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Influence of the Concentration of Electrolytes on the Electrification and the Rate of Diffusion of Water Through Collodion Membranes

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INFLUENCE OF THE CONCENTRATION OF ELECTROLYTES ON THE ELECTRIFICATION AND THE RATE OF DIFFUSION OF WATER THROUGH COLLODION MEMBRANES.

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I. Influence of the Concentration of Electrolytes upon the Rate of Diffusion of Positively Charged Particles of Water through Collodion Membranes.

When we fill a collodion flask, as described in a preceding publication,[1] with a solution of a non-electrolyte, *e.g.* cane sugar, grape sugar, or glycerol, and dip the flask into a beaker containing distilled water, the level of the liquid in the flask will rise, as is to be expected on the basis of the gas pressure theory of osmosis. When we close the opening of the collodion flask with a rubber stopper, perforated by a glass tube with a bore of about 2 mm. in diameter serving as manometer, the rate of diffusion of water into the solution can be conveniently followed. Since at the same time sugar will diffuse out of the flask into the surrounding distilled water, the rise of the column of liquid in the manometer will cease after some time (*e.g.* after about 70 minutes at 24°C.) and will be followed by a fall in the level of the liquid, until finally the solutions inside and outside the collodion flask become identical. It is therefore necessary to consider only the initial rise of liquid in the manometer as an indicator for the attractive action of the solution upon water, and in all the figures given in this paper the readings were made 20 minutes after commencement of the experiment. At the beginning of the experiment the level in the manometer was usually about 30 mm. above that of the distilled water in the beaker in order to discover possible cases of negative osmosis. All collodion flasks had practically the same sur-

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[1] Loeb, J., *J. Gen. Physiol.*, 1918–19, i, 717.

face, being cast inside of the same Erlenmeyer flask, and during the experiment the whole area of the flask was submersed in the beaker. The temperature was always 24°C.

In Fig. 1 the ordinates are the values for the rise in the level of the solution in the glass tube (after the first 20 minutes) which occurred when the collodion flasks filled with different concentrations of cane sugar, grape sugar, or glycerol were dipped into beakers containing distilled water. The abscissæ are the logarithms of the concentration of the sugar solution. The reader will notice that for concentrations below M/64 the curves run practically parallel to the base line while a sharp rise begins at about M/16 or M/8. If the rise is plotted over the concentration (instead of over the logarithms of the concentration) the curve is almost a straight line between concentrations of M/32 and 1 M (Fig. 2), as was to be expected on the basis of the gas pressure theory. When, however, we make the same experiments with solutions of *electrolytes*, separating them from pure water by collodion membranes, a curious phenomenon is observed, which was partly described in the first paper; namely, that at a very low concentration of electrolyte the rate of diffusion of water through the collodion membrane from pure solvent into the solution increases rapidly with increasing concentration and that it reaches a maximum at a comparatively low concentration[1] of the electrolyte. It is easier to follow the facts to be described with the help of the curves given in Fig. 3. The abscissæ are the logarithms of the concentration of the solution, while the ordinates give the height to which the liquid in the manometer has risen in 20 minutes. The reader will notice that the curves for five sodium salts are given—NaCl, Na_2SO_4, Na_2 oxalate, Na_3 citrate, $Na_4Fe(CN)_6$. The solutions must not be acid for this experiment, and the hydrogen ion concentration of the solutions of NaCl, Na_2SO_4, and Na_2 oxalate was almost that of the point of neutrality (pH about 6.0, or between 6.0 and 7.0), while the two other solutions were slightly alkaline. Beginning with the lower concentrations of the solutions of these salts the curves rise sharply with the increase in concentration, reach a maximum at a concentration of about M/256, and then with a further increase in concentration the curves fall abruptly to reach a minimum, varying for the different salts between M/32 and M/8. After this the curves rise again.

