ELECTRO-ENDOSMOSIS ACROSS CEMENT MEMBRANES.

A THESIS

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by

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Part 1. Historical

The first observance of electro-endosmosis was by Reuss in 1808, who noticed that during electrolysis there was a transfer of liquid from one side of a porous membrane to the other. Poiret, Bequerel, Armstrong and Daniels, using membranes of various materials as dividing compartments for work in electrolysis, also reported transfer of the electrolyte through these partitions.

Thomas Graham (1) while working with solutions of electrolytes contained in porcelain vessels in experiments on osmosis, found that irregularities in the osmotic pressure occurred. These irregularities he attributed to some action of the porcelain membranes. They were most marked when using caustic alkalis.

These and other phenomena were carefully studied by Wiedman (2) and Quinke (3,4,5). Generally speaking the results of these investigations indicated, that when a current of electricity was passed through a liquid, separated into two portions by a porous septum, the flow of liquid through the septum was proportional to:-(1) the current intensity, (2) the specific resistance of the liquid and (3) the thickness of the membrane. They found the endosmosis to be inversely proportional to the porosity of the membrane. The flow was generally toward the cathode, but under certain conditions was toward the anode, or contrary to the flow of the current.

Alfred Coehn, in 1898 (6,7), showed that during electro-endosmosis the membrane and solution became oppositely charged; and that by changing the media this charge could be increased, diminished and even reversed.

J.C.Olson (8) encountered electro-endosmosis while preparing permanganic acid by the electrolysis of potassium permanganate, employing a porous cup to contain the electrode. F.J.Parkes (9) on attempting to improve on Olson's method, made use of two porous cups, one containing the anode, and the other the cathode. Under such conditions he found that endosmosis occurred simultaneously, in opposite directions.

Jean Perrin (10,11) used thick membranes of a large number of substances, and, from a study of the endosmosis occurring in each case, made the generalisation that the flow of liquid was either with or against the current, according to the charge held by the membrane. Perrin postulated that the charge was itself determined by the membrane being in contact with either hydrogen or hydroxyl ions.

A peculiar case was reported by Reed in 1902 (12) in which endosmosis appeared to flow to neither cathode or anode, but away from both.

Bancroft (13), commenting on the work of both Reed and Perrin suggested that the direction of flow was determined by the adsorption of ions of the greatest concentration.

Bartell (14) described a series of experiments on osmosis where he actually obtained concentration of substances contained in a porous membrane on electrolysis of the solution.

Byers and Walter (15) performed experiments which show that the flow may be toward the cathode, anode or in both directions simultaneously. The membranes used throughout their work were of clay, and consequently they encountered complications due to stenalysis. Starting with very concentrated solutions they found electro-endosmosis to increase with dilution. They did not however take into consideration the possible effect of change in voltage, maintaining only the current density at a constant value. Theoretically they considered that the

charge on the membrane was responsible for the flow, but were at a loss to explain the mechanism by which the liquid actually traversed the septa.

Bartell (14), pointed out that the underlying cause of negative osmosis, and electro-endosmosis were the same. The cause of the charge he attributed to the formation of a "double layer" between membrane and solution to which the general nernst equation

applies.

He pointed out, also, that while this accounts for the charge on the membrane surface, it does not account for the flow of liquid through the membrane. The actual flow he considered a function of the tiny capillaries which make up such a membrane.

Bancroft, in a later article (16) considered electro-endosmosis to be a general colloidal property, and gave a very much wider view of the application of the adsorption theory to this phenomena than did Perrin. Bancroft showed that the charge on the membrane was not exclusively determined by concentrations od hydrogen and hydroxyl ions, but that any ion has the power to affect a membrane charge. Bancroft suggested that in cases where more than one ion is present, the ion having the greatest "adsorption value" is active in determining the membrane charge. He, however, did not go past the polorised surface, and did not show what happens within the septa.

In 1907, Bigelow had published a paper (17) which, read in the light of what we now know of adsorption, goes a long way toward clearing up the mystery of the mechanism of endosmosis. He considered that in any membrane there are an infinite number of microscopic capillaries in a very complex arrangement.

The adsorption of an ion at either end of such a capillary tube, would have the same effect as the introduction of a tiny anode

and cathode. This in turn would "polarise" neighboring capillaries. Only ions of high mobility would be able to modify the more central capillaries. In this way he explains "selective adsorption". The double layer having been established at the surface and the "pores" or capillaries within the membrane being polarised the liquid in contact with the membrane amy pass through.

The whole subject of endosmosis was considerably cleared up, and put on a workable basis by Bartell and Hocker in 1916 (18). The work was really done on negative osmosis but as Bartell pointed out previously, (14), the underlying theory of both negative osmosis and electro-endosmosis are identical. These workers premise two controlling factors (1), the potential difference between membrane and solution, i.e. the Helmhalst double layer effect and (2) the charge on the membrane material. So far as the effect of ions is concerned they held the views of Bancroft to be fundamental, while those of Perrin and Gerard (10,11) were found to be not always justified, as they showed that the concentration of hydrogen and hydroxyl ions do not exclusively determine the membrane charge. They also stressed the fact that endosmosis is a colloidal property of matter, and the counterpart of cataphoresis.

The authors had used porcelain membranes which, when finely ground showed marked cataphoresis. They were able to reverse the direction of migration by the addition of acids; and, not only that, but by calculation they found that the velocity of cataphoretic migration was of the same magnitude as the velocity of endosmosis, when the particles were bound together, as in the original membranes.

The principles of colloidal chemistry with respect to adsorption of ions, was definitely shown to apply in the case of these membranes. The valency rule held in all particulars and among the members of each valence, the ions of greatest mobility had the greatest effect. In summary experimental evidence was brought forward to show:-

(1) When neutral salt solutions were the media, negative osmosis and hence endosmosis increased with the dilution.

(2) The Hoffmeister series of ion activities held closely.

(3) Hydrogen and hydroxyl ion concentration do not exclusively determine the membrane charge.

(4) The greater the diffusion of ions through the membrane the greater its modification. Hence ions of high mobility have greater effect than those with lower velocity of migration.

Bartell and Hocker were able to measure the actual potential differences at the membrane - solution interface by the potentiometer method. Their set up was:

A - Hg - HgCl - N.KCl - Solution - Membrane

B - Membrane - Solution - N.HCl - HgCl - Hg.

Frank and Withrow (20), using Shepherd's device for making mercury amalgams by electrolysis (21), were surprised to find that electro-endosmosis did not occur when it was expected. This caused a further investigation of the cause of the phenomena. The result added but one new thing to those found by previous investigators, namely, the effect of change in the applied voltage. Frank and Withrow found that electro-endosmosis varied directly with the applied E.M.F.

The most recent investigation of electro-endosmosis was carried out by Strickler and Matthews (22), in 1922. They made use of a modified Briggs type of endosmosis apparatus (23), which, since we have used the same type of apparatus in this investigation we will not describe.

The media for the most part were organic in nature, having little or no conductivity. The membranes used were of Whatman filter paper.

The authors were successful in showing experimentally the effect of voltage, current density temperature and time on the endosmosis.

(For complete Bibliography see last page.)

Object of the Research

For some time the colloidal nature of cement has been generally accepted. For this reason it seems probable that colloidal reactions play a part in the deterioration of concrete in contact with ground waters.

The role of the charge on colloidal particles is most important. The repulsion of particles due to like charges is generally given as one explanation of the stability of suspensions. When the charge on the particle becomes, or approaches zero, coalescence takes place, brownian movement is retarted and precipitation occurs. The importance of the charge on the stability of colloidal systems becomes at once an important problem. Carrying this reasoning over to cement and concrete, it becomes immediately a point of interest to determine the effect of various solutions with which cements come in contact, on the isoelectric point, Furthermore, it would be of material interest to compare the conditions responsible for an isoelectric with their effect on concrete deterioration.

Calcium hydroxide, rapidly leaches from cement left in contact with water or solutions, and since certain concentrations of calcium hydroxide from part of the environment of cements, it seemed of interest to determine the effect of various concentrations of this material on the charge on the cement particles. Ground waters in various localities have different hydrogen ion concentrations and hence a study of the effect of various hydrogen ion concentrations on the charge on the cement seemed of importance.

Electroendosmosis across cement membranes in these various solutions seemed to be an effective way of attacking this problem.

