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XIX. *Researches upon Osmosis and Osmotic Pressure.* By
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Laboratory, Cambridge*) *.

[Plate VIII.]

Introduction.

1. **T**HE following paper gives some results obtained from a series of investigations upon osmotic properties. Most of the work has been done at the Physical Institute, Christiania; but some experiments carried out at the Cavendish Laboratory are also included.

These researches have been going on for about two years, as the construction of the cells and first pieces of apparatus was done as early as in March 1906. The reason why such a considerable time has been required to obtain the results is due to several circumstances. In the first place the difficulties to be dealt with were greater than anticipated, and secondly, for most of the time I had only a few hours of the day to devote to the work. The greater part of this time has been spent in preparing the cells and working out the method, and most of the experiments have been made during the past autumn and winter.

During the experiments I have had the advantage of gathering experience from the works of Morse and Frazer †, and later from the work by Berkeley and Hartley ‡.

Besides a description of the method used, the paper will deal with the following subjects:—

1. A study of the properties of the membrane by its behaviour for electric currents.
2. General theoretical considerations as to the direct measurements of osmotic pressure.
3. Measurements of the equilibrium pressure for the cane-sugar solutions.
4. Experimental determination of the velocities of osmotic flow corresponding to different pressures. (Velocity-Curves.)
5. The effect of temperature upon the reversion pressure (π_0').

* Communicated by Prof. J. J. Thomson, F.R.S.

† H. N. Morse and J. C. W. Frazer: "The Preparation of Cells for Measurements of High Osm. Press.," *Am. Ch. Journ.* July 1902; "The Osm. Press. and Freezing-points of Solutions of Cane Sugar," *Am. Ch. Journ.* July 1905.

‡ Earl of Berkeley and E. G. J. Hartley: "On the Osm. Press. of some Concentrated Aqueous Solutions," *Phil. Trans. of R. S. London*, series A, vol. ccvi. pp. 481-507.

§ 1.

2. The constructions of the various pieces of apparatus that have been tried have (all of them) been made upon the principle that the solution, and consequently the pressure, was to be placed outside the cell. This arrangement allows a better tightening of the cell, and at the same time the latter will be more capable of resisting great pressures, as by a proper construction we can always arrange matters so that the cell substance is only subject to compression. The same principle with other arrangements has been used by Berkeley and Hartley.

The construction of the apparatus finally used is shown in Pl. VIII. figs. 1, 2, 3. It consists essentially of three parts :

The osmometer itself (fig. 1), the compressor (fig. 2), and the manometer (fig. 3).

The osmometer again chiefly consists of three parts : the cell C and the two pieces A and B made of cast-steel.

The cup A, which has an inner volume of 118 cm.³, can be fixed to the disk B by means of six set-screws with nuts passing through perforations equally distributed round the circular edge of the cup and the disk. The tap (*c*) that serves for fastening the cell forms a part of the disk B, and is cast in the same piece.

The cell has at the top a cylindrical form, but the bottom is made spherical as to ensure that the cell is only acted upon by stresses tending to compress it. The upper part of the cell is glazed. The fastening of the cell to the osmometer is easily seen from fig. 1. I have used the principle to let the osmotic pressure itself take care of the fastening and tightening. To this end the steel tap as well as the glazed part of the cell are covered with a piece of rubber tubing of a suitable diameter. By this arrangement it is ensured that the pressure will have no tendency to produce any leak between the steel tap and the cell. An increase of pressure, on the contrary, will only cause the cell to be pressed with a great force up to the steel tap, and at the same time the extensible rubber is pressed with the whole pressure up to the walls of the cell and the steel tap.

In order to prevent every possibility of leak at this point the ends of the rubber tubing during the experiments have been tied round with a cotton thread.

By the arrangement here shown one of the corrections required by the method of Berkeley and Hartley has been eliminated, namely, the so-called "guard-ring leak."

The disk B besides the six screws already mentioned has three other cylindric perforations (*a*, *a'*, *b*) for three glass

capillaries. One (*b*) (inner diameter 0.49 mm.) is open at both ends and connects the interior of the cell with the air, the other two capillaries go to the compressor and to the manometer. In order to give these two capillaries a better support the two perforations end in two steel tubes.

The glass capillaries are fixed to the tube in the following manner. The tubes used were somewhat conical, and had such dimensions that only a certain length could pass the tube. The place where it stopped was noticed, and in the neighbourhood of it the capillary was heated and covered with sealing-wax. Simultaneously the steel tube was heated and the capillary pulled through from beneath.

In the course of the experiments the disk *B*, as well as the glass tubes, the compressor, and the manometer could be fixed. Only the steel cup *A* and the cell had to be taken down for each trial.

For the fastening of the osmometer three steel rods (length 31 cm., diam. 1.0 cm.) were fixed to the disk, the upper ends of which formed horizontal flanges with screw holes, and the other ends serving as set-screws for fixing the cup *A*.

The glass tubes went for some distance straight upwards, and were thus protected from damage by the three steel rods. Further, by this arrangement the osmometer could be put into a thermostat so as to secure a constant temperature.

The Compressor.

3. By means of the compressor the pressure could be raised to the height desired. The construction of it is shown in fig. 2. The apparatus is chiefly made of brass, only the screw (*f*) and the cylindrical piston (*g*) are made of steel. The piston (diam. 0.95 cm.) passes through a cylindrical perforation of exactly the same diameter as the piston. The piece (*E*) ends in a conical tap, that goes down into the cup (*D*). The tightening is brought about in the same manner as in the case of the cell; a piece of rubber tubing put on to the end of the brass tube covers the connexion with the piston. The pieces (*E*) and (*F*) are screwed to the cup and tightened by a leather ring. The cup had a perforation at the bottom for the glass capillary that led to the osmometer, and this tube was fixed with sealing-wax in the manner already described.

The Manometer.

4. For measuring the pressure I used the usual way of compressing air in a glass capillary. The length of the manometer was about 135 cm., exterior diam. 7.5 mm., and the average inner diameter 0.472 mm. It was given the form shown in fig. 3 (Pl. VIII.). In this form the manometer could be made long without being inconvenient, and the temperature accurately determined as the column of air in the vertical part of it could be put into a thermostat. With this form the vertical part must have a small diameter; it ought not to surpass 0.6 mm.

