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INFLUENCE OF A SLIGHT MODIFICATION OF THE COLLODION MEMBRANE ON THE SIGN OF THE ELECTRIFICATION OF WATER.

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(From the Laboratories of The Rockefeller Institute for Medical Research.)

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I.

When we separate a solution of an electrolyte from pure water by a collodion bag the water will as a rule diffuse into the solution. In a preceding paper¹ it was shown that the forces determining this diffusion are different for concentrations of electrolytes below or above a certain value (which is for certain sodium salts about $m/16$). The forces causing the diffusion of water into the solution below this critical concentration are predominantly electrical, while the forces causing the diffusion above the critical concentration are predominantly (or perhaps exclusively) molecular.

The electrical forces of diffusion depend upon the sign, the valency, a third property of the ions (which we arbitrarily designated as their radius), and in addition upon the concentration of the ions in solution. There is still another variable to be considered; namely, the nature of the membrane. We have already called attention to the fact that a collodion membrane which has once been treated with a gelatin solution shows a different osmotic behavior from a membrane not treated with gelatin. The gelatin treatment consisted in this that the collodion bags with which the experiments were made were filled over night with a 1 per cent gelatin solution (isoelectric or nearly isoelectric). The next day the gelatin solution was poured off and the interior of the bags washed out about six times or more with warm water to remove as much gelatin as possible. They were then put for days into water to dissolve still more and remove the last traces of gelatin.

¹ Loeb, J., *J. Gen. Physiol.*, 1919-20, ii, 173.

Such bags seemed to retain the effect of the gelatin treatment for a long time, and continued use and subsequent washing did not seem to remove this after effect of the gelatin treatment.

When collodion bags which had received this gelatin treatment were filled with solutions of electrolytes (of the theoretical osmotic pressure of that of a $M/64$ sugar solution) and were dipped into beakers with distilled water, the influence of the nature of the electrolyte upon the initial rate of diffusion of water into the bag could be expressed by the following two rules.²

1. Solutions of neutral salts possessing a univalent or bivalent cation influence the rate of diffusion of water through a collodion membrane, as if the water particles were charged positively and were attracted by the anion and repelled by the cation of the electrolyte; the attractive and repulsive action increasing with the number of charges of the ion. The same rule applies to solutions of alkalies.

2. Solutions of neutral or acid salts possessing a trivalent or tetravalent cation influence the rate of diffusion of water through a collodion membrane as if the particles of water were charged negatively and were attracted by the cation and repelled by the anion of the electrolyte; the attractive and repulsive action increasing with the number of charges of the ion. Solutions of acids obey the same rule.

When the same experiments were repeated with collodion bags which had not come in contact with gelatin, the influence of the electrolytes mentioned in Rule 1 on the diffusion of water was the same as when the membrane had been treated with gelatin. Rule 2, however, was not valid when the collodion membranes had *not* been treated with gelatin. It was of interest to discover the cause of this difference.

The curves in Figs. 1 and 2 show that Rule 1 holds also for collodion membranes *not* treated with gelatin. The solutions of salts used were neutral or slightly alkaline (in the case of Na_3 citrate). The abscissæ in the figures are the logarithms of the concentration, the ordinates the height to which the level of liquid in the manometer rose in the first 20 minutes. The curves in Fig. 1 show that the levels

²Loeb, J., *J. Gen. Physiol.*, 1918-19, i, 717.