Part 11. Experimental

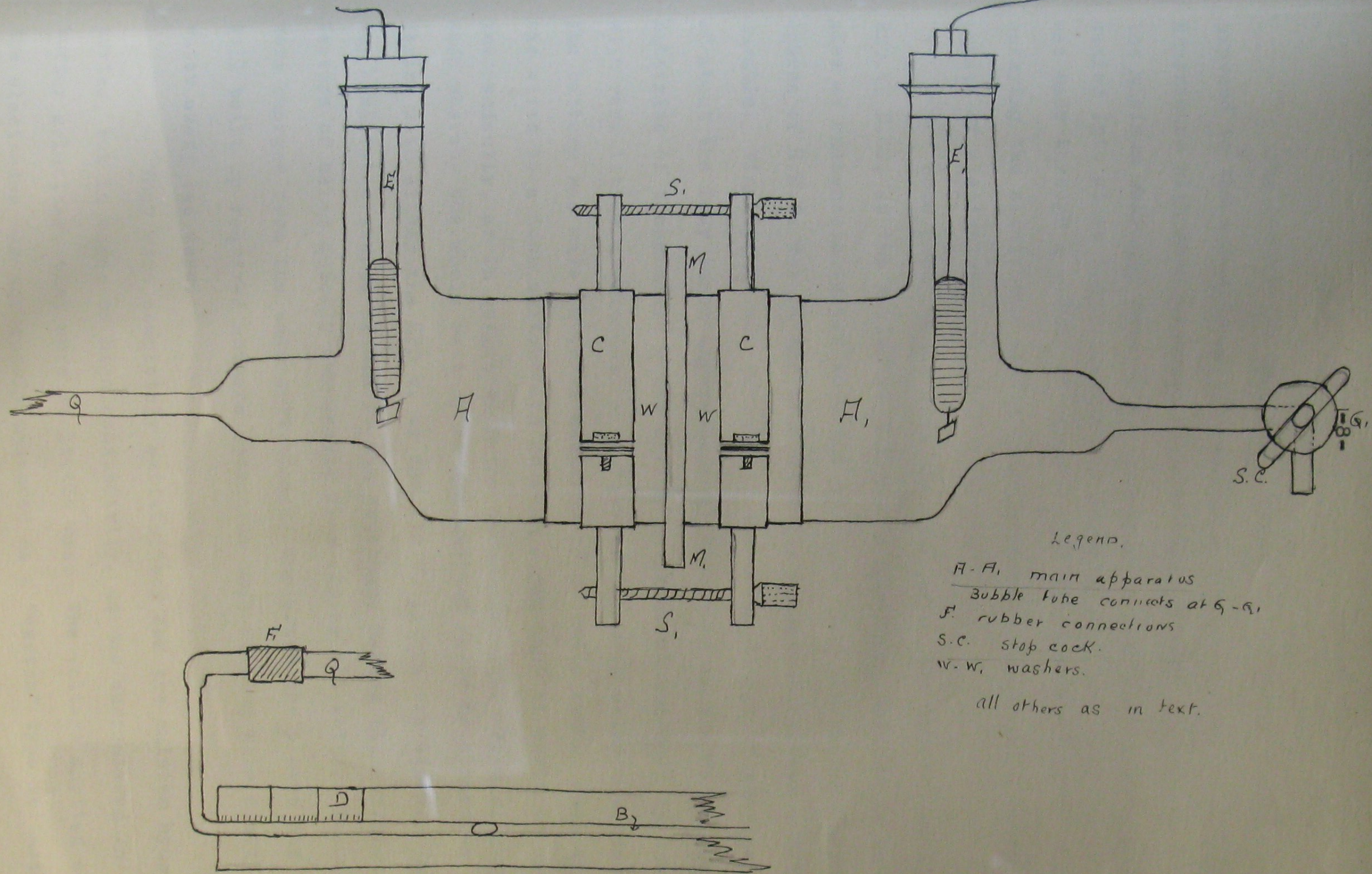
Apparatus

After some consideration of the apparatus used by previous investigators, that employed by Strickler and Matthews (loc.cit), was thought to be most suitable for our purpose. It was easily assembled and cleaned, and with a few slight modifications was used satisfactorily for endosmosis of solutions having a high conductivity, causing evolution of electrolytic gases.

The main portion of the apparatus was in two parts (A) and (A_1) when the membrane (M_1) was placed in position it represented a large cell divided into two portions by a cement septa. This main portion of the apparatus was fitted with two electrodes (E) and (E_1) for applying the external voltage. The ends of this main position was connected by short rubber joints to a small bore glass tube, in which rested a bubble, completely filling the bore. When, a potential having been applied to E and E_1, endosmosis took place through the membrane, the pressure of water on the one side of the membrane would force the bubble along the tube B. By observing the initial and final positions of the bubble, the endosmosis over a given time could be determined.

The apparatus was assembled by specially prepared clamps (C) and (C_1), which permitted an even strain being placed on glass and membrane. The glass, beneath the clamps, was protected by a thin washer of gooch crucible rubber, so arranged that the rubber collapsed over the end of the glass vessel next to the membrane, thus forming an effective gasket. To further prevent any possibility of leak, a thin coat of paraffin was applied to the point of juncture between rubber and membrane.

The bubble tube was mounted on a scale graduated in millimeters enabling the position of the bubble to be read easily to half a millimeter.



Legend.

A - A, main apparatus

Bubble tube connects at G - G,

F. rubber connections

S.C. stop cock.

W - W, washers.

all others as in text.

The electrodes were made from heavy platinum wire the end exposed to the solution in the apparatus being slightly flattened. Experience with several types of electrodes showed us that these gave the minimum wear and tear on the batteries. The wires were carefully sealed into glass tubes, mounted on corks to fit the apparatus. Contact was made through a column of mercury half filling the tubes. The corks carrying the electrodes were doubly perforated to afford a means of egress of electrolytic gases.

Some preliminary work was done using the laboratory line of 220.V. D.C., as the source of E.M.F., it was found however to be too slow as endosmosis varies with the voltage. The use of dry cells as a source of E.M.F. was at the same time too expensive and not sufficiently durable. Finally, it was decided to use a small type of storage cell, of about the four tenth ampere-hour size, having an e.m.f. of two volts. Batteries of these cells could easily be prepared and kept in condition with very little attention. A battery of 240 such cells was constructed. The battery was made in three sections of 80 cells each. Each section was wired to a desk switchboard in such a way that it could be used independently, or in series with the other sections. Provision was also made whereby the whole battery or any section could be connected in series with either the 220 V. or the 110 V. laboratory lines. In this way a variable source of E.M.F. was provided, having the additional feature of being quickly changeable from 110 to 700 volts. The cells were charged from the same switchboard, and after the plates had been well built up required no more attention than filling with distilled water every two days.

They were completely satisfactory for the calcium hydroxide series, but in cases of high conductivity, as was encountered in the buffer solutions, they were of little use. The voltage applied across the electrodes was accurately measured on a "Weston" type voltmeter, whose 150 volt range was increased to 1500 V. by the use of external

resistance. It was afterwards calibrated against a known E.M.F.

The runs were timed by a stop watch. The interval being previously agreed, and the reading taken and recorded when this time had elapsed.

Membranes

The membranes used in these determinations were made from "neat" cement. The cement employed was a "Canada" Portland, Engineering Laboratory No.465. The cement was mixed to a consistency of a little wet of normal, with distilled water, the average being about 27 per cent water. It was then poured into little brass moulds of diameter $2^1/8$ inches, but of varying heighths 1/16 inch and 1/8 inch, and 1/4 inch being the heighths used. The cement was allowed to set over night in the moulds and then the disks so formed were taken out and cured. The curing lasted ten days in all cases, in distilled water. After this partial hydration was complete the disks were removed, washed with distilled water, then with ether to remove any grease remaining from the moulds, a careful washing with alcohol followed, to remove the last traces of ether, the washed disks were then placed in distilled water until required. Experiments were tried on the various thicknesses of disks and the 1/16 inch and 1/4 inch sizes were eliminated, the one being too thin to withstand the strain of assembly and the latter too thick to give a reasonable flow with the voltage at our disposal. In a similar manner the right consistency had been arrived at. Disks having a consistency on the dry side of normal were apt to powder up quickly, and being porous, allowed the water to flow back through the membrane, instead of through the bubble tube.

Before a prepared membrane was used, it was carefully ground down with fine and course emery, washed, and soaked in distilled water for twelve hours before use. This was found to aid a great deal in preventing leaking, and also the membrane being wetted through made

it more permeable to the solutions. It will be remembered that paraffin seals are also used to prevent leaking, when this is done the greatest care must be exercised to prevent the apparatus ever reaching the melting point of paraffin, as in this event a film of paraffin will be deposited on the membrane surface completely spoiling the run.

Procedure

It was decided early in the work to use a standardised method of procedure, in order to ensure, as far as possible, the reproducibility of results.

The first run was always made with distilled water in the apparatus, to make sure that the prepared membrane was thoroughly soaked through, and sufficiently permeable, then, and between all subsequent runs, the solution in the apparatus was drained off, and the main apparatus washed twice with distilled water and finally with the new solution. It was found impossible to wash the bubble tube, due to the right angled bends, so this part of the apparatus was washed twice with a stream of distilled water. Between series the apparatus was filled with cleaning solution and carefully washed out before again being used.

The apparatus was assembled and one side filled with the solution to be worked with. The solution was permitted to run through the bubble tube and the stop cock turned to permit the first ten cubic centimeters or so to run out of the apparatus. The other side of the apparatus was then filled with solution to a higher level than the first side, at the same time a bubble of air was caught in the stop cock bore. When the stop cock was turned to connect this side with the bubble tube, the trapped bubble was swept into the bubble tube, The solution levels were approximately balanced, and the electrodes inserted. The bubble was then allowed to come to equilibrium. It was found best

to use a bubble of from four to six millimeters in length. The position of the bubble was then recorded to the nearest half of a millimeter. The difference between two readings of the bubble, over a given time interval was taken to be the measure of the endosmosis over that length of time.

EXPERIMENTAL

PRELIMINARY EXPERIMENTS

Preliminary experiments were run with a voltage of 220 as the storage cells subsequently used had not been installed. No accurate timing device was employed, the object being merely to see if the determination of endosmosis was at all feasible. The runs were of long duration being continued until the apparatus heated up to such an extent as to render further work impossible. In these experiments it was found that the bubble moved in what we called the "negative" direction, meaning that the liquid flowed to the negative electrode, then after a while its direction reversed and flowed in a "positive" direction, i.e. to the positive pole. The time elapsing between the first negative movement and the reversal was considerable but we at first considered that this negative movement was due to some physical cause. Later it was thought that the leaching out of $Ca(OH)_2$ from the membrane might have some contributing effect. By ignoring this first negative flow and considering that the positive one was the true endosmosis the natural assumption was that the membrane itself was positive, and that the leaching out of calcium hydroxide would cause a lessening of the flow. This assumption was not corroborated by experiment as when saturated calcium hydroxide was added to the solution the result was the decrease of the first negative flow to give rise to a much increased positive flow. We then concluded that the negative flow was due not to physical happenings in the apparatus but that in distilled water and slight concentrations of calcium

hydroxide (i.e. in low pH) the membrane was not positive but negative, and that it adsorbed the calcium ion from solution to become less and less negative until finally its charge was reversed and the flow went in a positive direction. Having arrived at this conclusion it was decided to start a series of experiments beginning with distilled water and continuing through various concentrations of calcium hydroxide with concentrations increasing toward saturation point.

Preliminary Calcium Hydroxide Series

Preparation of Materials

"Baker's C.P." calcium hydroxide was heated over a blast lamp for several hours in an open platinum dish. The center of the remaining substance was removed and reheated in a covered platinum crucible for one hour until no further loss in weight was noticeable. The cooled calcium oxide was then shaken slowly into two liters of distilled water, and thoroughly shaken. The suspension was allowed to settle, the supernatured liquid ultrated and found to contain 1.6570 grams $Ca(OH)_2$ per liter. The total carbonate and bicarbonate impurities was represented by a liter of fiftieth normal acid of 0.66 cubic centimeters. The titration was run at 22°C which was the average room temperature.

The stock solution was preserved in corked flasks, carefully sealed with paraffin to exclude carbon dioxide from the air.