The manometer joined on to a U-shaped capillary with an inner diameter 1.01 mm., that was filled with mercury, and thus the mercury level in the U tube had only to move a relatively short distance to fill the whole manometer with mercury.

As the exactitude of the results greatly depends upon the manometer, I shall give a more minute description of its construction.

The capillary itself was graduated, the distance between each mark being 0.5 cm. The marks were cut in wax by means of a cutting-machine marking with an accuracy of about $\frac{1}{50}$ of a mm., and the marks etched to the glass. The manometer was then given its final form, cleaned and calibrated.

The calibration was carried out in the following manner. The manometer-tube was placed horizontally on a table. By means of a rubber tubing put on one end, the column of mercury could be given the position desired. The ends of the mercury column were measured relatively to the nearest marks on the manometer by means of a microscope with a vertical filament movable along a horizontal steel rod and furnished with a micrometer-screw. By these means I was able to measure with an accuracy of about $\frac{1}{50}$ mm.

For each position the mercury column was pushed forward as nearly as possible its own length. In the calculation, the length from the end of one position to the beginning of the next was considered to have the average diameter of the neighbouring position. The end where the volume of air was to be measured was calibrated with a smaller mercury column.

The calibration finished, the U-tube was put on at the point *h*. The capillary was well cleaned and a current of air drawn through it, the air being dried by passing through a solution of NaOH and over dry CaCl₂. Without disturbing the connexion to the drying apparatus the U-tube

was filled with well-cleaned mercury, taking care in doing this that no air from without followed the mercury. Then the manometer was left to itself till the following day, and the temperature in the room, which was found to keep fairly constant, examined.

Just before closing the manometer the following observations were made:—

1. The pressure of the air observed by means of a mercury barometer by which the pressure could be read with an accuracy of $1/25$ mm.; the barometer was compared with the standard barometer at the Meteorological Institute, Christiania.
2. Reading of the temperature of the room.
3. Reading of the mercury level in the manometer.
4. Reading of the position of the open end.

The end was closed very quickly by putting a drop of melted glass into the opening and at the same time using the flame. It took no more than 10 seconds from the time the gas-flame was lighted till the end was quite closed. Furthermore, the manometer was protected from change in temperature by means of an asbestos plate put on the end of the manometer.

The manometer then was sealed to the capillary from the osmometer, and the latter filled with water. This was done by drawing back the mercury with a water-pump and letting the water flow back into the tube. This was done to reduce the volume to be filled by the osmotic flow.

The constants of the manometer are the following:—

The air-pressure on closing... $B_0 = 754.6$ mm. Hg at 0° ;
 „ abs. temperature „ ... $T_0 = 287.5$;
 „ volume of air „ ... $v_0 = 22.762$ vol. units.

For the pressure q in the manometer at a temperature T and a volume v we have

$$q = \frac{B_0}{760} \frac{v_0}{T_0} \frac{T}{v} (1 + \kappa) = 0.07861 \frac{T}{v} (1 + \kappa).$$

κ is a correction introduced because the air does not exactly follow Boyle's law. I have put

$$1 + \kappa = \frac{pv}{p_0 v_0},$$

where p_0 is one atmosphere and all pressures are made at 0° , and this value I have taken from the measurements made by Regnault and Amagat.

The volume v was determined by observing the position of the mercury column by means of a cathetometer furnished with a filament movable by a micrometer-screw reading with an accuracy of about $1/50$ mm. It was somewhat more difficult, however, to get an exact determination of the other end of the air column as the tube, on account of the melting, ended in a tip. It is especially at high pressures that an exact determination is of importance. The position of the lowest point, as well as the point where the diameter began to diminish, could be determined with great precision. This lowest part had very nearly the form of a cone, and thus the position of the end could be found if the tube had been throughout cylindrical. Furthermore, I afterwards succeeded in calibrating the manometer quite up to the tip. The two methods gave results for the end reading differing only by $1/10$ mm. In the calculation I have used the mean value.

As this error that may arise from the determination of the end point when measuring somewhat high pressures is predominant, we can conclude that even for pressures up to 50 atmospheres the error in q would not exceed 0.2 atm., and lower pressures could be measured much more accurately.

In the following table is given the volume of air corresponding to a series of readings at the temperature of 15° centigrade. All the numbers are derived directly from observations. The values of v for intermediate readings have been found by interpolation. The volume is expressed in an arbitrary unit, which is the volume of the largest mercury column used in the calibration.

Reading.	Volume.	Reading.	Volume.
1.592 cm.	0.2380	60.282 cm.	9.9580
3.060 "	0.4761	66.077 "	10.9512
4.520 "	0.7141	72.140 "	11.9898
5.988 "	0.9522	78.073 "	12.9968
7.439 "	1.1902	83.914 "	13.9952
8.887 "	1.4283	89.712 "	14.9877
10.329 "	1.6663	95.488 "	15.9797
11.768 "	1.9044	101.305 "	16.9778
12.160 "	1.9692	107.205 "	17.9783
18.306 "	2.9666	112.674 "	18.9030
24.399 "	3.9654	118.114 "	19.8285
30.489 "	4.9642	123.553 "	20.7484
36.572 "	5.9639	128.952 "	21.6743
42.601 "	6.9603	134.313 "	22.6025
48.535 "	7.9569	139.587 "	23.5290
54.434 "	8.9580		

The temperature of the air when the manometer was closed was $14^{\circ}.5$ C.; at other temperatures the volume per length-

unit will be altered on account of the dilatation of the glass. For the temperatures actually used this change need not be considered.

The whole apparatus as it was put up at the Physical Institute at Christiania is shown in the photograph fig. 4 (Pl. VIII.).

§ 2.

The Semipermeable Membrane.

5. The membrane used in these measurements is the usual one consisting of copper-ferrocyanide. In preparing the cells I used electrolysis, practically the same method as used by Morse and Frazer, and later by Berkeley and Hartley.

It proved, however, to be very difficult to get a cell which gave a good membrane, and I tried several sorts, till I found one which gave satisfactory results.

At first I tried cells made of porcelain, but these proved either too weak or else so hard as not to permit of the fluid passing through.

Some cells of fayence made at the Fayence Factory, Egersund, showed better qualities, but were not fully satisfactory.