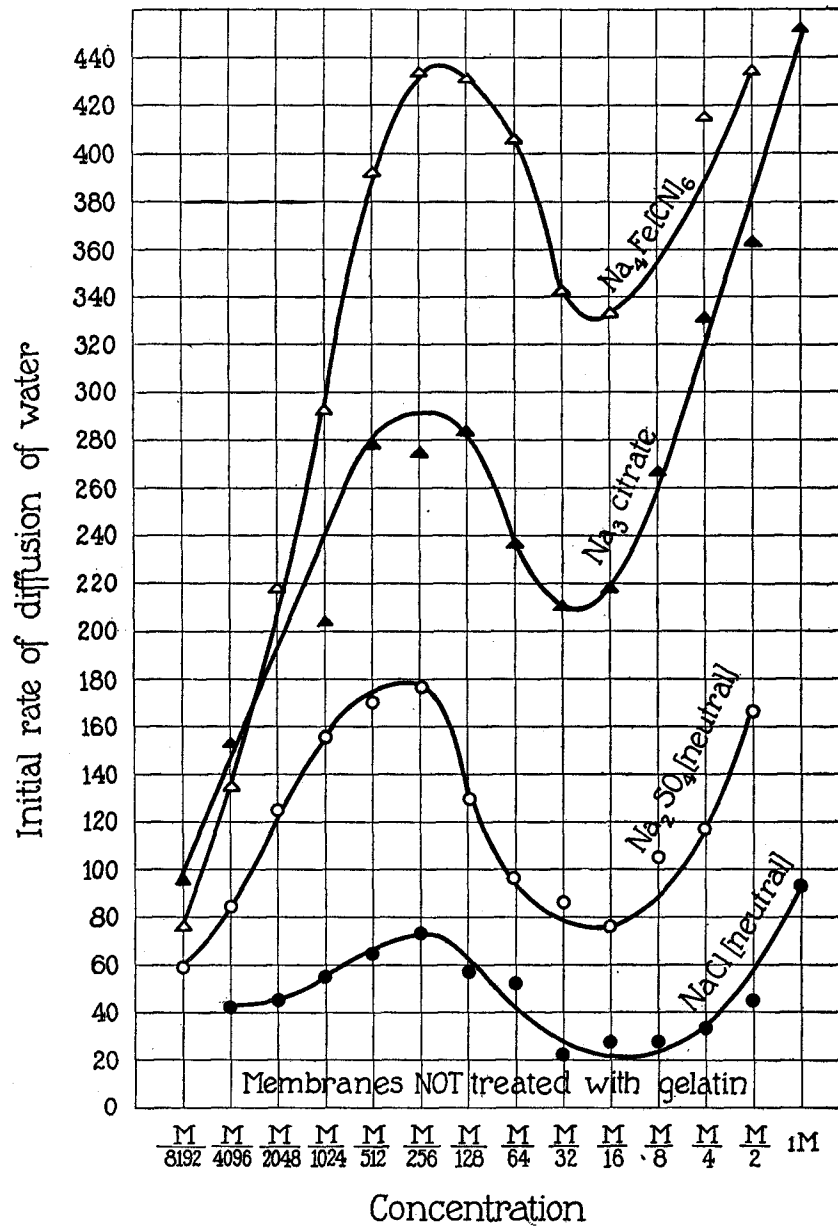


FIG. 1. Curves representing influence of concentration of solutions of different Na salts upon the initial rate of diffusion of water from pure water into solution through membranes not treated with gelatin. The curves are essentially the same as those obtained with collodion membranes which had been treated with gelatin.³ Abscissæ are the logarithms of concentration, ordinates the rise of height of level of solution in 20 minutes. Inside of collodion bag salt solution, outside H_2O .

³ Loeb, J., *J. Gen. Physiol.*, 1919-20, ii, 177, Fig. 3.

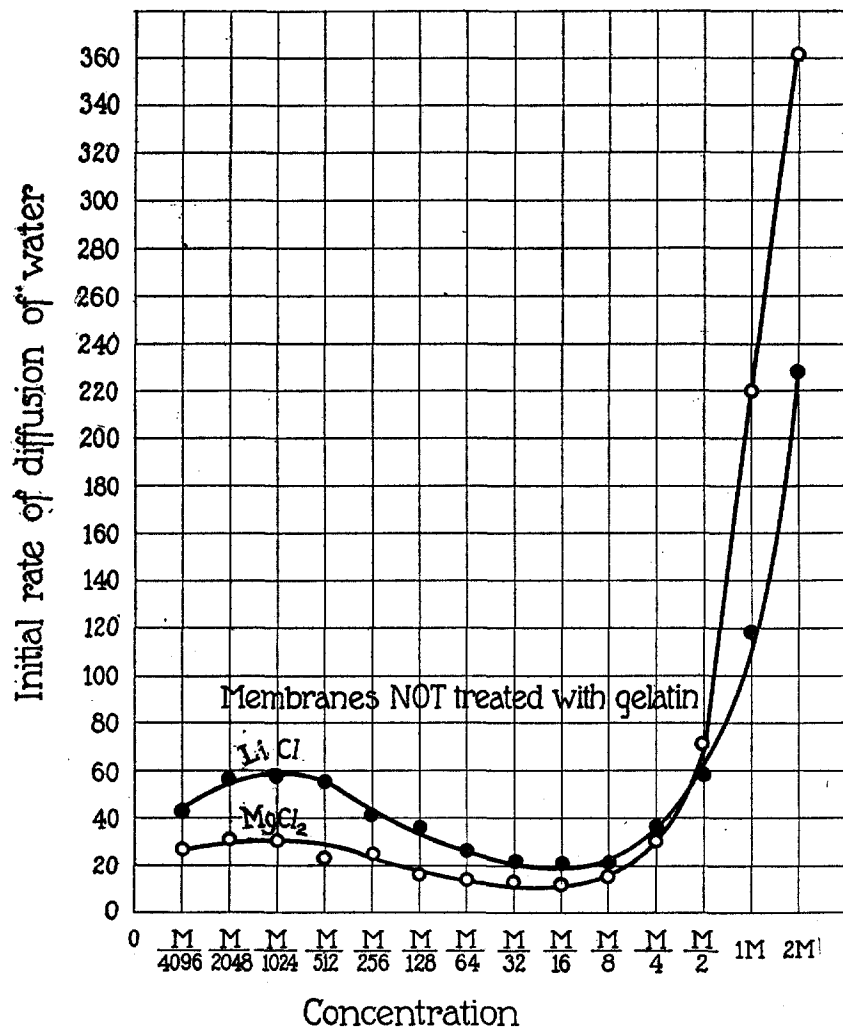


FIG 2. Same curves as in Fig. 1 for LiCl and MgCl₂. Curves identical for membranes treated and not treated with gelatin.