The solutions used in the series were then prepared by diluting a measured amount of the stock solution and making up to 500 ccs. in a calibrated flask. These solutions were kept in small sealed flasks until used. A 500 cc. portion was usually sufficient for a run in duplicate.

Nomenclature

Each series was designated with a letter. For example Distilled water series was reported as the "A" series. The Preliminary

Calcium Hydroxide as the "B" series, and so on throughout the work. Each member of the series was given a number corresponding to a definite concentration of $Ca(OH)_2$ or a definite pH as the case might be. Hence in the Preliminary Calcium Hydroxide series B - 7 would represent a concentration of $Ca(OH)_2$ of 0.00497 grams per liter and B - 8 a concentration of 0.006628, the number increasing with the concentration. The original run was numbered 1, the duplicate 2, while the first trial, original and duplicate, was lettered "a" , the second trial "b". Hence the member of the preliminary calcium hydroxide series of concentration 0.00497 grams per liter, the original of first trial would be numbered B-7-1-a, the duplicate B-7-2-a and so on.

The method of procedure outlined above was used in all cases. After a sample of solution had been removed the flask was again resealed to prevent contamination. Readings of electroendosmosis were made over a definite time interval, usually one minute, but in cases of high conductivity this time was shortened. In recording data all time intervals were calculated over to one minute.

Definition

Throughout this work frequent use is made of the terms "positive" and "negative" endosmosis. "Positive" is taken to mean the flow of liquid to the positive pole and "negative" the flow to the negative pole. By so defining these terms it follows that when the endosmosis is positive, the charge on the membrane is positive and vice versa.

It is regrettable that during the run of B-6, the apparatus heated up sufficiently to cause the paraffin seal to melt over the membrane surface. A new membrane was inserted at B-7 and the results from B-1 to B-6 inclusive were discarded.

Interpretation of Results

The actual experimental data of the series are given in Table 1, and graph, while the summary is given in Table 11 and graph. It will be noticed that in all cases there is an irregularity at the beginning of the run followed by a period lasting for the balance of the run, of relative constant values. As it was not at all certain that these initial regularities can be attributed to endosmosis, it was decided to omit them in the summary of results. From a study of the graph, accompanying Table 1, it will be noticed that there are a series of maxima followed by minima points. Since the graph represents the actual flow during each time interval rather than the additive flow during the whole period, it was decided to average the readings of the last 10 or 15 minutes of each run and calculate the endosmosis per minute from this. These results are given in the summary Table 11.

Date on Series B.

Table 1.

values neg. except where marked

Membrane	Medium	Volts	Time	Endosmosis in Cm.
B-7-1-A 1/8" membrane Canada Portland cement No.465	$Ca(OH)_2$ 0.00497 grams per liter	700 volts	60 second intervals.	0.25 0.25 0.20 0.10 0.24 0.40 0.25 0.36 0.15 0.15 0.35 0.25 0.20 0.32 0.20 0.25 0.45 0.25 0.13 0.22 0.10 0.12
B-7-2-A 1/8" membrane Canada Portland cement No.465	$Ca(OH)_2$ 0.00497 grams per liter	700 volts	60 second intervals.	0.02 0.13 0.08 0.00 0.38 0.12 0.02 0.10 0.10 0.00 0.20 0.10 0.02 0.23 0.01 0.14 0.01 0.20 0.10 0.13
B-8-1-A 1/8" membrane Canada Portland cement. No.465	$Ca(OH)_2$ 0.006628 grams per liter	700 volts	60 second intervals.	0.30 0.04 0.08 0.20 0.11 0.10 0.15 0.20 0.10 0.15 0.08 0.09 0.01 0.12 0.01 0.10 0.00 0.10 0.10 0.11 0.15 0.11
B-8-2-A 1/8" membrane Canada Portland cement No.465	$Ca(OH)_2$ 0.006628 grams per liter	700 volts	60 second intervals	0.05 0.15 0.10 0.00 0.10 0.11 0.00 0.04 0.08 0.00 0.06 0.10 0.00 0.13 0.10 0.00 0.12 0.09 0.15 0.09 0.10 0.14 0.10
B-9-1-A 1/8" Canada Portland cement. No.465	$Ca(OH)_2$ 0.00942 grams per liter	700 volts	60 second intervals.	0.00 ±0.00 +0.02 ±0.00 ±0.00 ±0.00 +0.02 ±0.00 +0.02 ±0.00 ±0.00 ±0.00 +0.04 ±0.00 ±0.00 +0.03 ±0.00 +0.01 +0.02 ±0.00

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Table 1.

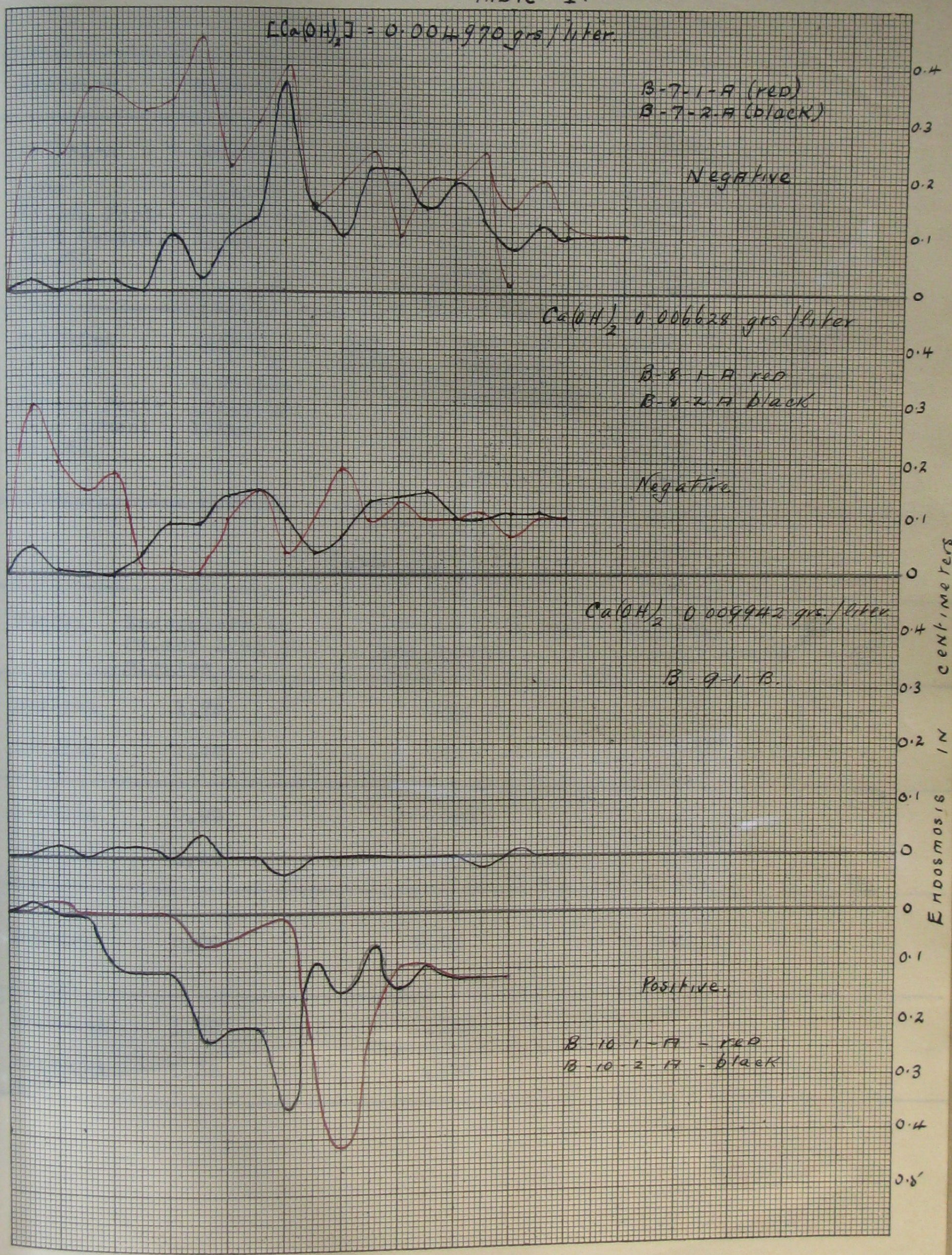

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Table 1. Cont'd.

Membrane	Medium	Volts	Time	Endosmosis in Cm.
B-10-1-A 1/8" Canada Portland Cement, No.465	$Ca(OH)_2$ 0.016570 grams per liter	700 volts	60 second intervals	-0.01 +0.04 +0.11 -0.02 +0.02 +0.11 0.00 ±0.00 +0.11 0.00 +0.42 0.00 +0.21 0.00 +0.09 +0.05 +0.09
B-10-2-A 1/8" Canada Portland cement No.465	$Ca(OH)_2$ 0.016570 grams per liter	700 volts	60 second intervals	-0.02 0.20 0.11 ±0.00 0.35 0.11 ±0.00 0.08 0.11 +0.09 0.14 +0.10 0.05 0.10 0.14 0.22 0.09

Table 11.