At last I got cells, made of "Pukalische Masse," from C. Desaga, Heidelberg, that proved very good.

For the electrolysis a somewhat variable potential was used, arranging matters so that the voltage increased with increasing resistance in the cell until for resistances of about 50,000 ohms it kept a fairly constant value of 115 volts. This method was originally chosen, as I had to use currents of 230 volts; but I also consider it good for the forming of the membrane, as the voltage is small as long as the membrane is weak.

The arrangement is shown in fig. 5. R_1 and R_2 are two equal resistances, consisting of two 16 candle-power incandescent lamps. By means of two commutators, K_1 and K_2 , the cell C can be put as a shunt to one of the lamps. The resistance of the membrane as well as the voltage at a certain moment could be measured by means of a torsion galvanometer G, furnished with a resistance-box with resistances of 900, 9900, and 99,900 ohms, the resistance of the galvanometer being 100 ohms.

I have not treated more than four cells of this type, and all of them have attained an electric resistance of more than 125,000 ohms; one of them especially, which I shall call S, has shown very good qualities as the resistance has gone up to 400,000 ohms. This resistance, however, was first obtained after it had been long in use, and after it had several times been tested for osmosis. This, my first cell, has been used in all my measurements.

It seems as if I have succeeded in finding a type of cell *with constant qualities and very convenient for the production of semipermeable membranes*. The cell substance has a suitable porousness, is very homogeneous, and can at the same time stand great pressures.

In making the membrane the following method of proceeding has been used,

The forming of the first beginning of the membrane for three of the cells was done in the way described by Berkeley and Hartley*.

One of my cells (A), however, has been treated in a somewhat different way. In this case I took the dry cell and let it soak the two solutions simultaneously, the potassium ferrocyanide from the outside and the copper sulphate from the inside, whereupon the cell was placed in distilled water and the whole placed in the vacuum for about twenty-four hours. The result was very satisfactory, the resistance rose more suddenly than in any of the other cells.

The solution of copper sulphate used contained 50 gr. in one litre, and the solution of potassium ferrocyanide 42 gr. in the litre. The positive electrode consisted of a copper rod, and the vessel containing the solution served as the negative electrode. In order to prevent the potassium hydrate produced by the electrolysis from acting upon the membrane, the cell was separated from the vessel by a porous cup also filled with potassium ferrocyanide solution. In the electrolysis the positive electrode was fixed to the cell by a cork with perforations, and the cell hung up by the current wire.

At the beginning of the electrolysis the resistance suddenly rose within two minutes to about 3-4000 ohms, and then increased more slowly until after $1\frac{1}{2}$ -2 hours it reached a maximum value. As an instance I shall give the observations for the first electrolysis of the cell A :

Electrolysis begun Nov. 10, 1907, 1^h 8^m P.M.

Time.	Temp.	Potential.	Resistance.
1 ^h 9 ^m	9° C.	65 volts	3,000 ohms
11	7	96 "	4,500 "
33	6	107 "	11,400 "
48	5	110 "	13,500 "
2 25	4	111 "	18,800 "
3 30	3.5	111.5 "	20,200 "

If the electrolysis is continued after maximum resistance

* Earl of Berkeley and E. G. J. Hartley, *loc. cit.* p. 486.

is reached we shall generally notice a fall in the resistance, especially when the maximum resistance is small. In the best cell I could not detect any fall, although the electrolysis was continued for one hour after the maximum resistance was reached.

When the electrolysis has finished the resistance falls very rapidly, as will be seen from the curve fig. 6 (Pl. VIII.). And for each time the process is repeated, we shall have an increase of resistance from a value which is only a small fraction of the maximum value of the resistance. Even in the case when it got up to 400,000 ohms it was only 51,000 to begin with.

In the following tables is shown the development of the membrane for the two cells S and A, these being chosen because they have been subject to a somewhat different treatment.

CELL S.

Date.	Duration of electrolysis.	Temp.	Potential.	Resistance.
1906, Nov. 21...	0 ^h 30 ^m	...	→ 96 volts	4,500 ohms
" " 22...	1 10	...	→ 114 "	60,000 "
" " 23...	1 0	9°	→ 111 "	56,000 "
" Dec. 5...	...	6°	→ 114 "	45,000 "
" " 11...	1 5	...	→ 114 "	40,000 "
" " 11...	0 20	...	230 "	65,000 "
" " 28...	1 0	12°·2	115 "	100,000 "
1907, June 11...	1 2	16°	"	97,000 "
" " 15...	2 5	...	"	180,000 "
" Sept. 19...	1 0	10°	"	220,000 "
" Oct. 14...	1 40	4°·5	"	320,000 "
" " 24...	1 18	3°	"	290,000 "
" Nov. 12...	1 52	1°·6	"	400,000 "
" " 28...	3 0	0°·9	"	290,000 "
" Dec. 4...	2 50	2°·5	"	360,000 "

CELL A.

Date.	Duration of electrolysis.	Temp.	Potential.	Resistance.	
1907, Nov. 10...	2 ^h 20 ^m	5°	→ 111·5 volts	20,000 ohms	} Solutions interchanged.
" " 15...	1 5	11°	→ 114 "	36,000 "	
" " 17...	2 30	1°·1	115 "	75,700 "	
" " 18...	1 37	1°·5	116 & 230 "	118,000 "	
" " 21...	2 30	2°·0	115 "	178,000 "	
" " 23...	1 30	2°·5	"	182,000 "	
" " 25...	3 0	3°	"	230,000 "	
" " 29...	2 0	0°·9	"	276,000 "	

For general use I have found that the least voltage is about 115 volts. When the maximum resistance has reached a value of about 50,000 ohms, I have found it to have a good effect for about 20 or 30 minutes, to use the double voltage (230 volts). After this treatment I have generally observed a considerable increase in the maximum resistance when going back to 115 volts.

For the cell A the solutions have been interchanged, the copper-sulphate solution being used on the outside. Before the change the cell ought to be placed for one or two days in distilled water ; further, in the electrolyses I had repeatedly to change the solution of potassium ferrocyanide as to prevent action from potassium hydrate. This was also done for one of my other cells, and effected in both cases a considerable increase in the maximum resistance.

The Effect of Temperature upon the Membrane.

