soc. biol., **62**, 432, (1907).

Pharmacopoeia. Seventy-five cc. of ethyl ether were poured over 3 g. of commercial pyroxylin[1] in a flask with a cork to prevent the rapid evaporation of the solvent. After ten or fifteen minutes 25 cc. of ethyl alcohol were added and the pyroxylin dissolved quickly and completely to a clear, rather mobile, liquid requiring no filtration. The preliminary soaking in ether materially hastens the solvent action. Other proportions of solvents and solute may be used. A few cc. of this collodion solution were poured upon a clean dry piece of plate glass and were spread by tilting the glass to and fro, over an area about half again as large as the membrane we wished to make. This layer was allowed to dry until it was of a gelatinous consistency and did not wrinkle when the finger was rubbed lightly across it. Its edges were then loosened and it was peeled off. The largest membrane we made was perhaps 20 cm. in diameter, but larger ones could have been made if they had been wanted. The membranes were fairly uniform in thickness, between 0.2 and 0.4 mm. as measured by a micrometer caliper. After the work described in this article had been completed, one of us found that membranes of great uniformity of thickness could be made by pouring the collodion onto a surface of mercury in a shallow dish.

Three dialysers of the common type and of nearly the same size (9 cm. in diameter) were selected. A collodion membrane was made and placed immediately on a dialyser, the surface that had been next the plate being next the rim. It was stretched tightly, and drawn up over the rounded sides to which it conformed without wrinkles, owing to its plasticity. A coating of collodion painted on the joint made this secure, and tying with string was not necessary. While the membrane was being attached to the dialyser, its surface was kept moist by laying upon it a piece of moist filter paper.

Gold beater's skin, such as is sold in strips by surgical supply houses. was tied on the second dialyser with numerous turns of strong thread. Parchment paper was attached in the same manner to the third dialyser.

One hundred cc. of a solution of red colloidal gold, made according to the directions given by Zsigmondy[2] were put in each of the dialysers, and all three were suspended in one large low ice jar of distilled water. The rate of dialysis was followed by determining the conductivities of the solutions by means of a Kohlrausch "Tauchelektrode" every twenty-four hours. The water in the jar was changed each day, immediately after the determinations of the conductivities. When the conductivity of the solutions had fallen to nearly that of ordinary distilled water, this was replaced by water showing a conductivity of 1.2×10^{-6}. The results

[1] Detailed and interesting information regarding pyroxylin is given in a recent article by G. Lunge. "Zur Kenntniss der Kollodionwolle". Z. angew. Chem., 19, 2051-58. (1906).

[2] Z. anal. Chem., 40, 697-719. (1901).

obtained are given in Table 1. All the values for the conductivities should be multiplied by the common factor 10^{-6}.

TABLE 1.

Time of dialysis in days	Gold-beater's skin. Conductivity.	Collodion. Conductivity	Parchment paper Conductivity
0	984.2	984.2	984.2
1	304.7	415.6	850.0
2	81.3	207.8	467.5
4	55.3	102.4	255.8
5	29.9	85.0	158.5
10	22.7	26.3	47.1
11	16.7	(30.4)	(50.5)
12	*11.0*	21.0	43.1
13	10.1	17.3	27.1
14	7.9	14.0	17.3
17	8.1	*11.0*	14.9
18	8.0	12.4	13.9
19	...	11.0	*11.0*

Some intermediate values obtained are omitted from the table. We have no explanation to offer for the high values to which we call attention by enclosing them in brackets.

If we consider the time required for dialysis to proceed to the same point, say until the conductivity has been diminished to 11×10^{-6} we see that this is accomplished by the gold beater's skin first, in 12, by the collodion second, in 17, and by the parchment paper last, in 19 days. If we compare the conductivities of the solutions in the three dialyzers on the fourth day we find the conductivity in the parchment to be about twice what it is in the collodion, and in the collodion about twice what it is in the gold beater's skin. Approximately this relationship is maintained for eight days.