at first rise sharply with an increase in concentration and the more so the higher the valency of the anion. The maximum of the curves is reached at about $m/256$, then the curves fall with a further increase in the concentration until a minimum is reached again at about $m/16$, and then another rise begins. This second rise expresses the gas pressure effect of the solute. When we use membranes treated with gelatin, we get a similar system of curves for the same solutions,¹ and the explanation of the curves is the same for both kinds of membrane. The particles of water diffuse through the membrane as if they were positively charged, being attracted by the anion of the salt and repelled by the cation, the attraction increasing with the valency of the anion. That the repulsion increases with the valency of the cation is shown in Fig. 2 where the lower curve represents the rate of diffusion of water in 20 minutes into $MgCl_2$ solutions and the upper curve the initial rate of diffusion of water in 20 minutes into solutions of $LiCl$ through membranes not treated with gelatin. These curves are also practically identical with those obtained for the same salt solutions when the collodion membrane had previously been treated with gelatin.¹ Hence Rule 1 holds in all essentials equally for membranes treated and not treated with gelatin.

The situation is altogether different for solutions of those electrolytes whose influence is described in Rule 2; namely, acids and neutral or acid solutions of salts with trivalent or tetravalent cation.

When we separate solutions of different concentrations of Al_2Cl_6 from H_2O by collodion bags treated with gelatin, water diffuses very rapidly into the solution and the level of liquid in the manometer rises steeply with an increase in concentration, as is shown by the upper curve in Fig. 3. Water is negatively charged and is powerfully attracted by the trivalent cation Al . When we repeat the same experiment with membranes *not* treated with gelatin (lower curve of Fig. 3), we notice that in that range of concentrations of Al_2Cl_6 where the diffusion is determined chiefly (or exclusively) by electrical forces no rise occurs until the concentration of the solution of Al_2Cl_6 is about $m/64$; at about this concentration the gas pressure effect of solutions of cane sugar begins to be noticeable. It, therefore, looks as if solutions of Al_2Cl_6 showed no electrical but only the gas pressure effect when separated from pure water by a membrane not treated with

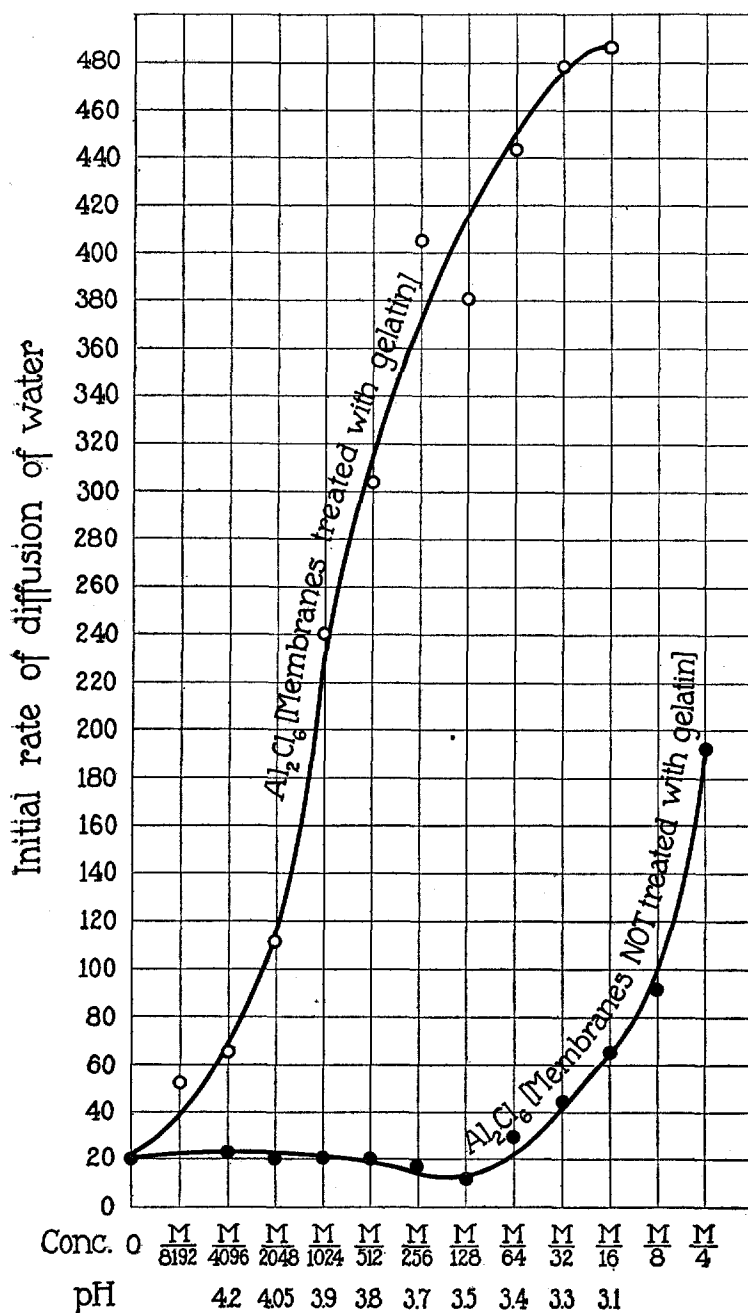


FIG. 3. Showing difference in osmotic behavior of collodion membranes treated and not treated with gelatin. Membranes separating solutions of Al_2Cl_6 from pure water. Upper curve, initial rate of diffusion of water (first 20 minutes) into solution through membranes treated with gelatin; lower curve, diffusion of water during the first 20 minutes into same solution of Al_2Cl_6 through membranes *not* treated with gelatin. In second case only the gas pressure effect of solution is apparent, while electrical attraction of water by solution is lacking.