6. The temperature has a great influence upon the maximum resistance obtainable. In order to examine the effect more closely I have made some experiments with my two other cells, which I may call M and N. The experiments were in the following manner :—The cell was electrolysed at first at a temperature near 0° until maximum was reached. Then the temperature was raised as quickly as possible and the electrolysis continued until maximum. By this somewhat hard treatment the cell might change its original quality, and for that reason the electrolysis was repeated by going down to 0°. The results of these measurements are given in the following tables and graphically represented by the curve fig. 6 (Pl. VIII.).

CELL M.

Jan. 7, 1908.—Mean Potential 118 volts.

Temperature 0°·9.		Temperature 12°·2.		Temperature 1°·3.	
Time.	Resistance.	Time.	Resistance.	Time.	Resistance.
h m		h m		h m	
10 48 A.M.	13 × 10 ³ ohms	5 25 P.M.	48 × 10 ³ ohms	8 30 P.M.	45 × 10 ³ ohms
11 8 "	53 " "	5 44 "	48 " "	8 40 "	49 " "
11 30 "	74 " "	6 4 "	58 " "	9 45 "	74 " "
11 55 "	100 " "	6 14 "	62 " "	10 0 "	78 " "
12 25 P.M.	122 " "	6 24 "	67 " "	10 15 "	83 " "
12 55 "	133 " "	6 34 "	68·8 " "	10 30 "	80·7 " "
1 40 "	139 " "	6 44 "	71·8 " "	10 45 "	93 " "
2 30 "	150 " "	6 49 "	78 " "	11 10 "	100 " "
3 10 "	150 " "	7 14 "	83 " "	11 30 "	106 " "
3 40 "	150 " "	7 30 "	78 " "		

CELL N.
Mean Potential 115 volts.

Jan. 8.				Jan. 9.			
Temperature 0°-9.		Temperature 14°-3.		Temperature 1°-1.			
Time.	Resistance.	Time.	Resistance.	Time.	Resistance.		
h m		h m		h m			
11 55 A.M.	24.5×10 ³ ohms	6 15 P.M.	73 ×10 ³ ohms	12 48 P.M.	10.8×10 ³ ohms		
12 40 P.M.	88.5 " "	6 25 "	62.2 " "	1 0 "	17.0 " "		
1 25 "	109 " "	6 35 "	56.5 " "	1 15 "	27.0 " "		
2 30 "	119 " "	6 45 "	53.0 " "	1 45 "	28.2 " "		
3 10 "	135 " "	7 0 "	52.0 " "	2 15 "	35.3 " "		
3 40 "	143 " "	7 30 "	48.6 " "	4 25 "	46.0 " "		
4 15 "	147 " "	8 5 "	42.5 " "				
4 55 "	147 " "	8 30 "	44.0 " "				
5 45 "	128 " "	9 30 "	38.5 " "				

In both cases the temperature has a great influence upon the maximum resistance. We see from the last experiment that the effect of temperature partly consists in a weakening of the membrane. The resistance is broken down and does not regain its original size when going back to the low temperature.

In the first experiment the membrane seems to have kept more constant during the treatment; but still we notice a very great temperature effect upon the maximum resistance. The membrane is, however, not unaltered, so the maximum resistance will not exactly correspond to equal membranes. Comparing the two curves for the low temperature, we see that the cell during the treatment has undergone a change; for in the last curve the resistance increases more slowly.

Unfortunately the experiment could not be continued till maximum was reached; but when the experiment was broken off (11^h 30^m p.m.) the resistance was still increasing, and the curve seems to show that the resistance has a tendency to regain a value near to its original maximum value.

It seems then that the temperature, even if the mechanical structure could be kept constant, would exercise a great influence upon the resistance at the membrane.

That this is the fact is brought to full evidence by an experiment carried out at the Cavendish Laboratory.

The cell A was first electrolysed at 11°-3 up to maximum of resistance, then the temperature was brought down to 1° C. During the time-interval the temperature was lowered the

electrolysis was stopped. The experiment had the result shown in the table.

Electrolysis begun 10^h 30^m A.M.

Temperature 11°·3.		Temperature 1°·0.	
Time.	Resistance.	Time.	Resistance.
h m		h m	
11 15 A.M.	171 × 10 ³ ohms.	12 54 P.M.	310 × 10 ³ ohms.
11 50 "	192 " "	1 15 "	320 " "
12 15 P.M.	196 " "	1 30 "	314 " "
12 34 "	192 " "	1 45 "	319 " "
		3 20 "	276 " "
12 44 P.M.	El. stopped.		

It appears from the table that the resistance on lowering the temperature rose from 192 to 310 thousand ohms. As the electrolysis had been stopped during the interval, this increase cannot be due to any building up of the membrane. On the contrary, the resistance will fall with time, but this will only cause a diminution in the effect, and we see that the resistance at the low temperature first increases for some time. As resistances that most nearly correspond to the same system we should also this time have to take the maximum resistances.

If in the experiment with the cells M and A we assume that the maximum resistances at the two temperatures correspond to nearly equal membranes, the temperature effect calculated from the maximum values should nearly give the temperature coefficient corresponding to a constant system. When the temperature effect is defined in the usual way, the two experiments give the following result :—

Cell.	Temperature Coefficient.
M	—0·072
A	—0·063

Since continuing the electrolysis after maximum we generally get some decrease in the resistance, the value found for cell M will be somewhat too large and the value for A too small ; and we see that the temperature effect found is greater for cell M than for cell A. The temperature effect

that the membrane would show if we were able to maintain a constant structure should lie between the two values.

In order to explain this large temperature effect it would be necessary to know the nature of the conductivity at maximum.

As long as the resistance is small and increasing, we can be sure that the conductivity is mainly of electrolytic nature; but it is also possible that electricity can pass through the membrane without being carried by the ions of the fluids, and when the membrane becomes tighter this nonelectrolytic conductivity might even be predominant.

That at maximum resistance a considerable *electrolytic* conductivity must take place is evident from the following fact.

As we have seen (fig. 6) the resistance after electrolysis has been stopped will very rapidly diminish; but we must necessarily assume that this breaking-down process is also going on under the electrolysis, only that we now have a counteracting process in the new building of the membrane. At maximum of resistance there must be an *electrolytic conduction* just sufficient for balancing the breaking-down process. And further, if we would imagine that for a moment the conductivity was mainly due to a conduction through the membrane substance, the current would call forth disturbances in the porous structure of the membrane, and the latter would very soon break down and give rise to electrolytic conduction.