Number	Endosmosis in Cm. for last 10 minutes	Endosmosis in Cm. per minute	Endosmosis in Cm. per minute
B-7-1-A	1.75	.17	- .16
B-7-2-A	1.40	.14	
B-8-1-A	0.99	.099	- .10
B-8-2-A	1.09	.109	
B-9-1-A	0.00	0.00	± 0.00
B-10-1-A	1.20	.120	+ .13
B-10-2-A	1.38	.138	

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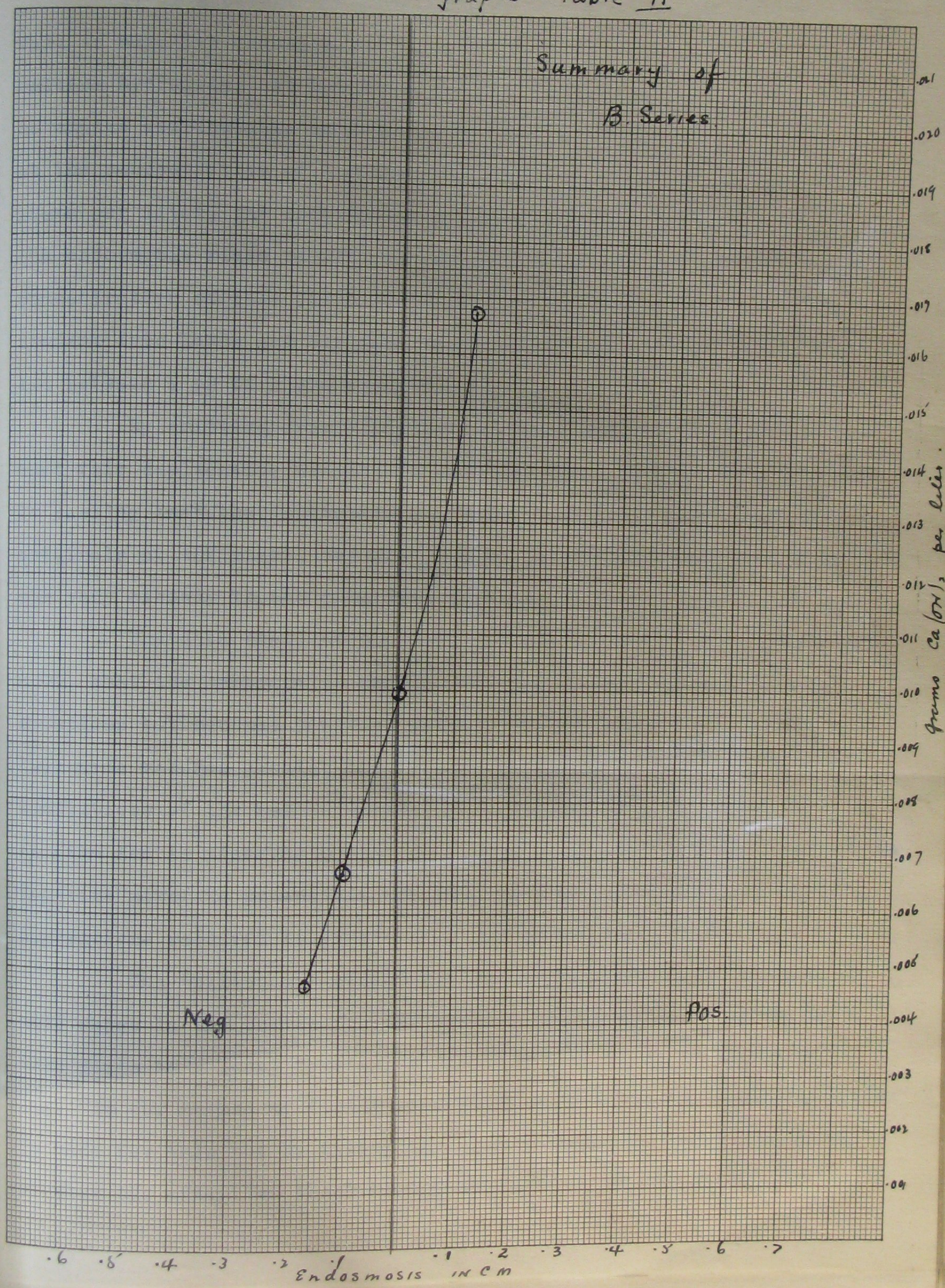
Graphs - Table II



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It is apparent that running through the series there is a fall in negative endosmosis with an increasing concentration of calcium hydroxide. At B-9 there is an apparant transition point, no change attributable to endosmosis is noticed. We may state that at the concentration of a calcium hydroxide represented at B-9,0.009942 grams per liter, the endosmosis is zero. After this point is passed the endosmosis rises rapidly in a positive direction. The hydrogen ion concentration of this point of transition ions taken roughly on a student type Leeds and Northrup hydrogen ion apparatus, and found to lie between a pH of 8 and a pH of 9.

By omitting irregularities stated above, it will be noticed that fair duplication of results was possible. It might be mentioned in passing that the duplicates are always a little lower than the originals at the start, but that during the run they balance up and run very closely to the same mean values.

The data seems to bear out our assumption of the preliminary work, that the membrane is negative in dilute calcium hydroxide solutions but becomes positive when the concentration of calcium hydroxide becomes greater than 0.0099 grams per liter. With all the limitations of the method allowed for there is evidence that the calcium ion is adsorbed by the membrane, resulting in a decrease of the negative membrane potential. It will also be noticed that the concentrations required to effect this change are very small.

The "piling up" effect noticed by Strickler and Matthews is well shown in the curves for the series. The endosmosis seems to take place in a jerky fashion, a distinct flow being followed by a lag. In our method of timing over sixty second intervals no correction is made for this but by taking the average over the last ten minutes of flow the effect of these maxima and minima are effaced.

C. Series

Calcium Hydroxide.

It is quite apparent that some relationship exists between the concentration of $Ca(OH)_2$ and the charge on membrane. The B series show a decided fall in negative endosmosis with increasing concentration of $Ca(OH)_2$. The C series attempts to duplicate the results on the position of the isoelectric point and as far as possible cover the same range of investigation as before.

The calcium hydroxide used was prepared in the manner described above. In addition it was shaken over night and removed, allowed to clear and the supernatant liquid analysed.. The analysis gave a concentration of 1.6565 grams $Ca(OH)_2$ per liter.

From this stock solution the flasks used for each determination were filled and the concetration of $Ca(OH)_2$ in each was calculated from the dilution. The method used was in all particulars the same as stated above.

The high conductivity of the solutions from C-4 to end caused considerable trouble with the storage cells. It was found impossible to place any resistance in series with the apparatus, due to the distribution of the current over the various resistances. Accordingly runs were timed over 30 second intervals and two such readings were added together to give the minute readings.

In C-5 and C-6 some violent reaction took place in the apparatus, at start of the run, this was not noticed in any other members of the series. There is always a slight negative endosmosis at the beginning of a run but in these cases it amounted to over 0.70 cm. in a minute.. After the first few minutes the curve became normal again.

Table 111.

Calcium Hydroxide Series "C".

Membrane	Medium	Voltage	Time	Endosmosis in Cm.			
				values neg.			
C-2-1-A 1-8" Canada Port-land. No.465	$Ca(OH)_2$ 0.0016570 grams per liter	700 volts	60 sec.	0.30			
				0.20			
				0.30			
				0.08			
				0.00			
				0.21			
			30 sec.	0.02	0.02	0.28	0.10
				0.07	0.08	0.01	0.10
				0.10	0.10	0.08	0.10
				0.01	0.05	0.01	0.11
				0.10	0.06	0.10	
C-2-2-A 1/8" Canada Port-land. No.465	$Ca(OH)_2$ 0.0016570 grams per liter	700 volts	60 sec.	0.28			
				0.10			
			30 sec.	0.05	0.04	0.14	
				0.05	0.04	0.06	
				0.05	0.07	0.09	
				0.05	0.09	0.16	
				0.10	0.00	0.15	
				0.11	0.10	0.10	
				0.01	0.06	0.10	
C-3-1-A 1/8" Canada Port-land cement. No.465	$Ca(OH)_2$ 0.0033140 grams per liter	700 volts	60 sec.	0.13	0.32	0.25	
				0.15	0.12	0.25	
				0.10	0.20	0.20	
				0.19	0.20	0.20	
				0.07	0.20	0.30	
C-3-2-A 1/8" Canada Port-land. No.465	$Ca(OH)_2$ 0.0033140 grams per liter	700 volts	60 sec.	0.60	0.19	0.07	
				0.15	0.12	0.08	
				0.20	0.18	0.17	
				0.10	0.11	0.18	
				0.21	0.12	0.17	
				0.14	0.20	0.07	
				0.05	0.14	0.07	
				0.20	0.17	0.11	
C-4-1-A 1/8" Canada Port-land No.465	$Ca(OH)_2$ 0.006628 grams per liter	700 volts	60 sec.	0.31	0.03	0.05	
				0.19	0.00	0.05	
				0.16	0.02	0.07	
				0.08	0.00	0.03	
				0.00	0.24	0.05	
				0.03	0.01	0.05	
						0.00	