gelatin. We shall see later that the electrical effect in the lower range of concentrations of Al_2Cl_6 is not lacking, but that the low ordinates are due to the action of the trivalent cation. Curves for the diffusion of water into solutions of LaCl_3 (Fig. 4), which are nearly neutral, show the same difference as those just described for Al_2Cl_6 solutions. When LaCl_3 solutions are separated from water by membranes not treated with gelatin, the ordinates (lower curve in Fig. 4) are low in the region of the electrical effect, while they rise steeply in the same region when the membranes have been treated with gelatin (upper curve in Fig. 4).

The difference in the osmotic behavior of the two kinds of membranes is still more striking when we use solutions of acids. When we separate solutions of strong acids (*e.g.* HCl , HNO_3 , H_2SO_4) from distilled water by collodion membranes previously treated with gelatin, we notice no rise but only a drop (Fig. 5)—negative osmosis—which commences for H_2SO_4 and H_3PO_4 at a concentration of about $M/256$. In the experiments represented in Fig. 5, the pressure head of the solution of acids inside the bag was about 70 mm. at the beginning. It dropped in 20 minutes to about 10 mm. at concentrations of about $M/8$ or $M/4$ for H_2SO_4 and H_3PO_4 (Fig. 5). Owing to the fact that the drop is due to the repelling action of the anion of the acid upon the negatively charged particles of water, the drop in the curves is greater when the anion of the acid is bivalent or trivalent than when it is monovalent. When we separate various concentrations of the same acids from pure water by membranes *not* treated with gelatin we get results of an altogether different order (Fig. 6). Instead of negative osmosis we notice a powerful positive osmosis, *i.e.* a rapid diffusion of water into the solution, and the acids behave almost like the sodium salts with the same anion. By comparing Fig. 1 and Fig. 6 the reader will notice the same steep rise of the curves until the concentration is about $M/256$; this rise is more considerable in the case of Na_2SO_4 and H_2SO_4 than in the case of NaCl and HCl . In the case of these two salts and acids, the rise is followed by a drop, until for the acids at $M/32$ and for the salts at $M/16$ the gas pressure effect of the solution commences. The drop is not noticeable in the case of H_3PO_4 .

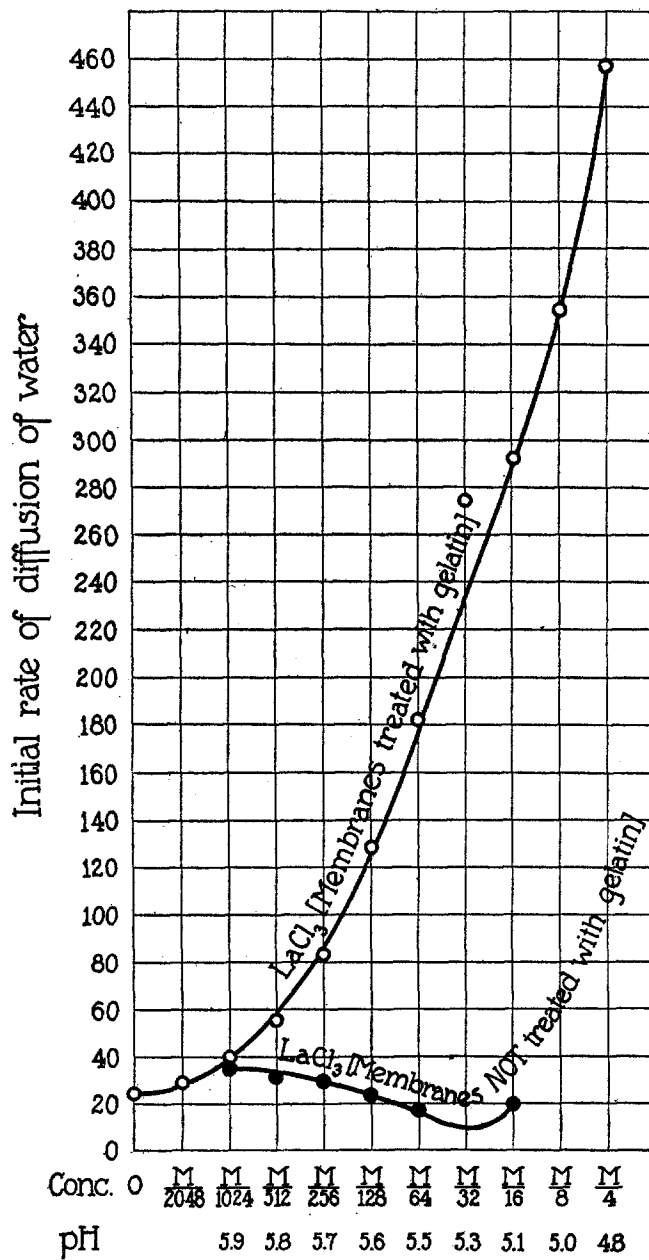


FIG. 4. Showing the same difference of membranes treated and not treated with gelatin for solutions of LaCl₃.