From this it seems probable that the conductivity even at maximum resistance is chiefly of electrolytic nature. The electric conductivity would then measure the degree of permeability of the membrane for the two ions $\overset{+}{\text{Ca}}$ and $\text{Fe}(\bar{\text{CN}})_6$, and the temperature effect would mean that *by increasing temperature the permeability of the membrane is largely increased.*

The Dependence of the Resistance upon the Potential.

7. In an experiment carried out for preparing the membrane with a higher potential, it was noticed that the latter had a great effect upon the resistance of the membrane. In this experiment, the cell N was electrolysed first by 110 volts until a maximum of resistance of 126,000 ohms was reached, then the potential was raised to 220, and the electrolysis continued for about 15 minutes until the membrane had got a resistance of 116,000 ohms. It might seem as if the high potential had diminished the resistance, but by going back to the original potential the resistance suddenly rose to 196,000 ohms.

This experiment shows the good effect of using a higher potential for a short time. This will have a similar effect as the remaking of the membrane under pressure which is used by Berkley and Hartley. But at the same time the experiments show that the resistance of the membrane, when the latter is kept unaltered, largely depends upon the potential.

The effect is examined more closely by some measurements carried out at the Cavendish Laboratory. The mode of proceeding was about the same as in the first experiment. The cell A was electrolysed at constant temperature up to maximum of resistance. Then the potential was changed as suddenly as possible and the resistance measured. The measurements were made by a d'Arsonval galvanometer put as a shunt to the head circuit, and the resistance was directly compared with a standard resistance of 100,000 ohms put into the circuit instead of the cell. With different potentials I had to use a different shunt-resistance so as to get a suitable deflexion, but the deflexion for the standard resistance was found for each potential, the resistance being thus directly compared with the standard.

As the electrolysis had to be stopped for some minutes during the experiments, some change in the membrane resistance was to be feared, and, as a matter of fact, by going back to the original potential the resistance had fallen about 1.4 per cent. ; but as the time for each reading was noticed, by assuming a constant rate of fall the measurements could be reduced to the same point of time. The result is given in the table.

Temperature 11°5.

Potential.	Resistance.	$\alpha = \frac{1}{R}$.
41 volts.	208×10^3 ohms.	4.81×10^{-6}
85 "	200 " "	5.00 "
117 "	191 " "	5.24 "
153 "	176 " "	5.68 "
199 "	147 " "	6.80 "

As we see, the current system does not follow Ohm's law, the resistance falls with increasing potential, and the greater the potential the more rapid the fall.

The table also contains the quantity $\alpha = \frac{1}{R}$, which measures the conductivity of the system. The experiments give α as a

function of the potential v , this function can be given the form

$$\alpha = \alpha_0 + \alpha_1 v + \alpha_2 v^2 + \dots$$

α_0 would then be the conductivity corresponding to $v=0$. By putting the values found into a curve we should get for this special case $\alpha_0 = 4.75 \cdot 10^{-6} \text{ ohm}^{-1}$.

If an electromotive force were required to make the system a conductor, we should get $\alpha_0=0$, then $\alpha - \alpha_0$ will give the conductivity produced by the electromotive force, and we see that the conductivity for higher potentials is made up of two parts, one part $\alpha - \alpha_0$ produced by the electromotive force and one part α_0 belonging to the system.

In our case α_0 is great in comparison to $\alpha - \alpha_0$ even for potentials up to 175 volts. For $v=115$ volts $\frac{\alpha - \alpha_0}{\alpha_0} = 0.1$.

From this we can conclude that the large temperature effect which is measured by a potential of 115 volts must be mainly due to the effect upon α_0 .

In view of the constitution of the membrane, a natural explanation of the potential effect can be got by assuming that it is due to an inner motion in the membrane produced by the mechanical action of the electric force. This also gives an explanation of the fact that the resistance generally will decrease when electrolysis is continued after maximum, and most rapidly in the weakest membranes.

As the potential effect as well as the temperature effect corresponds to a nearly constant membrane, we see that, as far as the electric resistance can be considered a criterion of a good membrane, the resistances must be compared at the same temperature and the same potential.

§ 3.

General Remarks as to the Treatment of the Observations.

8. Before going on to describe more minutely the special observations, we shall see which quantities are to be measured. By the term osmotic pressure we shall understand the difference between the hydrostatic pressures on the two sides of a perfect semipermeable membrane when the solution and solvent are in thermodynamic equilibrium. As this pressure is a limiting value for the pressures measurable by our membranes, we shall in the following call it the ideal equilibrium pressure (π_0) and we have :

$$\pi_0 = p - p_0 = \phi(C, T, p_0) \dots \dots \dots (1 a)$$

The problem to be solved is to determine by experiment the function ϕ . C denotes the concentration defined in one

$$\pi_0 = \phi_0(C, T), \quad (1b)$$

(1) The osmotic pressure π_0 .

(2) The concentration actually present under the experiment.

(3) The temperature.

On the Calculation of the Osmotic Pressure.

At first we shall make some remarks as regards the leak. The leak may be due to a mere mechanical defect in the membrane. In this case the leak, if it is too small to call forth any motion in the fluids, can be considered as taking place independently of the osmosis. By putting the apparatus up under a certain pressure and measuring the amount of solute that has passed through in a certain time, we should be able to find the velocity of leak by assuming that it has passed through the membrane with the concentration of the solution.

For this kind of leak that will not effect the osmotic activity we shall adopt the name used by Berkeley and Hartley and call it the Solution Leak.

There may, however, be another kind of leak due to the fact that the membrane substance itself, even in the good parts of it, does not give conditions for perfect semipermeability. This leak will be a function of the osmotic process, and the latter will most likely be influenced by the leak. This leak cannot be regarded as a leak of solution, but rather as a leak of solute. This kind of leak we shall call the Osmotic Leak. To get a strict definition of this leak, we shall *assume* that the solute also in this case is connected with so much of the solvent as to give a solution of

the same concentration as the solution in the osmometer. This assumption will only cause some difference as to what we understand by the velocity of osmotic flow. The leak defined in this manner will be proportional to the actual leak, and they will both of them disappear simultaneously. When the leaks are defined in this manner we can consider the total leak as a measurable quantity, when we are able to determine the amount of solute that has passed through by a certain pressure in a certain time.