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Table III

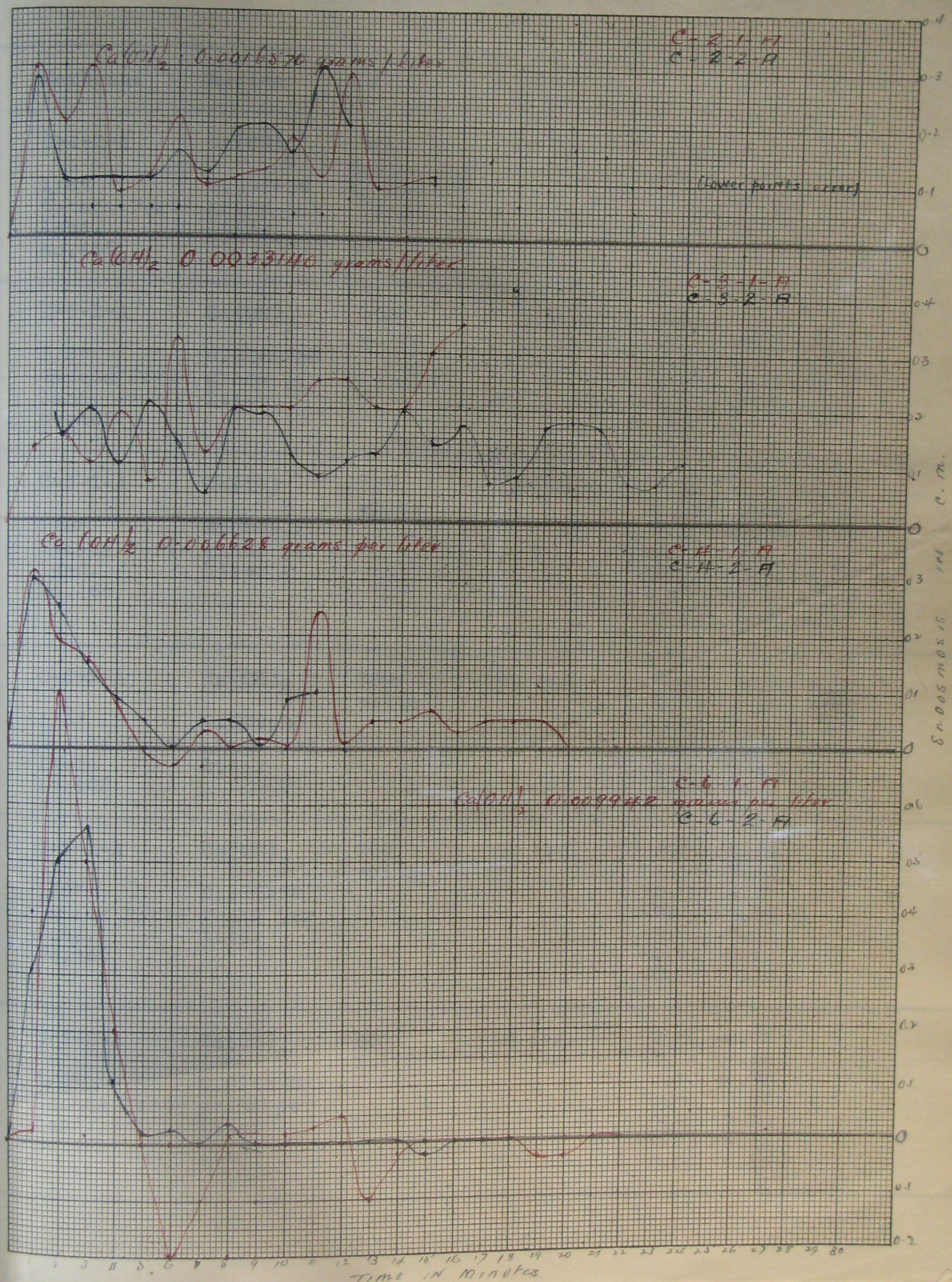

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Table 111. Cont'd.

Membrane	Medium	Voltage	Time	Endosmosis in Cm.
C-4-2-A 1/8" Canada Port-land. no.465	$Ca(OH)_2$ 0.006628 grams per liter	700 decreasing to 650 at end.	60 sec.	values neg. 0.30 0.00 0.10 0.25 0.05 0.00 0.15 0.05 0.05 0.09 0.01 0.05 0.09
C-5-1-A 1/8" Canada Port-land. No.465	$Ca(OH)_2$ 0.0082850 grams per liter	700 volts	60 sec.	0.34 0.05 0.01 0.31 0.02 0.04 0.06 0.16 0.04 0.09 0.01 0.02 0.05 0.01 0.01
C-6-1-A 1/8" Canada Port-land. No.465	$Ca(OH)_2$ 0.0099420 grams per liter	700 volts	60 sec.	0.00 0.02 0.00 0.80 0.03 0.00 0.50 0.05 0.03 0.20 0.10 0.03 0.00 0.02 0.00 0.20 0.00 0.00 0.10 0.00 0.00
C-6-2-A 1/8" Canada Port-land. No.465	$Ca(OH)_2$ 0.009420 grams per liter	700 volts	60 sec.	0.00 0.03 0.00 0.31 0.00 0.00 0.50 0.04 0.00 0.56 0.00 0.02 0.11 0.00 0.00 0.02 0.00 0.00
C-7-1-A 1/8" Canada Port-land. No.465	$Ca(OH)_2$ 0.016570 grams per liter	700 volts	60 sec.	-0.04 +0.35 -0.04 +0.25 ±0.00 +0.11 +0.10 +0.20 +0.05 +0.11 +0.22 +0.13 +0.05 +0.10
C-7-2-A 1/8" Canada Port-land. No.465	$Ca(OH)_2$ 0.016570 grams per liter	700 volts	60 sec.	-0.01 ±0.00 -0.04 +0.40 ±0.00 +0.35 ±0.00 +0.20 ±0.00 +0.10 +0.05 +0.10 +0.05 +0.10

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Table III Ctd

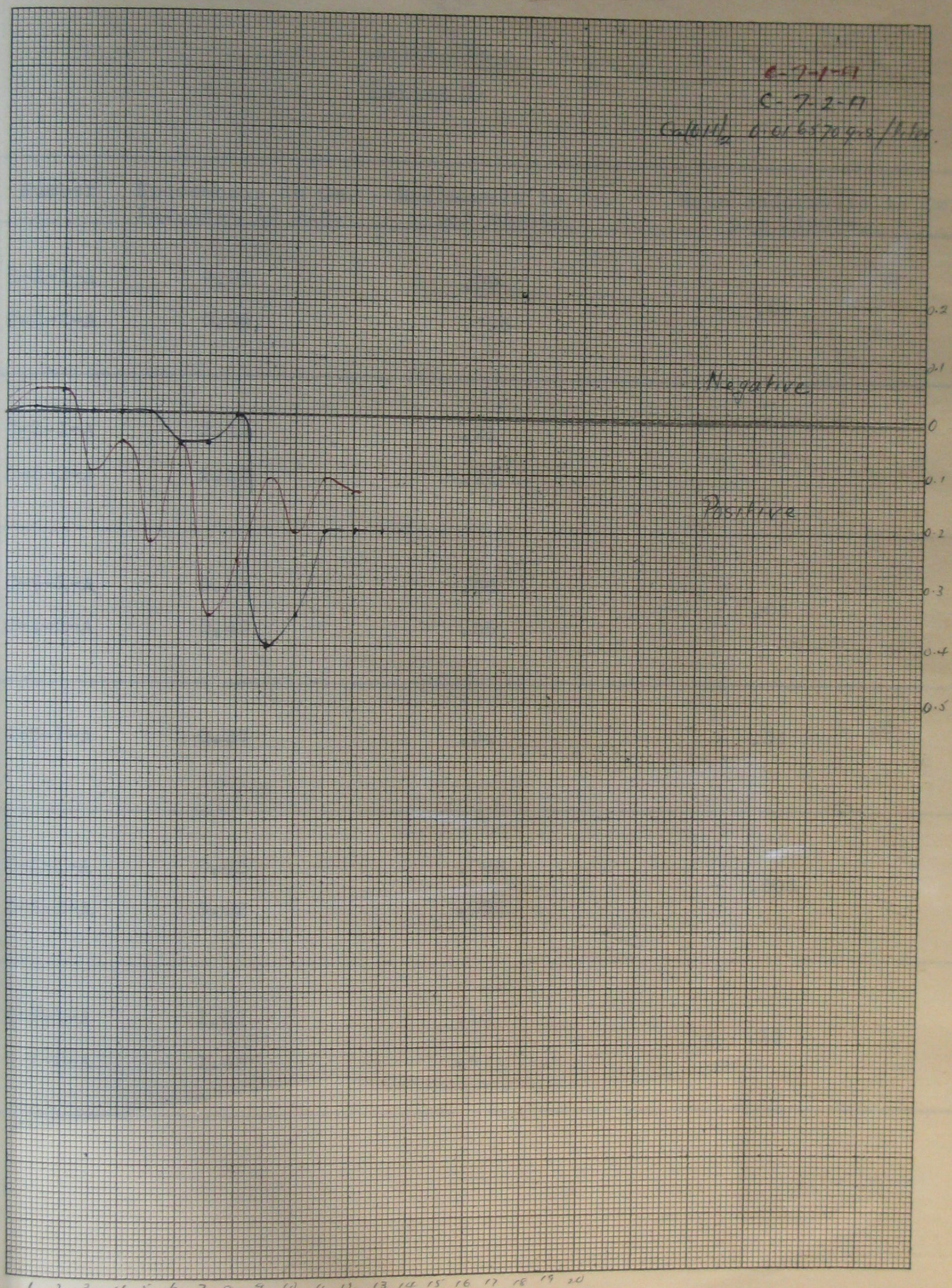

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Table IV.

Series C.

Number	Endosmosis in Cm. for last 10 min.	Endosmosis in Cm. per minute	Mean endosmosis in Cm. per minute.
C-2-1-A	0.90	.09	- .09
C-2-2-A	0.95	.095	
C-3-1-A	2.12	.21	- .15
C-3-2-A	1.23	.12	
C-4-1-A	0.57	.06	- .05
C-4-2-A	0.49	.05	
C-5-1-A	0.37	.04	- .04
C-6-1-A	0.08	.008	- .003
C-6-2-A	0.02	.002	
C-7-1-A	1.57	.16	+ .15
C-7-2-A	1.45	.4	

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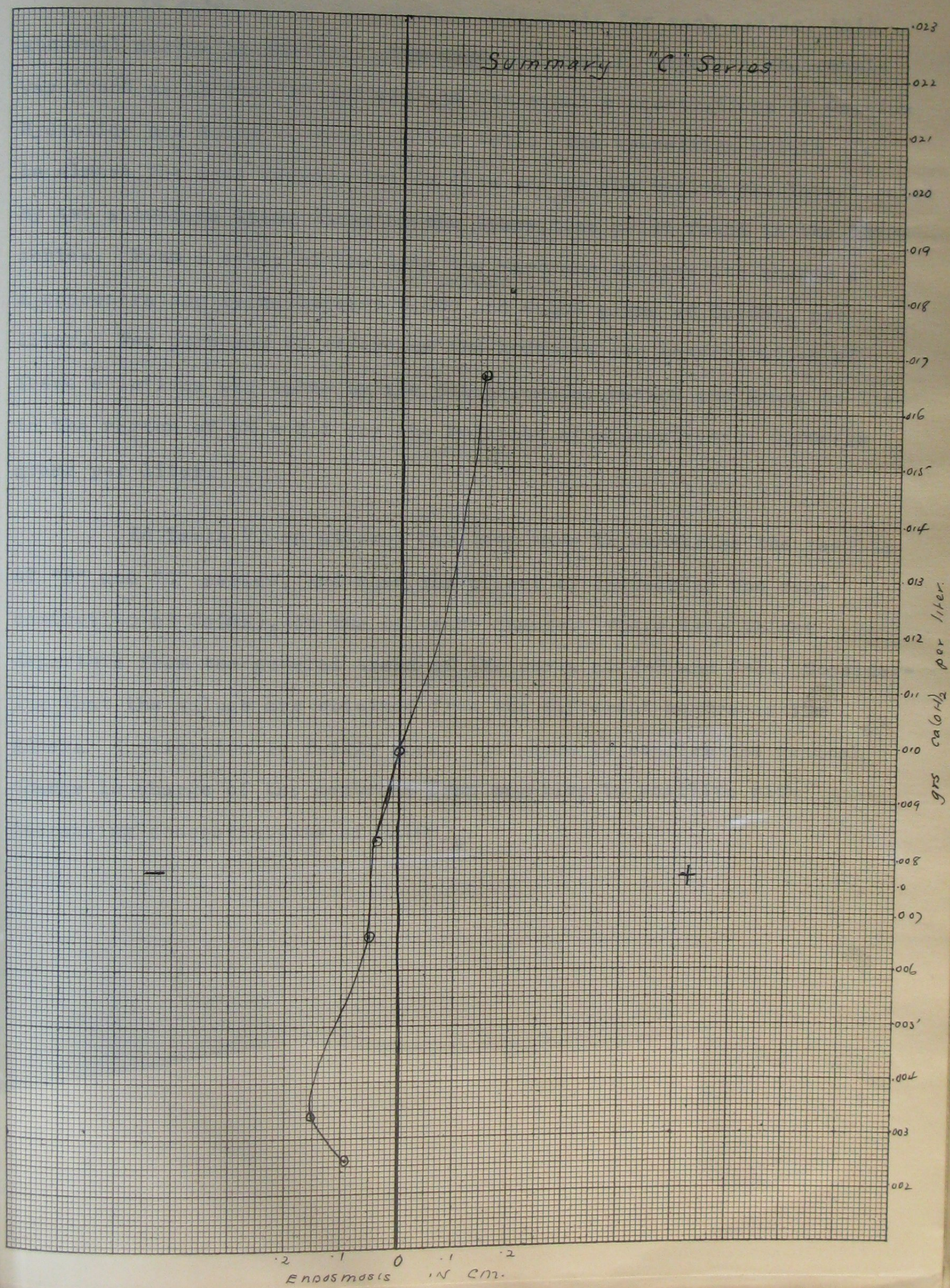
Table IV