We carried out similar experiments with $Fe(OH)_3$ and $Al(OH)_3$ as the colloids. The volumes of liquid in the dialyzers with the gold beater's skin and with collodion membranes increased rapidly owing to osmosis, and these dialyzers repeatedly overflowed. It is worth noting that the dialyzers with parchment membranes did not do this. The following is an example of the results we obtained: In 20 days the conductivity of a solution containing colloidal ferric hydroxide fell off 287×10^{-6} in the gold beater's skin dialyzer, 265×10^{-6} in the collodion dialyzer, and only 55×10^{-6} in the parchment dialyzer.

These comparisons measure the relative merits of the three membranes for effecting separations by dialysis. Gold beater's skin is the best membrane, collodion is next and parchment paper, which is undoubtedly the most generally used, is the least good.

A. Zott[1] carried out an extensive investigation, comparing dialysis

[1] Ueber die relative Permeabilität verschiedener Diaphragmen und deren Verwendbarkeit als dialytische Scheidewände. Wied. Annal., **27**, 229-289, (1886).

through fifteen different membranes. Collodion was not included among them. He says that only three are useful in practise, namely, gold beater's skin, pig's bladder and parchment paper, and, of these three, gold beater's skin is distinctly the best, while parchment paper is the poorest.

We tried to strengthen collodion membranes by making them with cotton net inside and so enlarge their field of usefulness. The net was easily incorporated in the collodion by laying it on the plate glass and pouring the solution on it. We found, however, that the meshes of the fabric were not readily covered, and that we could not be sure that we had perfect membranes without leaks. Our membranes, as we were making them, appeared strong enough for all ordinary purposes, indeed collodion membranes are tougher than one not familiar with them would suppose, and so we did not pursue this work further. If a membrane requires reinforcement, this can be given by letting the membrane and dialyzer rest on wire gauze, as is frequently done in experiments upon osmosis.

The Effect of Changes in Temperature and Pressure on the Permeability of Collodion Membranes.

Apparatus and Method of Measurement.—We made some quantitative determinations upon the rate at which water passes through collodion membranes, at a definite temperature and pressure, and also upon the effects of changes of pressure and of temperature on this rate. Very little bearing upon these questions is to found in the literature. Schmidt[1], who studied the rate at which water and various solutions pass through animal membranes, did not work with collodion, and Schumacher[2] and Baranetzky[2] confined their attention to determining the quantities of dissolved salts which passed through their membranes.[3]

The arrangement of the apparatus is shown in Figure 1.

A,A,A, are the membrane holders. C,C,C, are pinch cocks by means of which any one holder can be cut out. D is a safety bottle. E is a mercury manometer measuring the diminished pressure in the apparatus. F is a stone jug of about 20 liters capacity. G is a tube provided with a stop cock leading to a water aspirator. H is an Ostwald thermostat of the usual type with the usual temperature regulation and system of stirring. I is a glass jar immersed in the thermostat and containing distilled water into which the membrane holders dip.

The membrane holders were made by sealing pieces of common glass tubing, about 2.5 cm. long, the smallest having an internal diameter of

[1] W. Schmidt. Versuche über Filtrationsgeschwindigkeit verschiedener Flüssigkeiten durch thierische Membran. Pogg. Ann., **99**, 337-88 (1856).

[2] Loc. cit.

[3] This literature will be considered more fully in an article by one of us to appear in the next number of this journal.

11.67 mm., the largest an internal diameter of 11.89 mm., onto capillary tubing. The capillary tubes were 28 cm. long and of such internal diameter that approximately two cc. were contained in a length of 21 cm. Thus one mm. length contained about 0.0097 cc. It was easy to read the height of a water column within these tubes to less than ½ mm.; therefore our measurements of volume were within 0.005 cc. of right.