Let us in general assume that the total leak is l and the total amount of solution leak l_0 . Further, we shall assume that there are a certain number of leaks $l_1 l_2 \dots l_n$ which each influence the osmotic flow in its own manner. According to their nature the leaks must be absolute quantities that cannot change their signs, so when $l=0$ all the other leaks must be equal to zero.

The apparent velocity of osmotic flow we shall call λ' . This is the velocity directly examined. The velocity of osmotic flow λ we shall define by the equation

$$\lambda = \lambda' - l. \quad \dots \dots \dots (2a)$$

In general we must be able to put

$$\left. \begin{aligned} \lambda &= \psi(\pi, l_1, l_2, \dots, l_n, C, T, k_1 k_2 \dots) \\ l_1 &= \epsilon_1(\pi, \lambda, C, T, k_1', k_2' \dots) \\ l_2 &= \epsilon_2(\pi, \lambda, C, T, k_1^{(2)}, k_2^{(2)} \dots) \\ &\dots \quad \dots \quad \dots \quad \dots \quad \dots \\ l_n &= \epsilon_n(\pi, \lambda, C, T, k_1^{(n)}, k_2^{(n)} \dots) \\ l_0 &= \epsilon_0(\pi, C, T, k_1^0, k_2^0 \dots) \end{aligned} \right\} \dots \dots (2b)$$

π denotes an arbitrary pressure difference between the solution and the solvent; $k, k_1 \dots k_1', k_2' \dots$ &c., are parameters dependent upon the qualities of the membrane and the mechanism of osmotic flow.

In order to find a mathematical expression for the relation between π_0 and π' , we must be able to define the ideal equilibrium pressure by means of the quantities in equations 2a and 2b. This definition we get by fixing the conception of semipermeability. We shall have perfect semipermeability when $l=0$, and λ is a function of π defined as a single-valued function in the neighbourhood of the reversion point, and further we must have $\left(\frac{d\lambda}{d\pi}\right)_{\pi_0}$ different from zero. Then the manipulations necessary for the thermodynamic treatment can be carried out.

For perfect permeability we shall have that the ideal equilibrium pressure is defined by the equation $\lambda=0$.

For all the intervals in which the function ψ has a physical interpretation ψ must, on account of the continuity of nature, be a continuous function with regard to the variables. We shall in general consider the equation

$$\psi(\pi l_1 l_2 \dots l_n C.T k_1 k_2 \dots) = 0.$$

By this equation the pressure is implicitly given as a function of $C.T l_1 \dots l_n$ and $k_1 k_2 \dots$. This pressure we shall call π_0' . In the interval of physical interpretation π_0' is a continuous and single-valued function of the named variables. But as we cannot produce perfect semipermeability we cannot be sure that the continuity with regard to the leaks will hold quite up to the point $l_1=l_2=\dots=l_n=0$. If it was not allowed to assume continuity up to this point it would mean that the conception perfect semipermeability, as applied to nature in the case considered, would be an absurdity. It might also be that for certain membranes and solutions the assumption is not allowed, while it is allowed for others. At all events, if we cannot assume continuity up to the point $l=0$, we have no means of combining the ideal equilibrium pressure with the reversion pressure actually measured.

The following development is restricted to those cases for which π_0' can be considered a continuous function of the leaks quite up to the point $l_1=l_2=\dots=l_n=0$. This condition we can write

$$l-l_0=0.$$

Under these conditions the ideal equilibrium pressure is defined by the equation

$$\psi(\pi l_1 l_2 \dots l_n C.T k_1 k_2 \dots) = 0 \quad \text{for } l-l_0=0 \quad (3)$$

With perfect semipermeability π_0 is a function of C and T , provided p_0 is constant, and then we see that if the ideal equilibrium pressure can be defined by equation 3, ψ must be such a function of $k_1 k_2 \dots k_m$ that for $l-l_0=0$ and $\lambda=0$ the quantities dependent on the membrane must disappear. And consequently, if ψ is continuous with regard to the leaks up to the point of ideality, we must have that the influence of the membrane upon the reversion pressure actually measured must disappear with the leak.

Let us, on the other hand, assume that the membrane has such properties that when the leaks diminish the pressure π_0' approaches a value π_0'' where

$$\pi_0 - \pi_0'' = a,$$

where α is a finite quantity, and as being due to the leaks it would be a quantity characteristic of the membrane, and would necessarily change with the properties of the membrane, and we might expect that a change in the membrane constants would give rise to a change in the reversion pressure of the same order.

If, then, we are able to show that the reversion pressure keeps constant while the qualities of the membrane or the mechanism of osmotic flow in some way are altered, it will give a strong evidence for the correctness of the assumption as to the continuity of π_0' to the point of ideal semipermeability, so the pressure measured by a small total leak must be near to the ideal pressure. We shall later have an occasion to come back to this question.

In general the quantities $k_1 k_2 \dots$ &c., even during one experiment, will vary with time. In the following we shall find the properties of the membrane at a certain moment, or, in other words, we shall find the properties under the assumption that $k_1 k_2 \dots$ can be kept constant. Further, we shall consider C and T constant. As to the concentration it will change on account of λ and l , but we shall assume that this variation is so small as not to produce any appreciable effect upon the velocities. Then we may write the equations 2a and 2b

$$\left. \begin{aligned} \lambda &= \psi(\pi l_1 l_2 \dots l_n) \\ l_1 &= \epsilon_1(\pi \lambda) \\ l_2 &= \epsilon_2(\pi \lambda) \\ &\vdots \dots \dots \\ l_n &= \epsilon_n(\pi \lambda) \\ l_0 &= \epsilon_0(\pi) \\ \lambda' &= \lambda + l \end{aligned} \right\} \dots \dots \dots (2c)$$

If we put into the functions $\epsilon_1 \epsilon_2 \dots \epsilon_n$ the value of λ from the first equation, we get n equations between the $n+1$ quantities $l_1 l_2 \dots l_n$ and π . And by this means $l_1 l_2 \dots l_n$, and thence λ , can be found in terms of π . From this it follows that we always can put

$$\begin{aligned} \lambda' &= \zeta(\pi) \\ l &= \eta(\pi). \end{aligned}$$

These two functions can be found by experiment. λ' can be found by determining the apparent velocity corresponding to different pressures, and to find $\eta(\pi)$ we should have to

analyse the solvent when the solution has been standing for a given time under a certain pressure.