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In calculating the average endosmosis for each series, this abnormal maxima is omitted. The same decrease in negative endosmosis was found as in the "B" series, and for equal concentrations of Calcium Hydroxide are found to agree failry well. The transition points lie in almost the same region, but in this series the region was investigated by two solutions lying close to the transition point found in the "B" series. From a study of the data the membrane changes its charge at a concentration lying between 0.006 and 0.009 grams of $Ca(OH)_2$ per liter. For purposes of reference the hydrogen ion concentration of these solutions was taken by the potentiometer method and found to lie in the region of pH = 8.5 for the solution of concentration 0.006628 grams per liter.

In Table V. an attempt has been made to summarise the results of "B" and "C" series, and show the effect of increasing the concentration of $Ca(OH)_2$ on the membrane charge. There is a slight departure from the general trend of the curve at C-2 and C-3. Considering that the values are obtained from two different membranes the general duplication is fairly good, and seems to confirm the gradual change in charge of the membrane from negative to positive with increasing concentrations of $Ca(OH)_2$.

Table V.

Variation of Endosmosis with Increase in Concentration of Calcium Hydroxide.

(From both B & C Series.)

Concentration of Calcium Hydroxide in grams per liter	Series	Number	x Mean Endosmosis in Cm. per minute	Mean Endosmosis in Cm. per minute.
0.0016570	C	C-2-1-A C-2-2-A	0.09 ?	- 0.09 ?
0.0033140	C	C-3-1-A C-3-2-A	0.15 ?	- 0.15 ?
0.004970	B	B-7-1-A B-7-2-A	0.16	- 0.16
0.006628	B	B-8-1-A B-8-2-A	0.10	- 0.07
	C	C-4-1-A C-4-2-A	0.05	
0.0082850	C	C-5-1-A	0.04	- 0.04
0.009942	B	B-9-1-B	0.00	± 0.00
	C	C-6-1-A C-6-2-A	0.003	
0.016570	B	B-10-1-A B-10-2-A	0.13	+ 0.14
	C	C-7-1-A C-7-2-A	0.15	

x From Tables 11 and 1V.

Summary of $Ca(OH)_2$ Series.
(Table V)

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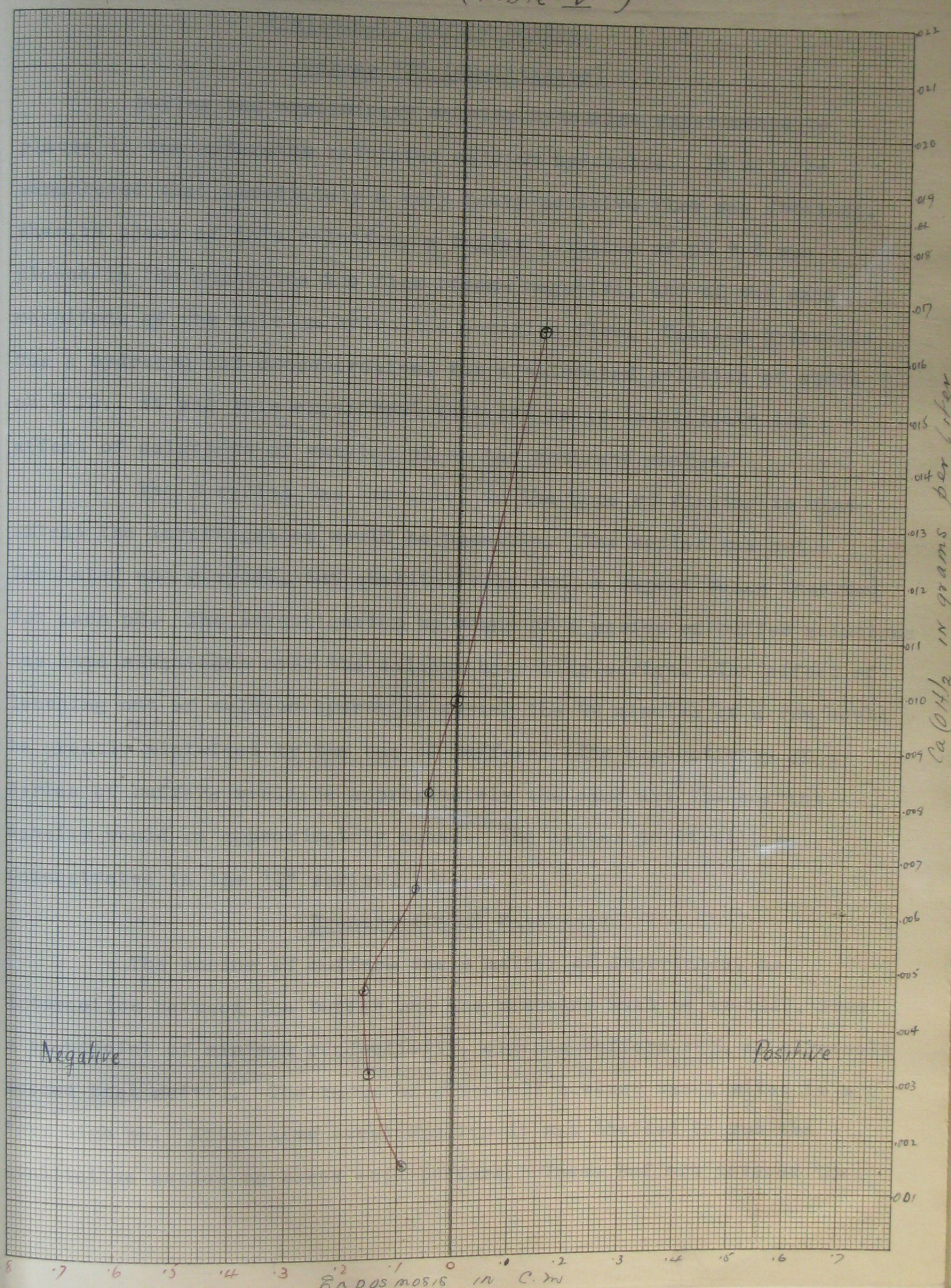

Preliminary Buffer Series.

Series "D" (Qualitative)

During the preliminary calcium hydroxide experiments we placed in the apparatus saturated calcium hydroxide. It will be remembered that immediately a very heavy positive flow was obtained. When, in place of this solution, a buffer solution of pH = 6 was placed in the apparatus the flow became negative, and of the same magnitude as the calcium hydroxide positive flow. Calcium hydroxide has a hydrogen ion concentration, for a saturated solution of about pH = 12. It was this experiment that led us to investigate the effect of solutions of varying pH on the membrane charge.

The D series was commenced in the hope of finding to what extent the investigation would be possible. The series was not tabulated and graphed, but qualitatively run, a report being inserted for each pH. The investigation by means of a series of buffer solutions has some advantages over the calcium hydroxide series. The effect of leaching out of calcium hydroxide during the 22 minutes of a run could be greatly minimised by the use of buffers. The conductivity of a series of buffers would be approximately the same and the current density would be approximately equal. The latter point will be demonstrated in the "G" series.

Preparation of Materials

The choice of buffers was a matter of importance, as interaction between the buffer and the membrane must be avoided. From a standpoint of minimum conductivity, organic buffers such as glycocoll seemed best suited. The range of glycocoll however was limited to a very high pH. After some consideration it was decided to run the qualitative series on boric acid buffers. These Buffers covered the

required range, did not react with the membrane to any appreciable extent, and were quite easily standardised to any required pH.

The method of preparation was that outlined by Clarke[1]. Two stock solutions were made up and the series buffer solutions were prepared by mixing the calculated amount of each.

Solution No.1

1000 ccs. distilled water containing 19.108 grams of $Na_2B_2O_7$

Solution No.11

1000 ccs. distilled water containing 12.404 grams H_3BO_3 and 2.925 grams NaCl.

Each of the series solutions contained about 300 ccs. of buffer solution, which was enough for two short runs. Each series solution after preparation was checked for its pH on one of the hydrogen ion machines. The results of these measurements, the preparation data, and a comparison between the theoretical and observed pH is given in the accompanying table (Table 6).

Table VI.

Preparation of Buffer Solutions

No. of Flask	Preparation	Observed pH	Theoretical pH
1	200 cc. solution 1 + 0 cc. Solution 2	9.06	9.24
2	180 " " 1 + 120 cc. " 2	8.68	8.69
3	90 " " 1 + 210 cc. " 2	8.03	8.08
4	30 " " 1 + 270 cc. " 2	7.36	7.36
5	9 " " 1 + 291 cc. " 2	6.73	6.77

In view of the high conductivity of such solutions it was obvious at the outset that the storage batteries could not be used. Accordingly the whole series was run with a voltage of 225. The amperage was kept constant at 0.8 amperes.