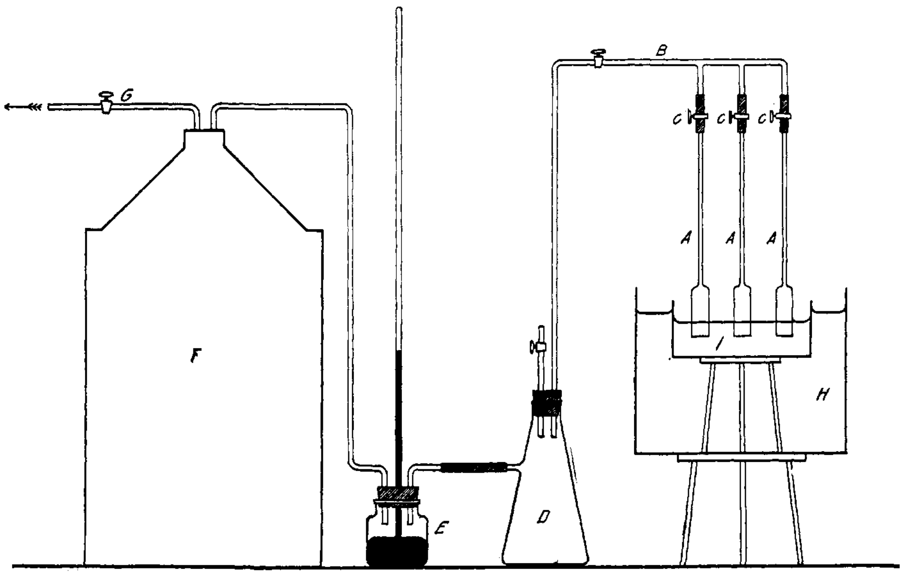

FIGURE 1.

We etched scales on these tubes and then calibrated them for intervals of 0.2 cc. by weighing them out with mercury. The membranes, made as already described, were fastened on in the same manner in which we fastened them onto other dialyzers, only we found it desirable to wind the joint with thread besides painting it with collodion.

The method of carrying out an experiment is evident from the figure. The tubes were filled with water nearly up to the lowest mark on the scale, and were then attached to the arm B. Suction was applied until the manometer showed the desired diminution of pressure within the apparatus. The difference between the barometric height and the height of the mercury in the manometer, we have called the "driving pressure" in the tables. A few moments were allowed for the flow of water through the membranes to become regular before the initial readings were taken. Readings were made at the expiration of five or fifteen minute intervals, measured by means of a stop watch. The volume of the jug being large, the very small diminution in volume caused by the entrance of water into the experimental tubes was quite negligible. The pressure within the apparatus frequently remained practically unchanged for twenty-four hours. During no experiment, which was accepted as of value, did the pressure fall off as much as five mm.

Varying the pressure, temperature being held constant.—The results of a typical series of experiments with three membranes are contained in Table 2. Reading were made at intervals of five minutes and were corrected by the calibrations of the tubes.

TABLE 2.

TEMPERATURE 25° ± 0°.2. DRIVING PRESSURE 150 MM. ± 2.5 MM.

Tube I		Tube II		Tube III	
Readings	Diff. or volume in cc.	Readings	Diff. or volume in cc.	Readings	Diff. or volume in cc.
1.500		1.685		1.790	
	0.085		0.075		0.075
1.415		1.610		1.715	
	0.065		0.065		0.040
1.350		1.545		1.675	
	0.080		0.095		0.045
1.270		1.450		1.630	
	[0.030]		[0.120]		[0.090]
1.240		1.330		1.540	
	[0.190]		0.065		0.065
1.050		1.265		1.475	
	0.080		0.080		0.040
0.970		1.185		1.435	
	0.075		0.055		0.030
0.895		1.130		1.405	
	0.075		0.055		0.040
0.820		1.075		1.365	
Mean values	0.084 cc.		0.076 cc.		0.056 cc.

The bracketed values show wide divergence from the rest. We call attention to them as being the largest fluctuations, without obvious cause, which we observed in our numerous measurements.