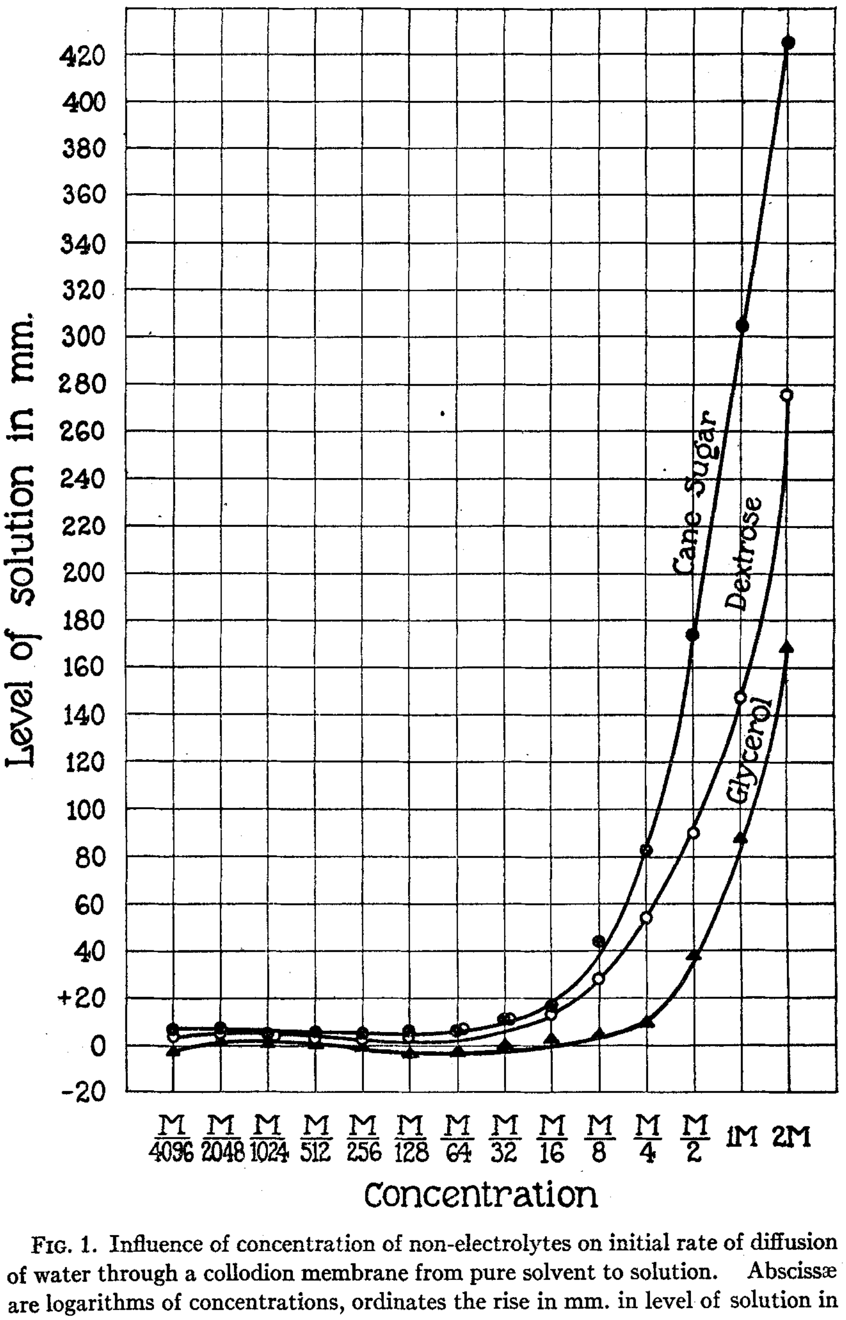

FIG. 1. Influence of concentration of non-electrolytes on initial rate of diffusion of water through a collodion membrane from pure solvent to solution. Abscissæ are logarithms of concentrations, ordinates the rise in mm. in level of solution in the manometer tube after 20 minutes.