(1) "Determination of Hydrogen Ions" - Clarke.

Qualitative Results.

The results of the series were not altogether satisfactory. The high conductivity caused great heating effects which melted out our paraffin seals. The membranes, due to the temperature change, and a possible uneven strain on the clamps, broke very easily. Due to these occurrences, the 300 ccs. of buffer solution provided for each trial was insufficient, and in some cases the effect of a trial could not be determined.

The numbers by which this series is reported refer to the number of the flasks given in Table Vl. D-5 was spoiled due to the membrane breaking. D-4 gave a steady negative endosmosis. D-3 gave the appearance of being a transition point while D-2 gave practically no flow at all. D-1 in the few minutes that the membrane held was decidedly positive. The qualitative results of the series is tabulated in Table Vll. Too much reliance cannot be placed on this series as the membranes were changed far too often, and to assume that all the membranes in a batch will behave exactly the same seems unreasonable.

Table Vll.

Preliminary Buffer Series. Series D. (Qualitative)

Number	Voltage	Direction of Flow	pH
D-1	225	Positive	9.24
D-2	225	Negligable	8.68
D-3	225	Negative to Zero	8.03
D-4	225	Negative	7.36
D-5	Membrane	Broken	-

So far as any conclusion on this series is permissable it seems to indicate that again there is a point of transition, or an isoelectric point slightly on the alkaline side of the neutral point. With the three unspoiled runs there seems to be a decrease in negative endosmosis with increasing alkalinity with a change to positive endosmosis, somewhere in the neighborhood of pH = 8.0 to pH = 8.7.

In any event it seems worth while to run some quantitative data on this work and attempt to locate the isoelectric point definitely. It may be remarked in passing that the indicated position of the isoelectric point so far as this series is concerned, is about the same as the calcium hydroxide series of concentration 0.006628 grams per liter. The pH of this solution was in the same region as D-2.

Final Buffer Series.

Series "G" (1)

It was quite obvious from the work done in series D that to obtain any quantitative data it would be necessary to take precautions to avoid melting out seals and breaking membranes by the excessive temperature developed during a run.

A small water bath was constructed to contain the apparatus leaving the bubble tube on the outside. Some runs were made with some of the old membranes, and solutions, and it was found that by not running the trials longer than four minutes and changing the water in the bath after each run, a uniform temperature of 20°C could be maintained. As a result seals remained intact and no accidents occurred to the membranes, furthermore much of the erratic nature of the curves shown in the B and C series was eliminated.

Preparation of Materials.

Following directions given in Clarke, two stock solutions, numbered 1 and 2 were made up. The highest grade C.P. chemicals were used. They were not however repurified.

The Stock Solutions.

No.1 - 1000 ccs. of solution containing 19.108 grams of Sodium bi-borate per liter.

No.2 - 1000 ccs. of solution containing 12.404 grams of Boric Acid and 2.925 grams of sodium chloride, per liter.

The actual preparation of the solutions used in each run is tabulated in Table V111.

(1) Series E and F were used for some experiments on Cataphoresis which will be given later.

Table V111.

Preparation of Palitzsch Buffers

Serial No.	Flask No.	Preparation	Observed Voltage	pH
G-1	6	9 ccs.I and 291 ccs.II	0.6800	6.75
G-2	5	30 " I and 270 ccs.II	0.6951	7.00
G-3	4	90 " I and 210 ccs.II	0.7385	7.73
G-4	3	180 " I and 120 ccs.II	0.7500	7.91
G-5	2	(Special, not a boric acid buffer)	0.7976	8.73
G-6	1	300 ccs.I and No ccs.II	0.8150	9.00

As soon as the solutions were made up and their hydrogen ion concentration determined, they were sealed in small flasks until required.

Procedure.

The apparatus was placed in the water bath and carefully washed and filled according to the general procedure given for the calcium hydroxide series. When the apparatus had been carefully tested for leaks, and the bubble was giving constant readings the water jacket was filled with cold water. Several readings of the bubble were taken to be sure that no water was leaking into the apparatus. The bubble still being constant the current was switched on both voltage and amperage being recorded and the bubble timed over fifteen second intervals. That this method was a decided improvement over previous ones is shown by the regularity of the curves. No duplicates were made of the individual runs but the whole series was run straight through with increasing pH.

Results.

In the case of G-1 and G-2 a fairly heavy precipitate was noticeable at the negative electrode but in the rest of the series no precipitate occurred. The charge on the membrane was positive in high pH and negative in low pH. Passing through the series the point of transition seems to lie between G-3 and G-4 - the approximate pH of this position is about 7.9. The same initial rise is noticed that was present in the series on calcium hydroxide. The time effect, that is the effect of running the series for a longer length of time in each solution, could not be determined, if the run was to be made at uniform temperature. In the D series the point of transition was about 8.03, this checks very well the position of the isoelectric point given by the calcium hydroxide. In the latter series the charge had reversed at a pH of about 8.5 corresponding to a concentration of $Ca(OH)_2$ of 0.006628 grams per liter. The experimental data of the series is given in Table 1X.

It must be remembered that the graphs in this series represent 15 second intervals and not minute intervals as heretofore.

In Table X is given the summary of the series. The points for each run were calculated as set forth in the B and C series. The average of the last ten readings was taken and the endosmosis per minute calculated.

There is no comparison between the magnitude of endosmosis in the calcium hydroxide and buffer series. In the buffer series with a third of the potential gradient the endosmosis is very much higher. Regardless of this however it seems probable that isoelectric cement exists at a fairly definite hydrogen ion concentration, no matter whether this state is arrived at by addition of calcium hydroxide or by increasing the hydrogen ion concentration. A comparison of the calcium hydroxide and buffer solutions is given in Table X1.

Table 1X.

Membrane	Medium	pH	Volts	Current Intensity	Time	Endosmosis in given interval	
						valves	positive
G-1-1-A 1/8" Canada Portland. No.465	Buffer Solution	9	225	0.8 amps	15 secs.	0.20 0.10 0.20 +0.30 → 0.30 0.60	0.50 0.60 0.60 0.60 0.60
G-2-1-A 1-8" Canada Portland. No.465	Buffer Solution	8.73	225	0.8 amps	15 secs.	0.20 0.30 0.20 0.10 0.10 0.10 0.10	0.30 0.20 0.50 0.40 0.40 0.40
G-3-1-A 1/8" Canada Portland. No.465	Buffer Solution	7.91	225	0.8 amps	15 secs.	0.30 0.20 0.10 0.05 0.10	0.00 0.00 0.10 0.10 0.05
G-4-1-A 1/8" Canada Portland. No.465	Buffer Solution	7.73	225	0.8 amps	15 secs.	±0.00 -0.01 -0.01 -0.01 -0.09 -0.10 -0.10	-0.10 -0.10 -0.20 -0.10 -0.10 -0.10 -0.10
G-5-1-A	Spoiled but flow slightly to positive	7.00					
G-6-1-A 1/8" Canada Portland. No.465	Buffer Solution	6.75	225	0.8 amps	15 secs.	-0.10 -0.10 -0.20 -0.08 -0.11 -0.51	-0.50-0.55 -0.40-0.55 -0.50-0.50 -0.50-0.50 -0.40 -0.50

Table IX

"G" series

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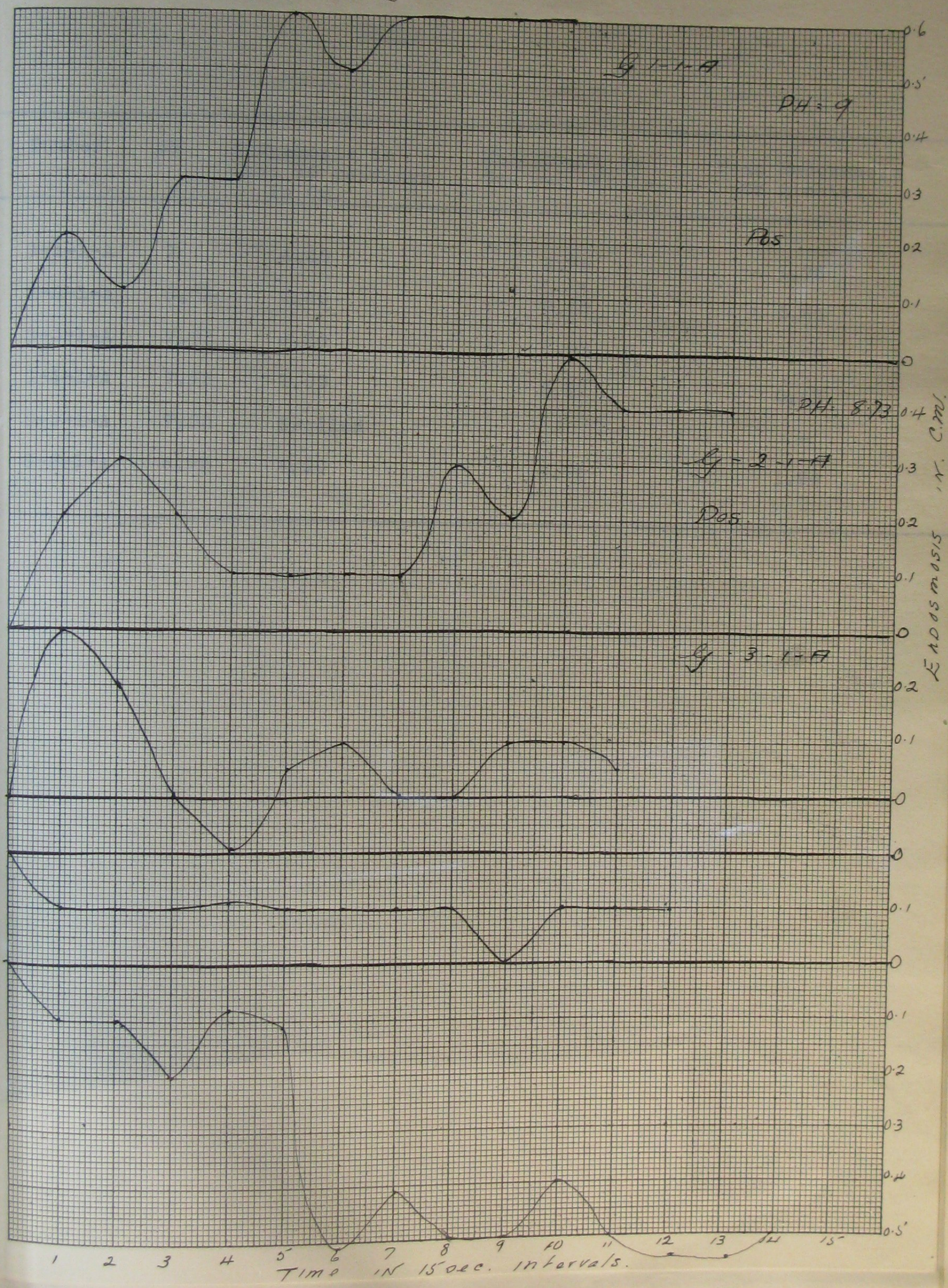

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Table X.