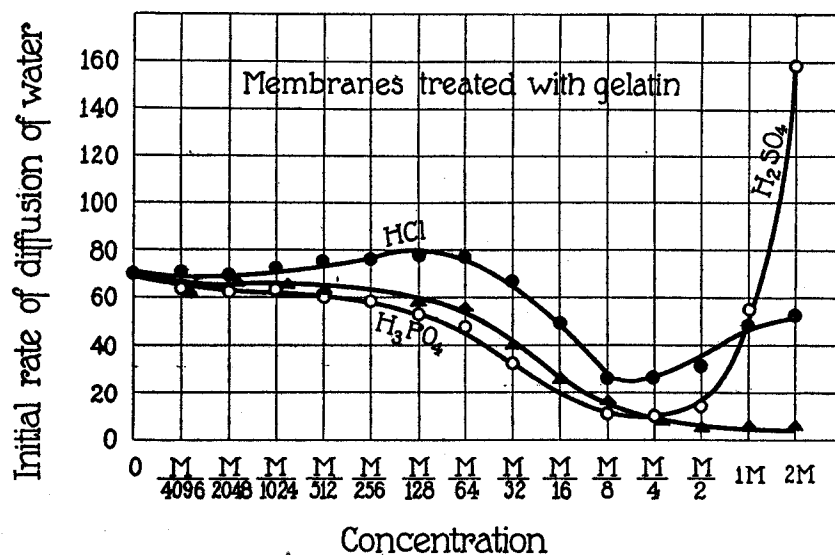


FIG. 5. Negative osmosis when acids (HCl, H₂SO₄, H₃PO₄) are separated from water by membranes treated with gelatin.

Fig. 7 gives the curves for several other acids when the membranes are treated with gelatin and Fig. 8 the curves for the same acids when the membranes are *not* treated with gelatin. When the membranes are *not* treated with gelatin the curve for oxalic acid (Fig. 8) becomes almost like that of Na₂SO₄ in Fig. 1; while the same acid shows the phenomenon of negative osmosis (Fig. 7) when the membrane has received a gelatin treatment previous to the experiment.

II.

What causes this profound difference in the osmotic behavior of collodion membranes according to whether they have or have *not* received a previous treatment with gelatin? It is so customary in biology to explain obscure phenomena by the assumption of variations of permeability that the writer felt it necessary to test the possibility of such an explanation in this case.

The phenomenon of positive osmosis for acid when the collodion bag separating the acid from pure water was not treated with gelatin, and the opposite phenomenon of negative osmosis when the collodion

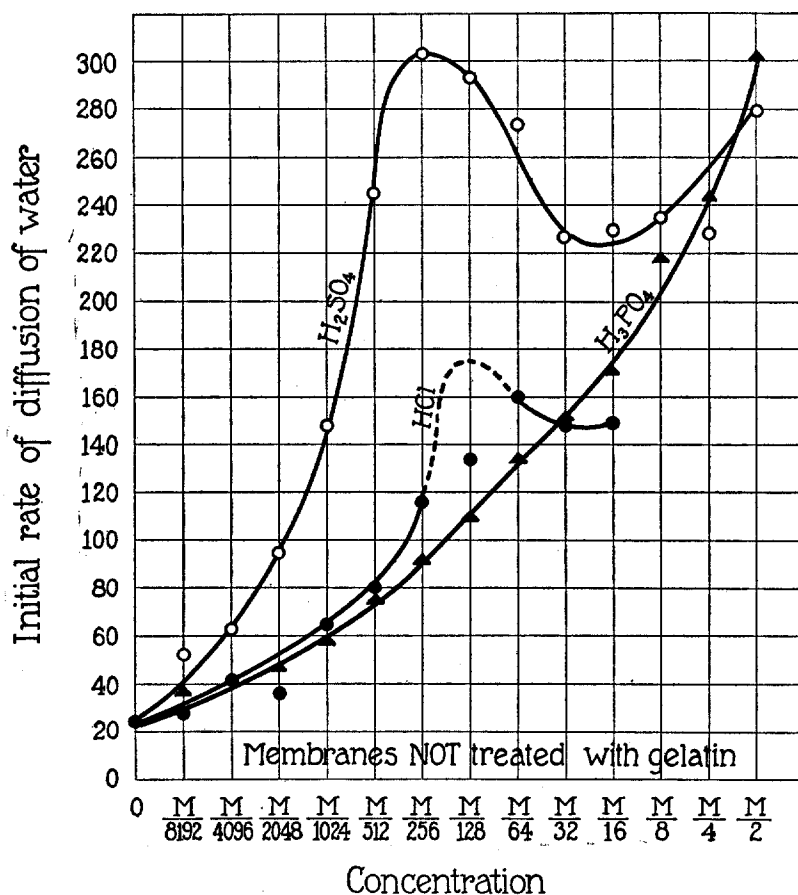


FIG. 6. Positive osmosis when the same acids as in Fig. 5 are separated from water by membranes *not* treated with gelatin. Curves similar to those obtained with sodium salts of the same anion (Fig. 1).