The two functions can be graphically represented by two curves, and the intersection of these two curves would give a point corresponding to a pressure π_0' and a total leak l' . This point will, on account of the last equation in 2c, satisfy the condition

$$\lambda = 0.$$

The point π_0' will in general be different from π_0 . There is only one case in which the point determined in this manner will give the ideal equilibrium pressure. That occurs when the total leak is a solution leak. Then we have

$$l \equiv l_0 \quad \text{and} \\ l_1 \equiv l_2 \equiv l_3 \equiv \dots \equiv l_n \equiv 0.$$

Then we see from equation 3 that the point that satisfies the equation $\lambda = 0$ will give the ideal equilibrium pressure.

Thus we see that in the case when the velocity of osmotic flow λ can be considered independent of the leak, it should be possible to determine the ideal equilibrium pressure even with a leak of the same order of size as λ itself. If the leak is not very great, we do not need to determine the whole leak curve; we only need to determine a point corresponding to the apparent equilibrium pressure.

On account of the nature of the leak we must have that l_0 as well as $\frac{\partial l_0}{\partial \pi}$ never can be negative. If, then, for a somewhat large value of π l is maintained fairly low, it seems allowable to conclude that $\frac{\partial l}{\partial \pi}$ is a very small quantity, and for the surroundings of the equilibrium point we can put

$$l = l_{\pi'} = \text{constant}.$$

We shall now treat the general case when we have only osmotic leaks.

In this case the intersection point will not give the ideal equilibrium pressure. If we knew the functions $\epsilon_1, \epsilon_2 \dots \epsilon_n$ we should by putting $\pi = \pi_0'$ and $\lambda = 0$ get a series of values $l_1', l_2' \dots l_n'$. The pressure π_0' must satisfy the equation

$$\psi(\pi_0' l_1' l_2' \dots l_n') = 0. \quad \dots \quad (3b)$$

The ideal equilibrium pressure, however, must satisfy the equation 3:

$$\psi(\pi_0, 0 \dots 0) = 0. \quad \dots \quad (3a)$$

And if the function ψ really varies with the leaks, the solution of equations 3a and 3b must give different pressures.

As earlier mentioned, as long as in the functions ψ the leaks are different from zero, the quantities dependent on the membrane will not disappear and the pressure π_0' will be a function of the membrane. π_0' is the pressure we should get if the total leak could be regarded as a solution leak not influencing the osmotic flow. This is the pressure which is measured by Berkeley and Hartley.

We see from this that if some of the quantities $l_1 l_2 \dots l_n$ are somewhat great, it may seem as if the pressure π_0' is a property mainly due to the membrane.

We shall find the mathematical expression for the ideal osmotic pressure in the case that the leaks are very small quantities. We have earlier assumed that the function ψ is continuous in the neighbourhood of the point $l=0$. We will now also assume that the first derivatives with regard to the pressure and the leaks are continuous.

Then we can apply to the equation 3b the formula of Taylor for the neighbourhood of the point $\pi=\pi_0$ and $l=0$, and we get

$$0 = \psi(\pi_0' l_1', l_2' \dots l_n') = \psi(\pi_0 0 0 \dots 0) + \left(\frac{\partial \psi}{\partial \pi}\right)_0 (\pi_0' - \pi_0) \\ + \left(\frac{\partial \psi}{\partial l_1}\right)_0 l_1' + \left(\frac{\partial \psi}{\partial l_2}\right)_0 l_2' + \dots \left(\frac{\partial \psi}{\partial l_n}\right)_0 l_n' + \omega_2.$$

But according to the definition of π_0

$$\psi(\pi_0 0 0 \dots 0) = 0.$$

If $\frac{\partial \psi}{\partial \pi}$ is a finite quantity different from zero, we see that

$\pi_0 - \pi_0'$ will be a quantity of the same order as the leaks and will disappear with the leaks. ω_2 consists of terms of second and higher order. If we restrict ourselves to terms of the first order we get

$$\pi_0 - \pi_0' = \frac{1}{\left(\frac{\partial \psi}{\partial \pi}\right)_0} \left\{ \left(\frac{\partial \psi}{\partial l_1}\right)_0 l_1' + \left(\frac{\partial \psi}{\partial l_2}\right)_0 l_2' + \dots \left(\frac{\partial \psi}{\partial l_n}\right)_0 l_n' \right\}. \quad (4)$$

The pressure π_0' is defined by the equation $\lambda=0$. As we have seen we can put

$$\begin{aligned} \lambda &= \zeta(\pi), \\ l &= \eta(\pi), \\ \lambda' &= \xi(\pi). \end{aligned}$$

We shall assume what is generally confirmed by experiment, that for a small leak $\frac{d\lambda'}{d\pi}$ and consequently $\frac{d\lambda}{d\pi}$ and $\frac{dl}{d\pi}$ are continuous in the interval

$$0 < \pi < \pi_0'.$$

We shall develop the functions λ and l in the neighbourhood of the point $\pi = \pi_0'$. Then we get

$$\lambda = \zeta(\pi_0') + \left(\frac{d\lambda}{d\pi}\right)_{\pi_0'} (\pi - \pi_0') + \alpha_2,$$

$$l = \eta(\pi_0') + \left(\frac{dl}{d\pi}\right)_{\pi_0'} (\pi - \pi_0') + \alpha_2'.$$

But according to the definition of π_0' we have

$$\zeta(\pi_0') = 0.$$

And remembering that

$$\frac{d\lambda}{d\pi} + \frac{dl}{d\pi} = \frac{d\lambda'}{d\pi},$$

we get

$$\lambda' = (\pi - \pi_0') \left(\frac{d\lambda'}{d\pi}\right)_{\pi_0'} + \eta(\pi_0') + \alpha_2 + \alpha_2'.$$

For the apparent equilibrium pressure we have

$$\lambda' = 0 \quad \text{and} \quad \pi = \pi',$$

which gives

$$\pi_0' = \pi' \frac{\eta(\pi_0')}{\left(\frac{d\lambda'}{d\pi}\right)_{\pi_0'}} + \alpha_2''.$$