The series was repeated 11 times giving us 11 tables similar to Table 2. The results may be summed up as follows :—The average of 78 separate readings for tube I showed that 0.074 cc. of water passed through the membrane in five minutes. The average of 80 readings for tube II showed that 0.068 cc. of water passed through its membrane in five minutes, and the average of 77 readings for tube III showed that 0.044 cc. of water passed through its membrane in five minutes.

Experiments similar to those of Table 2 were performed with the same membranes for pressures of 50 and 250 mm. Table 3 contains the results of one of 16 series with a pressure of 50 mm. Table 4 contains the results of one of 11 series with a pressure of 250 mm. The values are cc. of water passing through in five minutes.

TABLE 3.

TEMPERATURE 25° ± 0.°5. DRIVING PRESSURE 50 MM. ± 2.5 MM.

	Tube I	Tube II	Tube III
	0.030	0.030	0.020
	0.020	0.020	0.010
	0.040	0.040	0.030
	0.025	0.020	0.020
	0.030	0.020	0.010
	0.030	0.025	0.015
	0.020	0.015	0.010
	0.015	0.030	0.015
	....	0.025	0.015
Mean values,	0.026	0.025	0.016

TABLE 4.

TEMPERATURE 25.° ± 0.°5. DRIVING PRESSURE 250 MM. ± 2.5 MM.

	Tube I	Tube II	Tube III
	0.095	0.110	0.045
	0.085	0.070	0.055
	0.095	0.085	0.050
	0.090	0.075	0.055
	0.090	0.095	0.050
	0.100	0.090	0.065
	0.085	0.090	0.065
	....	....	0.045
	....	....	0.060
Mean values,	0.091	0.087	0.054

Table 5 contains the means of all the values obtained at the three pressures.

TABLE 5.

	50 mm.		150 mm.		250 mm.	
	Number of observations	cc. of water in 5 mins.	Number of observations	cc. of water in 5 mins.	Number of observations	cc. of water in 5 mins.
Tube I....	98	0.030	78	0.074	70	0.120
Tube II...	99	0.028	80	0.068	77	0.108
Tube III..	96	0.017	77	0.044	81	0.076

We are unable to say why the membrane on tube III showed a lower permeability than those on tubes I and II.

We divided the increase in volume of water passing per unit time by the corresponding increase in pressure, and calculated what percentage this was of the volume passing when the pressure was 150 mm. This gave us what might be called a pressure coefficient of the permeability. The results of these calculations are given in Table 6.

TABLE 6.

	Tube I			Tube II			Tube III		
Pressure	Obs. volume	Diff.	Press. coeff.	Obs. volume	Diff.	Press. Coeff.	Obs. volume	Diff.	Press. coeff.
50	0.030			0.028			0.017		
		0.044	0.59%		0.040	0.59%		0.027	0.61%
150	0.074			0.068			0.044		
		0.046	0.62%		0.040	0.59%		0.032	0.66%
250	0.120			0.108			0.076		
Mean values			0.60%			0.59%			0.63%

Temperature being held constant at 25°, a change of 1 mm. in the pressure causes a change in the rate at which water passes amounting to about 0.6 per cent. of the volume of water which passes when the driving pressure is 150 mm.

It is interesting that in spite of the divergence between the actual experimental values for different membranes, all the pressure coefficients are nearly the same.

The permeability of the membranes at constant temperature, appears to us to be very nearly, but not quite, a linear function of the driving pressure. This same conclusion was reached by Schmidt[1] for his animal membranes from less experimental evidence.

Varying the Temperature, Pressure Being Held Constant.—We used the same three membranes as before, the uniform driving pressure of 150 mm. mercury, and determined the volumes of water which passed through during fifteen minute intervals. We made six separate observations for each of the three tubes at 5°, and at 45°, and 18 separate observations for each of the three tubes at 15°, 25° and 35°. Table 7 contains a summary of the results. The volumes given are the means of all observations at each temperature.

TABLE 7.