bag separating the acid had been treated with gelatin, suggested that the gelatin treatment had rendered the collodion bag more permeable for acid. It was, therefore, expected that titration of the contents of the bag at the beginning and after 20 minutes would show a greater diminution of the concentration of acid inside the bag when the bag had been treated with gelatin than when it had received no such treatment. The test, however, disproved the correctness of this explanation. *The rate of diffusion of acid from solution into the distilled water was practically the same for collodion membranes treated and not treated with gelatin, as Table I shows.*

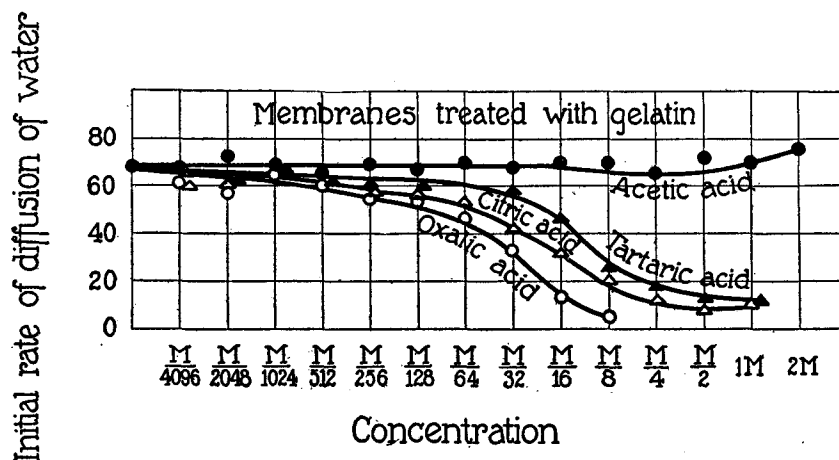


FIG. 7. Negative osmosis when solutions of acids (tartaric, citric, and oxalic) are separated from water by membranes treated with gelatin. The weak acetic acid behaves practically like a non-electrolyte.

The table shows that the amount of acid which diffused out from the collodion bag into the distilled water was (within the limits of accuracy of these experiments) the same for membranes treated and *not* treated with gelatin. Oxalic acid diffused a little more slowly than hydrochloric acid, but the rate of diffusion for each acid is approximately in direct proportion to its concentration. The fact that the same acids caused positive osmosis when the membranes were *not* treated with gelatin and negative osmosis when they were treated cannot be ascribed to differences in the permeability of the two types of collodion membranes.

Since solutions of Al_2Cl_6 and of $LaCl_3$ caused a vigorous diffusion of water from solvent into solution when the collodion membrane was treated with gelatin, but not when the membrane had *not* received a gelatin treatment, the idea suggested itself that the collodion membranes not treated with gelatin were so permeable for the molecules of the salt that an increase in volume of the solution by a diffusion of water into it was impossible. Titration experiments with Al_2Br_6 proved, however, that there was only a slight difference in the rate

TABLE I.

Loss of cc. of 0.01 N acid for 10 cc. of solution in 20 min.			
	n/32	n/64	n/128
Membranes treated with gelatin.			
HCl.....	10.2	5.0	2.3
H ₂ SO ₄	9.7	4.7	2.2
Oxalic acid.....	7.8	4.0	1.9
Membranes not treated with gelatin.			
HCl.....	11.0	4.9	2.3
H ₂ SO ₄	9.8	4.1	1.7
Oxalic acid.....	8.1	3.4	1.6

of diffusion of Al_2Br_6 through the two types of membranes; the non-treated membrane being slightly more permeable. The difference was, however, much too small to account for the difference in the osmotic behavior of the two types of membranes.

It was, therefore, necessary to look for another explanation in the different osmotic behavior of the two types of membranes. It seemed these differences would find their explanation if it could be proved that water diffuses through collodion membranes not treated with gelatin in the form of positively charged particles even in the presence of acids or salts with trivalent or tetravalent cation. For this purpose the method of electrical endosmose was applied. Identical solutions of $LaCl_3$ were put inside and outside a collodion bag not treated with gelatin and a current (of about 4.8 milliamperes and about 90 volts) was sent through the solution. The water migrated to the cathode, showing that its particles were positively charged in the presence of $LaCl_3$. When the same experiment was repeated with membranes previously treated with gelatin it was found that water is negatively charged in the presence of solutions of salts with trivalent cation. It was furthermore possible to show that in the presence of acids water diffuses through membranes not previously treated with gelatin in the form of positively charged particles.