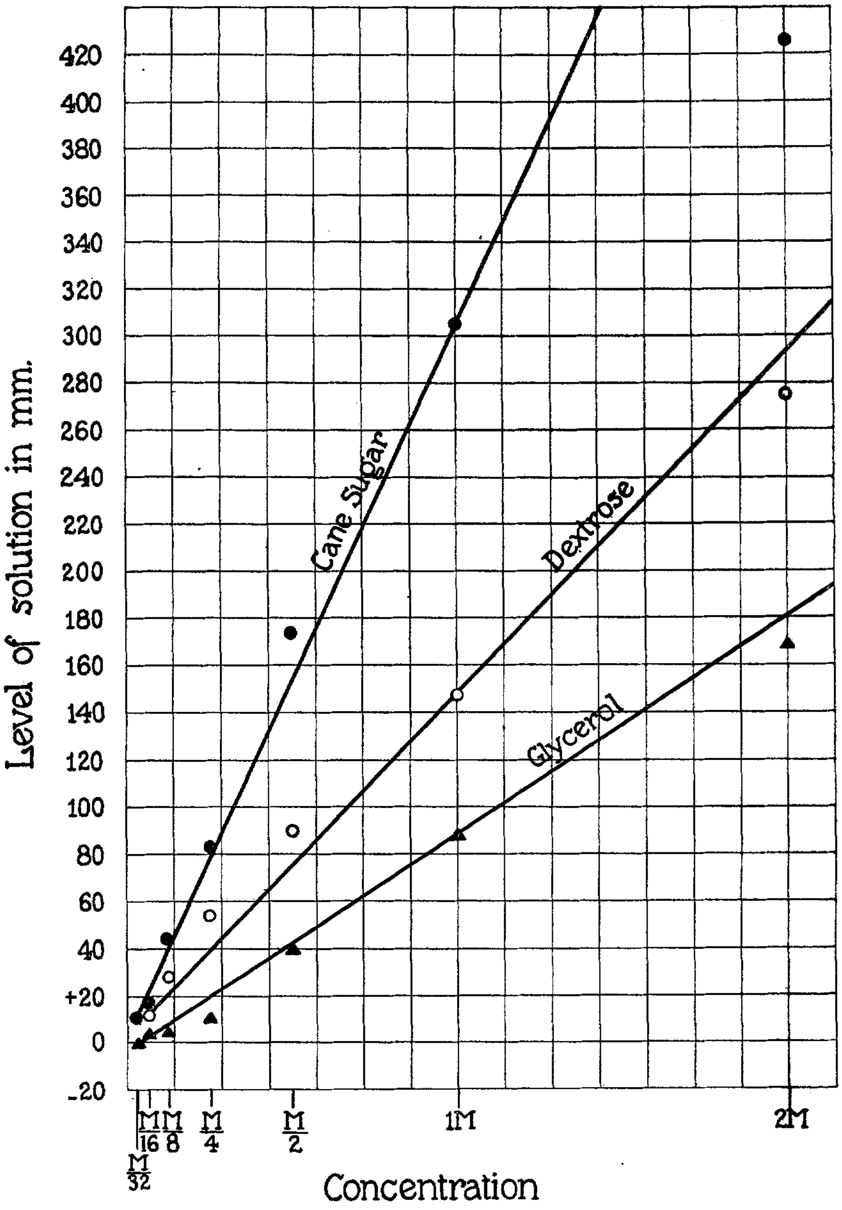

FIG. 2. The same as in Fig. 1, except that abscissæ in Fig. 2 are the concentrations instead of the logarithms of concentrations as in Fig. 1. Within concentrations of M/32 and 1 M the initial rise of liquid in 20 minutes is in direct proportion to the concentration, as van't Hoff's law demands.