	Tube I		Tube II		Tube III	
Temp.	cc. passing in 15 mins.	Diff.	cc. passing in 15 mins.	Diff.	cc. passing in 15 mins.	Diff.
5°	0.086		0.080		0.063	
		0.021		0.020		0.025
15°	0.107		0.100		0.088	
		0.043		0.033		0.022
25°	0.150		0.133		0.110	
		0.023		0.030		0.032
35°	0.173		0.163		0.142	
		0.034		0.062		0.036
45°	0.207		0.225		0.178	

The results are so irregular that we do not feel justified in calculating a temperature coefficient to correspond to our pressure coefficient. However, we think they show that such temperature coefficient is not a linear function, but increases slightly with the temperature. It will be observed also that the amount of water passing per unit time is about doubled when the temperature is increased 20° to 30°.

Varying the Thickness of the Membranes.—Attempts were made to determine the thickness of the membranes and its influence on the permeability. Of course the membranes are thicker when full of water and thinner when dried out. We secured six membranes of different thicknesses, by varying the amount of tilting to and fro of the glass plate on which they were made. We fixed these on six tubes and measured the amount of water which passed through in one hour at a temperature of 25°. We then removed the membranes from their tubes, pressed them lightly be-

[1] Loc. cit.

tween filter paper, and measured the thickness with a micrometer caliper at ten different points on each membrane. We allowed the membranes to dry for several days in a desiccator and weighed them, merely as a check on our micrometer measurements. The diameter of the largest membrane was 11.89 mm., of the smallest 11.67 mm. Table 8 contains the results. Only the means of each ten readings of the caliper are included.

TABLE 8.

Temperature 25°.

	1	2	3	4	5	6
Thickness in mm.	0.31	0.20	0.13	0.34	0.33	0.42
Cc. of water in one hour	0.45	2.04	1.25	0.83	0.86	1.05
Weight in mg. when dry	4.4	3.0	2.0	4.4	3.9	5.4

These values are not regular enough to establish any mathematical relations. They show that while the permeability undoubtedly falls off as the thickness increases, as is to be expected, other influences also are at work which have an even greater effect on the permeability than the thickness.

As already noted, Baranetzky[1] stated that if one membrane be allowed to dry out more than another before it is immersed in water it will be less permeable. We tested this experimentally, taking one membrane off the glass plate as soon as its consistency would permit, and leaving another on as long as we could. We found that the interval of varying moisture between which useful membranes can be taken off is rather narrow. They obviously cannot be taken off too soon, but on the other hand, if they dry out too much they are apt to stick to the plate and tear. The time interval however, is not inconveniently short, because the upper surface dries quickly, and this retards evaporation from the interior. Our numerical results are too irregular to serve as proof, but our experience leads us to believe that while the different degrees to which the membranes may have dried out, as we made them, affected their permeabilities to a certain extent, this alone is not sufficient to account for the irregularities in Table 8.

Different Collodions.—We observed marked differences in the permeabilities of membranes made from different samples of pyroxylin. In Table 9, tubes I, II and III carried membranes of collodion made from pyroxylin kindly furnished us by the School of Pharmacy of the University of Michigan. Tubes IV, V and VI carried membranes of collodion

TABLE 9.

Driving Pressure	I	II	III	IV	V	VI
50 mm.	0.078	0.075	0.048	0.018	0.018	0.008
	0.080	0.075	0.047	0.015	0.015	0.013
150 mm.	0.225	0.220	0.143	0.047	0.048	0.023
	0.207	0.185	0.122	0.043	0.040	0.020
250 mm.	0.357	0.345	0.190	0.067	0.073	0.032
	0.367	0.323	0.240	0.067	0.063	0.032

[1] Loc cit.

made from commercial pyroxylin. The values are cc. of water passing in 15 minutes at a temperature of 25°, each value given being the mean of three separate measurements.