We can now understand why it is that water cannot diffuse through collodion membranes not treated with gelatin into solutions of salts with trivalent cation, *e.g.* $AlCl_3$ or $LaCl_3$ (in the region of electrical effect), since these particles of water carrying a positive charge are

repelled by the trivalent cation. We understand also why the initial rate of diffusion of water through membranes *not* treated with gelatin is greater into a solution of H_2SO_4 than into a solution of HCl , since the positively charged particles of water are attracted by the anion of the acid and the more powerfully the higher the valency of the anion.

A very simple test will demonstrate that the water diffuses through collodion membranes *not* treated with gelatin in the form of positively charged particles even in the presence of $m/1,000$ acid. We know from Rule 1 (at the beginning of this paper) that positively charged particles

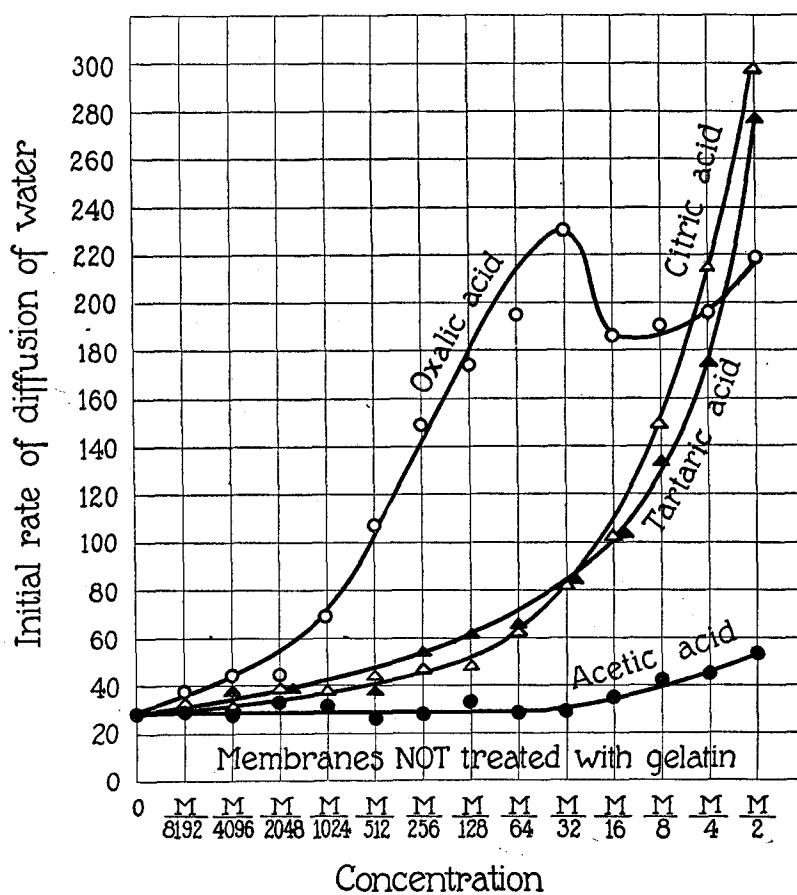


FIG. 8. Positive osmosis when solutions of the same acids as in Fig. 7 are separated from water by membranes *not* treated with gelatin.

of water are attracted more powerfully by Na_2SO_4 , less powerfully by NaCl , and still less powerfully by CaCl_2 . Hence when we make $m/128$ solutions of these three salts acid through the addition of HNO_3 , and if it is true that water diffuses through the membranes not treated with gelatin in the form of positively charged particles in the presence of strong acid, it should diffuse more rapidly into Na_2SO_4 , less rapidly into NaCl , and least rapidly into CaCl_2 . $m/128$ solutions of these three salts were brought to a pH of 2.9 through the addition of HNO_3 , and the experiment turned out as the theory demands. When the same experiment was made with collodion membranes treated with gelatin, the order of attraction of the three salts of pH 2.9 for water was reversed, water diffusing very rapidly into the acid solution of $m/128$ CaCl_2 , less rapidly into the acid solution of $m/128$ NaCl , and still less rapidly into the acid solution of $m/128$ Na_2SO_4 , since in this case the particles of water diffusing through the membrane were negatively charged. When the solutions of the three salts were neutral or alkaline, no difference in the osmotic behavior of the two types of membranes was noticed.

III.

In a previous paper¹ the writer had suggested that it was necessary to discriminate between the influence of cations upon the sign of electrification of water and upon the rate with which electrified water diffuses into the solution. This suggestion receives support from this paper, and it is impossible to understand the phenomenon of negative osmosis without this discrimination. Thus it is obvious that both H ions as well as trivalent cations cause the particles of water which normally have a positive charge, to assume a negative charge and it is not yet possible to state whether the H ions or the trivalent cations are more efficient in this direction. It follows, however, from the observations published in this paper that, as far as the rate of diffusion of the charged particles of water into the solution is concerned, the influence of the trivalent cations is much more powerful than that of the hydrogen ions. We express this influence in terms of electrostatic attraction and repulsion between the ions and the charged particles of water, not in order to offer thereby an explanation of this influence but merely to simplify the

presentation of the facts. With this reservation our experiments suggest that the apparent electrostatic effect of the hydrogen ions upon the motion of the electrified particles of water is small if compared with the effect of the trivalent cations; in fact it seems smaller even than that of other monovalent cations.