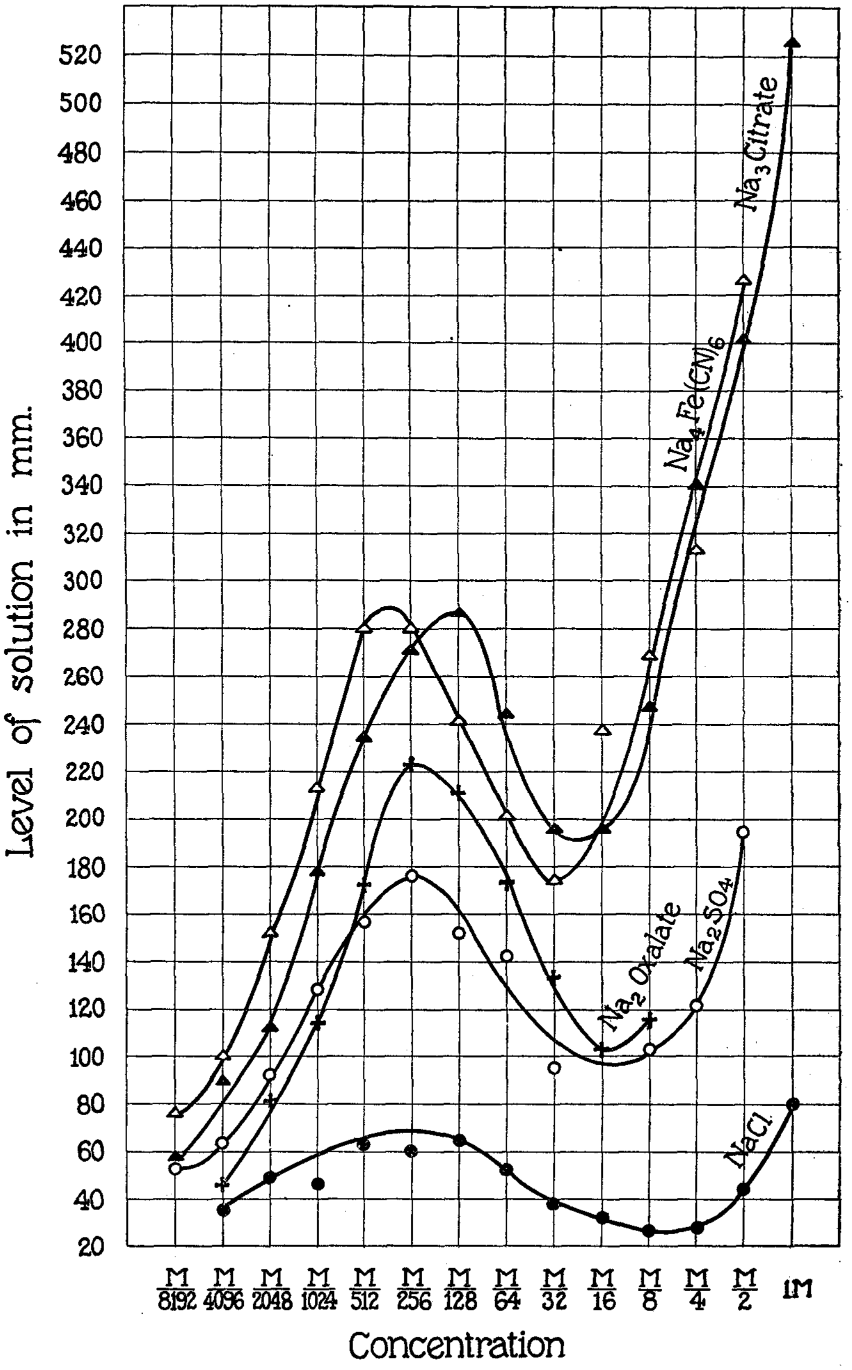

FIG. 3. Curves representing influence of concentration of five different sodium salts upon initial rate of diffusion of water through a collodion membrane from pure solvent to solution. Abscissæ are the logarithms of concentration. Ordinates represent level of solution in manometer tube after 20 minutes. The curves rise steeply until the concentration of M/256 is reached, then, with further increase in concentration, the curves drop, and rise again when the concentration is between M/16 and M/4.

While the ordinates of these curves represent the height in the manometer 20 minutes after the beginning of the experiments, the same form of curves is obtained when the readings are taken after 5, 10, or 30 minutes.

The interpretation of this complicated system of curves becomes simplified if we compare it with the curves for non-electrolytes in Fig. 1. We then notice that the character of both sets of curves agrees in the region of the higher concentrations above from M/32 to M/4, and we are therefore inclined to assume that the second rise in the curves for solutions of sodium salts beginning with M/32 to M/4 (according to the nature of the salt in solution) is due mainly to the gas pressure effect of the solution.