With the same accuracy as before we can put

$$\alpha_2'' = 0,$$

$$\eta(\pi_0') = \eta(\pi') = l_{\pi'},$$

$$\left(\frac{d\lambda'}{d\pi}\right)_{\pi_0'} = \left(\frac{d\lambda'}{d\pi}\right)_{\pi'},$$

and

$$\pi_0' = \pi' + \frac{l_{\pi'}}{\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By addition of equations 4 and 5 and by putting

$$\left(\frac{\partial \psi}{\partial l_1}\right)_0 l_1' + \left(\frac{\partial \psi}{\partial l_2}\right)_0 l_2' + \dots \left(\frac{\partial \psi}{\partial l_n}\right)_0 l_n' = \Sigma$$

we get

$$\pi_0 = \pi' + \frac{l_{\pi'}}{\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}} + \frac{\Sigma}{\left(\frac{\partial \psi}{\partial \pi}\right)_0} \dots \dots (6a)$$

When the leaks are very small we can regard $\frac{\partial \psi}{\partial \pi}$ as small quantities in comparison to $\frac{d\lambda'}{d\pi}$, then we can put

$$\left(\frac{\partial \psi}{\partial \pi}\right)_0 = \left(\frac{d\lambda'}{d\pi}\right)_{\pi'},$$

and we get

$$\pi_0 = \pi' + \frac{1}{\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}} (l_{\pi'} + \Sigma). \dots \dots (6b)$$

This equation is the most general, it contains also the case when the velocity of osmotic flow is independent of the leak; *e. g.*, if the leak l_1 could be regarded as a solution leak we should have in the sum Σ to put $\frac{\partial \psi}{\partial l_1} = 0$.

Even in the case of a small leak we are, at least with the present knowledge about the osmotic process, unable to find the correction due to that part of the leak which is able to influence the osmotic activity. We can only find the pressure π_0' .

As to the quantity Σ we know at present very little about its actual size. In the case of copper ferrocyanide and sugar solutions we have reason to believe that it will be positive. It is stated by Berkeley and Hartley* that in their experiments the corrected pressure (π_0') generally comes out smaller for a greater leak. It appears from this that as far as the leaks are able to influence the pressure π_0' the latter will be diminished by the leak. This is also confirmed by some experiments that will be described later.

As there probably always will be some osmotic leak we have

$$\pi_0 > \pi_0' > \pi'. \dots \dots (7)$$

And, as shown by the experiments, $\frac{d\lambda'}{d\pi}$ will be a positive quantity, then

$$\Sigma > 0.$$

* *Loc. cit.* p. 503.

If this can be considered a general rule it must take place when we have only one kind of leak, then we get

$$\left(\frac{\partial \Psi}{\partial l_r}\right)_0 > 0.$$

Remembering that the velocities are positive when the height of water-level is increased, we come to the very reasonable conclusion that the osmotic activity is diminished by the leak.

From (7) we see that by assuming the whole leak a solution leak and finding the pressure π_0' , we shall approach the ideal pressure, and in the treatment of the observations we shall use this correction.

The apparent equilibrium pressure is determined by the manometer pressure q , but to this must be added a quantity due to the liquids. For the manometer used at Christiania we get

$$\pi_0' = q - 0.44 + 0.0104a - p_0 + \Delta\pi \text{ atm.}$$

a is the manometer reading in cm. For somewhat high pressures we can put $p_0 = 1$. $\Delta\pi$ is the correction for the leak regarded as a solution leak. To find $\Delta\pi$ we shall have to find λ' in the neighbourhood of the apparent equilibrium point. Further, we shall have to find the leak corresponding to a pressure near to the equilibrium pressure. Then in the experiments we ought to keep the pressure on an average near to the equilibrium pressure. By analysing the water in the cell and by assuming a constant velocity of leak, the latter can be found.

On the Determination of the Actual Concentration.

10. The concentration difference between the two sides of the membrane in the case of cane-sugar can be altered in three different ways :

- (1) By the osmotic flow of water into the solution.
- (2) By the leaks.
- (3) By inversion.

To determine these corrections the following method was used :—

A possible inversion was tested with Fehling's solution, and in our experiments the first qualitative test gave no measurable precipitate. The change in concentration on account of dilution was found by measuring the angles of polarization α_0 and α before and after the osmosis. The concentration (g)

of the water in the cell was also determined by polarization. If $\frac{\alpha_0 - \alpha}{\alpha_0}$ is a small quantity and G is the original concentration, the actual concentration will be

$$C = G \frac{\alpha}{\alpha_0} - g.$$

When the compressor is used we shall generally find $\alpha_0 = \alpha$, and in most cases g has been so small as not to be detectable by polarization.

The angle of polarization is measured by Laurent's polarimeter, which enabled me to read with an accuracy of 1 or 2 minutes, when taking the mean of a number of readings. With the tube used it corresponds to a concentration of about 1/8—1/4 gr. in the litre.

[To be continued.]

XX. *On Bessel Functions of Equal Argument and Order.*
By J. W. NICHOLSON, D.Sc., B.A., Isaac Newton Student
in the University of Cambridge*.

THE solution of many physical problems depends upon a knowledge of the behaviour of the Bessel function commonly denoted by $J_n(z)$, and of other functions associated with it, when the argument z and order n are nearly equal. The only treatment of this question which the author has been able to discover is contained in a paper by Lorenz†, which only deals with a very special case in which n is half of an odd integer. But even in this restricted investigation, the method employed is highly unsatisfactory, and many of the steps made seem incapable of justification. For example, at one point Lorenz divides a definite integral, involving a Bessel function in the integrand, into two parts, say α and β . In α the range extends from zero to a "small quantity h ," and it is shown that to a certain order α may be neglected. The range in β extends from h to a quantity "not small," in fact $\frac{\pi}{2}$. Lorenz substitutes an asymptotic expansion for the Bessel function of zero order in β , but thereby renders the result liable to an error of the same magnitude as the terms retained, for in the lower portion of

* Communicated by the Author.

† "Sur la réflexion de la lumière par une sphère transparente," *Œuvres Scientifiques*, i. pp. 435 et seq.

FIG. 4.

FIG. 5.