Number	pH	Endosmosis in last 10 readings in Cm.	Endosmosis in Cm. per minute	Mean Endosmosis per minute.
G-1-1-A	9	4.40	1.76	+ 1.76
G-2-1-A	8.73	2.60	0.65	+ 0.65
G-3-1-A	7.91	0.20	0.08	+ 0.08
G-4-1-A	7.73	1.09	0.42	- 0.42
G-5-1-A	7.00	Spoiled	-	-
G-6-1-A	6.75	4.90	1.96	- 1.96

Table X.

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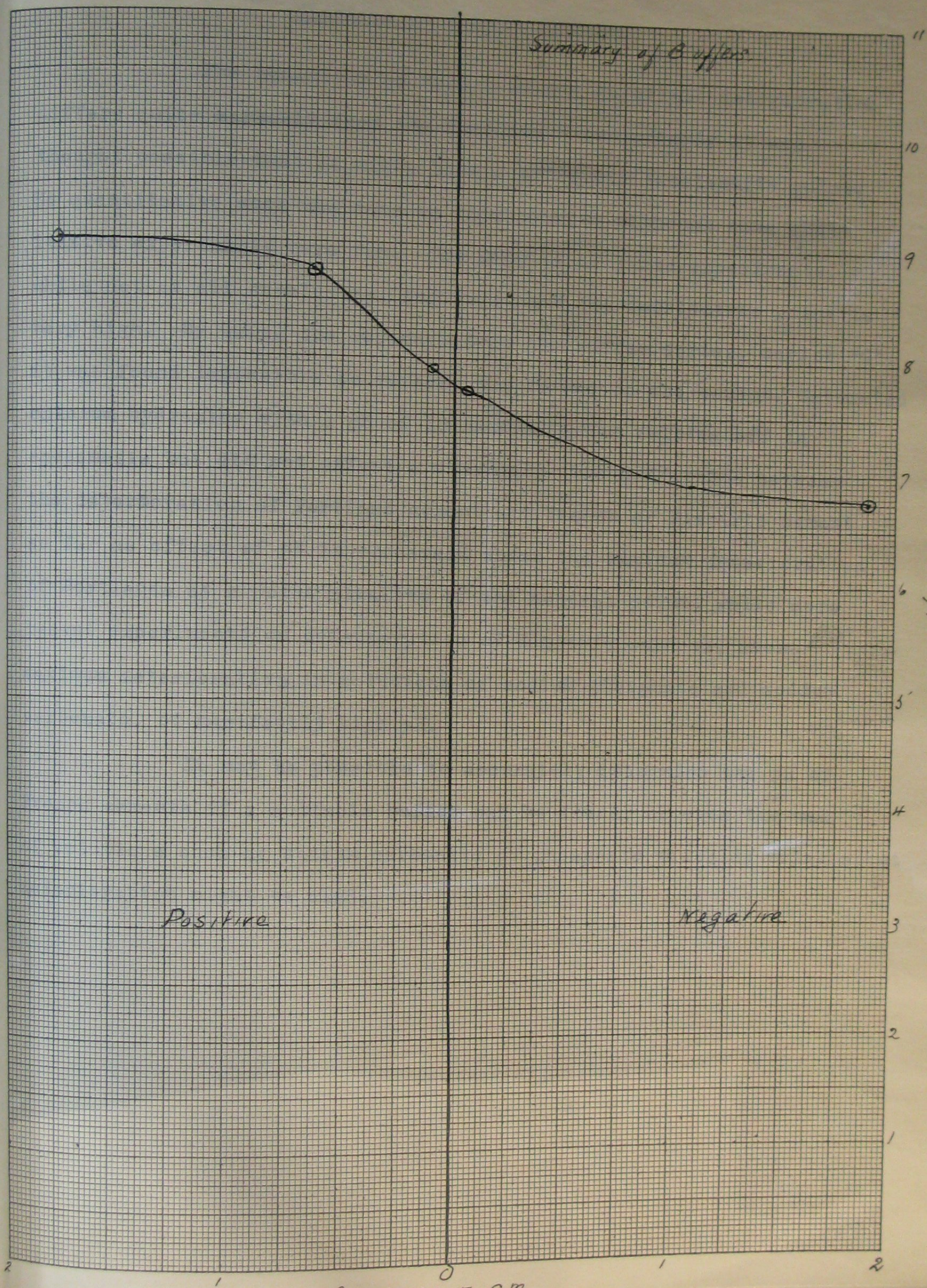

Electric or French Cements

The behaviour of French cement in alkali deterioration differs quite markedly from the Portland. Accordingly it was thought possible that it might have a different isoelectric point. No quantitative work was done on this problem although some qualitative experiments were run. The results of these experiments, while not at all conclusive, indicate that the isoelectric point is very high. By using the residues from the buffer series, series "G", it was found impossible to reverse the charge on the cement. Saturated calcium hydroxide with a pH of 12 caused marked falling off in endosmosis but did not effect a reversal. The difference between the determoration of Portland cement and French or Electric cement so far as effect of pH is concerned shows the maximum deterioration of Portlands at a point alkaline of the neutral point, while more recent experiments on deterioration of Electric cements, shows maximum deterioration in solutions of sodium phosphate and sodium carbonate, of manifestly high pH.

It may be possible to accurately determine the pH of French cements if a suitable buffer can be found, or even the use of solutions such as sodium carbonate or phosphate which do bring about deterioration might be used.

Cataphoresis

Series "F".

Bartell and Hocker (18) found it possible to obtain reasonably good agreement between the velocity of migration of membranes when subdivided to form suspensions and the endosmosis when these particles were combined in a solid membrane. A few experiments were tried on cataphoresis along these lines.

A membrane such as was used in endosmosis determinations was finely ground in an agate mortar, until no grit was noticed when a sample was placed between the teeth. This powder was then further ground in the powder mortar for one hour when it was considered fine enough to suspend.

A portion of this substance was then shaken well in about 500 ccs. of distilled water. The suspension so formed was filtered through a Whatman quantitative paper #40 into the flasks containing the buffer solutions. About 100 ccs. was added to each flask, when a slight opalescence appeared. The flasks were then placed in the rotary shaker and shaken for two hours. At the end of this time very little opalescence was noticed, but when the cone of light from an arc lamp was passed through the suspension a well marked Tyndal effect was obtained. Small portions of filter paper had also been added to the solutions, but these could readily be distinguished from the cement particles by their shape and size.

The reaction slide for the microscope consisted of two strips of platinum foil mounted 16 mm. apart on a Bausch and Lomb standard dark ground slide. The average width of the strips being 3 mm. Contact between the solution and the electrodes was ensured by using a large size cover slip of about $\frac{3}{4}$ inch side. The cell so

formed would hold three or four drops os solution and the depth was quite sufficient to give several layers of free moving particles.

The microscope used was one of the standard Bausch and Lomb student type microscopes. The tube length used was 160 mm and the eyepiece carried a micrometer head for measuring the size and velocity of migration of the particles. The microscope was further equipped with a Bausch and Lomb dark ground condenser and a substage illuminator. By means of this equipment the colloidal particles are very easily observed.

The dispersion media used were the residues from the buffer solutions series with a pH range from 6 - 9.

The potential fall across the electrodes was 110 volts, the laboratory line being used through a small resistance.

The results of this preliminary work follows in tabular form:-

PH of Media (old value)		Charge on Particle and Notes
(No.F-1)	6.73	Charge decidedly negative.Shortly after the run was started precipitation of some material occurred this precipitate appeared first as very small particles which were themselves charged but after a short time heavy flakes came down. An attempt was made to time the particles as they passed over the micrometer scale but the particles moved too fast, and it was impossible to watch any one of them in particular.
(No.F-2)	7.36	No apparent difference in either speed or magnitude of charge. This is not certain as had no way of accurately timing them
(No.F-3)	8.03	Could have actually timed them in this case, had there been no precipitate to interfere. In any event the movement was slower than in F-2. Not absolutely certain but would say that some of them moved in the other direction toward the end of the experiment.

PH of Media	(old value)	Charge on Particle and Notes
(No.F-4)	8.68	Particles uncertain what to do. At first they seem to be going in both directions but at the end in one. It may be that the latter case is incorrect and that it is the particles of ppt. which are moving in one direction. When the current is broken and then suddenly started they all jump toward the negative pole.

While there is a decrease in the negative charge as one passes through the series yet the complications occurring do not permit any final deductions to be made. Qualitatively the charge on the cement follows the same general trend as indicated by the buffer series. The chief trouble is the confusion arising through the precipitation occurring at the electrodes. This precipitate being charged also migrates across the field and in the initial stages of formation may be mistaken for cement particles. To obtain quantitative results on cataphoresis the particles should be suspended in some organic liquid and then solutions of buffers added to bring the pH to the desired value.

Summary

1. The charge on Portland cement in distilled water and slight concentrations of calcium hydroxide was found to be negative.

2. Addition of calcium hydroxide changed the sign of the charge on the membrane from negative to positive.

3. The isoelectric point for Portland cement was found to exist at a concentration of calcium hydroxide of 0.006628 to 0.009942 grams per liter.

4. The hydrogen ion concentration for the isoelectric point was found to be

   (a) from calcium hydroxide series at pH = 8.5

   (b) from buffer solution series at pH = 8.3

5. Cataphoresis of suspended cement, so far as it is possible to draw any conclusions at all, confirms the general change in charge on the cement particles.

6. French cements would seem to have their isoelectric point at a very high pH as compared with the Portland cements.

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