The abrupt rise and fall of the curves in Fig. 3 for lower concentrations than M/32 are not repeated in the case of the curves for the non-electrolytes in Fig. 1, and we are inclined to ascribe these peculiarities of the curves to the electrical action of the ions on the rate of diffusion of the electrified particles of water. Fig. 4 expresses this division of the curves diagrammatically.

In a preceding paper[1] we have shown that in the presence of neutral (or alkaline) salts with monovalent or bivalent cation 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 with a force which increases with the number of charges of the ion (and inversely with a quantity which we arbitrarily designated as the "radius" of the ion). The source of the electrification of the water particles as well as the specific mechanism by which the ions of the solution influence the rate of diffusion of water will not be discussed in this paper. It will, however, simplify the presentation of our experiments if it be permitted to describe our results as if the charged water particles were attracted or repelled electrostatically by the ions of the solution. We notice that in Fig. 3 the curves rise the more rapidly with increasing concentration the higher the valency of the anion of the salt, and with the reservation just mentioned we may ascribe this initial steep rise in the curves between a concentration of the solution of 0 to a concentration of M/256 to the fact that the attractive action of the anion of the sodium salts upon the rate of diffusion of the positively charged particles of water through the mem-

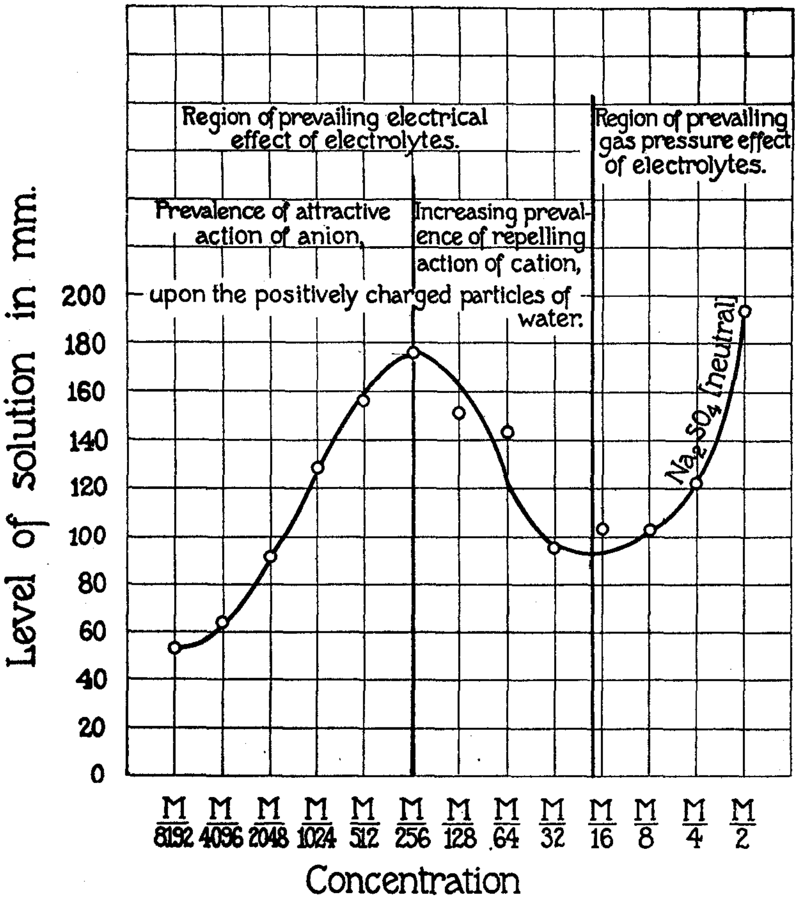

FIG. 4. Explanation of the curves in Fig. 3 given for the Na_2SO_4 curve. The first rise and fall between M/8,192 and M/16 represent the electrostatic action of ions of the solute upon the rate of diffusion of positively charged water particles. The second rise beyond M/16 represents the rise due to the gas pressure effect of the solute. The steep rise of the curve between 0 and M/256 is due to the prevalence of the attractive action of anion upon the positively charged molecules of water, while the drop beyond M/256 is due to the fact that the repelling action of cation upon the positively charged particles of water increases more rapidly with increasing concentration than the attractive action of SO_4 for the water.