In spite of the differences in the values obtained with different collodions, what we have called the pressure coefficient remains practically the same. Calculating the same way as before, we find a pressure coefficient for the membrane on tube IV of 0.57 per cent., for the membrane on tube V of 0.60 per cent., and for that on tube VI of 0.55 per cent.

The membranes made from the commercial collodion were less durable than the others. They frequently broke under low pressures before the third day, though some lasted as long as fifty days. Their average "life" was 20 days as compared to 50 or 60 days for membranes made from our other pyroxylin.[1]

Effect of Age on the Permeability.

The membranes become less permeable as they grow older. Table 10 contains results demonstrating this. The values given are cc. of water passing in five minutes, and all the values in this table were obtained with one membrane. The age of the membrane is given in days.

TABLE 10.

TEMPERATURE 25° ± 0.°5.

Driving pressure	50 mm.	150 mm.	250 mm.
Age 3 days	0.032 cc.		
	0.032		
4 days	0.027		
	0.043		
	0.024		
13 days	0.054	0.082 cc.	0.129 cc.
	0.034	0.086	
14 days	0.028	0.080	0.112
15 days	0.022	0.066	0.098
20 days	0.031	0.076	0.112
	0.024	0.074	0.107
21 days	0.028	0.062	0.106
	0.022	0.060	0.106
22 days	0.021	0.055	0.104
25 days	0.018	0.055	0.102
	0.017	0.043	0.099
		0.060	0.080
	0.021	0.056	0.085
29 days	0.017	0.047	0.073

[1] We were unable to obtain details regarding the particular method of preparation of the commercial pyroxylin, there being, apparently, some trade secret involved, and we are, therefore, not in a position to offer an explanation of the difference in permeabilities. Judging from the information contained in Lunge's article (loc. cit.) we are inclined to believe that the commercial pyroxylin was made by nitrating cotton for a longer time, or at a higher temperature, than that employed in the School of Pharmacy. We intend at some future time to make pyroxylin by different methods and compare the permeabilities of the resulting membranes.

In spite of some wide variations, for which we are unable to account, it is evident from this table that the permeability diminishes as the age increases. At the end of four weeks the membrane showed about half its original permeability.

Summary of Results.

1. Collodion membranes in the form of sacs, or flat films, for ordinary dialyzers, even of large size, are easily made. They may be attached to supports more neatly and more perfectly than parchment paper. Dialysis occurs through them more rapidly, and therefore they are to be preferred to the more commonly used material. Membranes of gold beater's skin, however, are still better for separations by dialysis.

2. The quantity of water passing through collodion membranes is nearly a linear function of the pressure, the temperature being held constant.

3. An attempt to calculate a "pressure coefficient" of permeability for 25° gave the result :—A change of 1 mm. in pressure causes a change in the volume of water passing equal to about 0.6 per cent. of the quantity which passes when the pressure is 150. mm. mercury.

4. The quantity of water passing, pressure being constant at 150 mm. is not a linear function of the temperature. A "temperature coefficient" was not established but an increase of 20° to 30° was required to about double the quantity of water passing per unit time.

5. Different samples of collodion showed different permeabilities, but in spite of the differences in the absolute values, a change of pressure or of temperature produced the same proportional effect in all.

6. As a collodion membrane grows older, its permeability diminishes gradually, but it lasts and remains useful for one to three months.

UNIVERSITY OF MICHIGAN.
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THE DETERMINATION OF CARBON MONOXIDE IN ATMOSPHERIC AIR.

BY J. LIVINGSTON R. MORGAN AND JOHN E. MCWHORTER.

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All the satisfactory methods for the quantitative estimation of small amounts of carbon monoxide are based upon the reaction,

$$I_2O_5 + 5CO = 5CO_2 + I_2,$$

which was first observed by Ditte,[1] and which, according to Kinnicutt and Sanford,[2] is only quantitative at 150° or above, although Gautier[3] re-

[1] Bull. soc. chim., **13**, 318 (1870).

[2] This Journal, **22**, 14 (1900).

[3] Compt rend., **128**, 487 (1899).