When acid is put into collodion bags *not* treated with gelatin, we observe a rapid diffusion of water into the acid solution as if the attraction of the positively charged water by the anion of the acid was very strong while its repulsion by the H ion was weak. When we put acids into collodion bags treated with gelatin we observe negative osmosis; *i.e.*, slight attraction of the negatively charged particles of water by the positive hydrogen ion, and a powerful repulsion of the water by the anion of the acid. In all these cases, the apparent electrostatic effect of the hydrogen ion upon the charged particles of water seems smaller than the electrostatic effect of any other ion. When we compare the electrostatic effect of trivalent cations on the rate of diffusion of water, we notice that it is much more powerful than that of the hydrogen ion. When water is negatively charged, it is attracted very powerfully by Al_2Cl_6 as well as by $\text{Al}_2(\text{SO}_4)_3$ though naturally more by the former than by the latter. While in the case of acids the SO_4 ion has a more powerful influence than the H ion, the electrostatic effect of a trivalent cation cannot be overcome by the effect of a bivalent anion. It can only be equalled by the influence of a trivalent anion; *e.g.*, the citrate. This comparatively weak electrostatic effect of the H ion is responsible for the phenomenon of negative osmosis observed in the case of acids. When we use membranes in which the electrified water is negatively charged in the presence of acid the attractive effect of the H ion is so small that the repulsive effect of the anion prevails in the critical range of concentrations, where the drop in the curve occurs. As a consequence no water can diffuse into the solution and the volume of the latter will diminish on account of the diffusion of solute into the pure solvent. Since we notice also negative osmosis in the case of $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, we conclude that the electrostatic effect of the OH ion on the movable stratum of the double layer is also small.

IV.

Gelatin is not the only substance which causes a reversal of the sign of the electrification of the particles of water diffusing through the collodion membrane in the presence of comparatively low concentrations of acid or of salts with trivalent or tetravalent cations. The same effect can be produced when the collodion membrane is treated with 1 per cent solutions of casein, egg albumin, blood albumin, and edestin; while treatment of the collodion membrane with 1 per cent solutions of Fairchild's peptone, of peptone (prepared by Dr. Northrop) from egg albumin digested with pepsin and neutralized, of alanine, of "soluble starch," of "potato starch," and of 0.50 per cent agar-agar did not cause the reversal. The proteins which modify the behavior of the membrane cannot diffuse through the latter but the writer is not yet ready to state that this is the decisive factor. It is of interest that a treatment of the collodion membrane with a 0.002 per cent solution of gelatin makes the membrane already noticeably amphoteric though to a considerably smaller degree than a treatment with a 1 per cent solution of gelatin.

SUMMARY.

1. It is shown that collodion membranes which have received one treatment with a 1 per cent gelatin solution show for a long time (if not permanently) afterwards a different osmotic behavior from collodion membranes not treated with gelatin. This difference shows itself only towards solutions of those electrolytes which have a tendency to induce a negative electrification of the water particles diffusing through the membrane, namely solutions of acids, acid salts, and of salts with trivalent and tetravalent cations; while the osmotic behavior of the two types of membranes towards solutions of salts and alkalis, which induce a positive electrification of the water particles diffusing through the membrane, is the same.

2. When we separate solutions of salts with trivalent cation, *e.g.* LaCl_3 or AlCl_3 , from pure water by a collodion membrane treated with gelatin, water diffuses rapidly into the solution; while no water diffuses into the solution when the collodion membrane has received no gelatin treatment.

3. When we separate solutions of acid from pure water by a membrane previously treated with gelatin, negative osmosis occurs; *i.e.*, practically no water can diffuse into the solution, while the molecules of solution and some water diffuse out. When we separate solutions of acid from pure water by collodion membranes not treated with gelatin, positive osmosis will occur; *i.e.*, water will diffuse rapidly into the solution and the more rapidly the higher the valency of the anion.

4. These differences occur only in that range of concentrations of electrolytes inside of which the forces determining the rate of diffusion of water through the membrane are predominantly electrical; *i.e.*, in concentrations from 0 to about $M/16$. For higher concentrations of the same electrolytes, where the forces determining the rate of diffusion are molecular, the osmotic behavior of the two types of membranes is essentially the same.

5. The differences in the osmotic behavior of the two types of membranes are not due to differences in the permeability of the membranes for solutes since it is shown that acids diffuse with the same rate through both kinds of membranes.

6. It is shown that the differences in the osmotic behavior of the two types of collodion membranes towards solutions of acids and of salts with trivalent cation are due to the fact that in the presence of these electrolytes water diffuses in the form of negatively charged particles through the membranes previously treated with gelatin, and in the form of positively charged particles through collodion membranes *not* treated with gelatin.

7. A treatment of the collodion membranes with casein, egg albumin, blood albumin, or edestin affects the behavior of the membrane towards salts with trivalent or tetravalent cations and towards acids in the same way as does a treatment with gelatin; while a treatment of the membranes with peptone prepared from egg albumin, with alanine, or with starch has no such effect.