brane is greater than the repelling action of the cation. The curves reach a maximum when the solution reaches a molecular concentration of about M/256 and from now on the curves drop rapidly with a further increase in the concentration of the solution. We assume that when the concentration of the solution of the sodium salts reaches a certain value the repelling action of the cation—in this case Na—increases more rapidly with increasing concentration than the attractive action of the anion upon the positively charged particles of water. This drop, however, is comparatively smaller the higher the valency of the anion. In the case of sodium chloride (Fig. 3) the curve is lower at M/8 (the minimum) than at M/4,096, while for SO_4 and oxalate the minimum reached by the curves (at M/16) is considerably above that

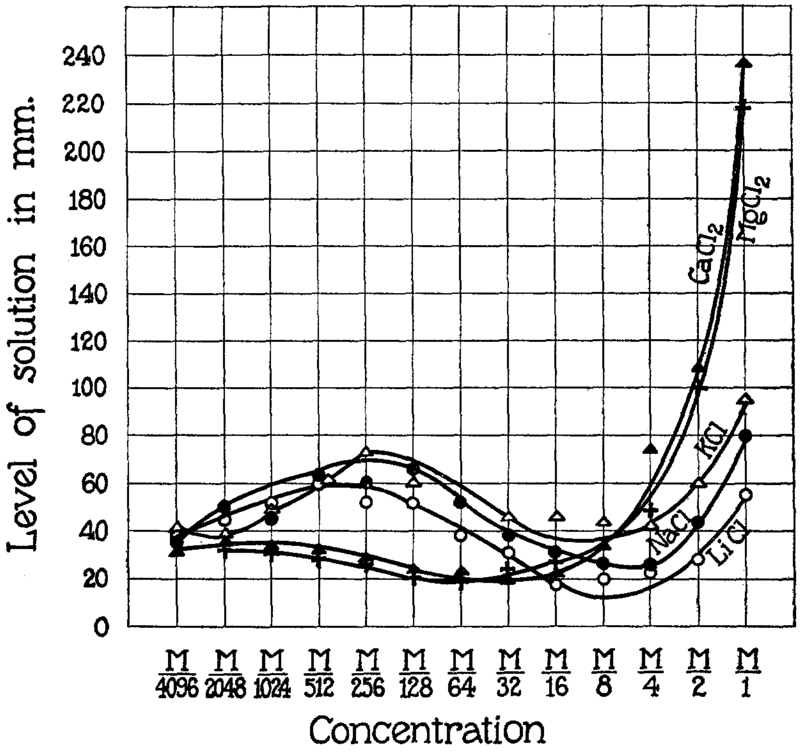

FIG. 5.

reached by the NaCl curve, and the minimum for the citrate and ferrocyanide is still higher. This was to be expected from the fact that the attractive action of the anion upon the positively charged particles of water is higher the greater the number of charges or the valency of the anion.

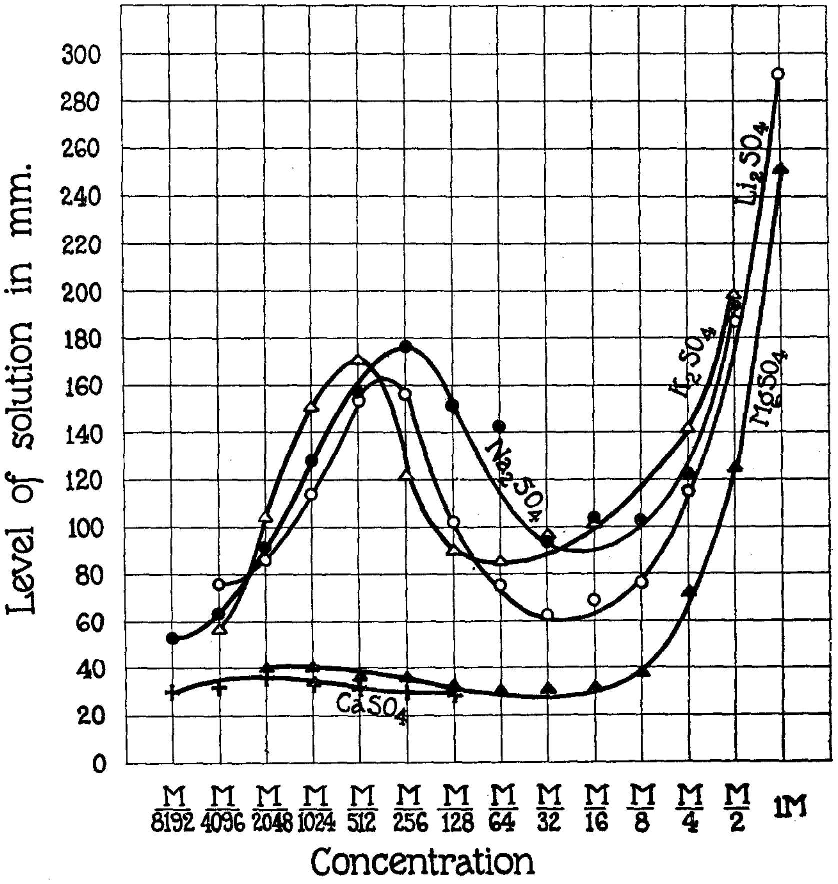

FIG. 6.

FIGS. 5 and 6. Curves representing influence of different chlorides (Fig. 5) and sulfates (Fig. 6) on initial rate of diffusion of water from pure solvent into solution, showing that the drop is greater in case of Li than of Na, or of K, and supporting the view that the drop is due to the repelling effect of the cation upon the positively charged particles of water.

The facts given are not peculiar to sodium salts but can be demonstrated in the case of all neutral or alkaline solutions of salts with monovalent or bivalent cation. Fig. 5 gives the curves for different chlorides and Fig. 6 for different sulfates. All the curves for these salts rise up to a concentration of about M/256 and then fall and finally rise again when the concentration is so high that the gas pressure effect begins to obliterate the electrical effect of the ions. The turning point for the commencement of the prevalence of the gas pressure effect is at a lower gram-molecular concentration for the sulfates than for the chlorides; Fig. 3 shows that the concentration of the turning point is the lower the higher the valency of the anion. It may be that this is simply the consequence of the fact that the higher the valency of the anion the greater the number of ions into which the salt dissociates electrolytically, but it is not yet certain that this is the full explanation. Another fact, however, is certain; namely, that the depression of the curves when the concentration exceeds M/256 is greater for the lithium salts than for the sodium salts, and greater for the sodium salts than for the potassium salts. This was to be expected if the drop is due to the repelling action of the cation on the positively charged particles of water, since the repelling action of cations on the positively charged particles of water increases inversely with a quantity which we arbitrarily designate as the "ionic radius." This "ionic radius" is less for Li than for Na and presumably less for Na than for K.

In the case of neutral solutions of salts with bivalent cation the repelling action of the cation is so great that it balances or exceeds the initial attractive action of a bivalent or monovalent anion for positively charged particles of water; the depressing action of the cation in concentrations above M/256 upon positively charged particles of water remains, however, noticeable especially in the SO_4 curves.

II. Influence of the Concentration of Electrolytes upon the Rate of Diffusion of Negatively Charged Particles of Water through Collodion Membranes.

The curves given in Figs. 3 to 6 contain a paradoxical fact, which can be expressed as follows: *when solutions of neutral or alkaline salts with monovalent or bivalent cation are separated by a collodion membrane* *from pure water the attraction of the solution for water diminishes with increasing concentration for concentrations between* M/256 *to about* M/32 *or above, according to the nature of the electrolyte.* This is exactly the reverse of what we should expect on the basis of van't Hoff's law which demands that the attraction of the solution for water should increase with the concentration. Such a reversal occurs only in the case of electrolytes and we assume provisionally that it is due to the fact that the repelling action of the cation of the electrolyte upon the positively charged particles of water increases inside the critical range of concentrations more rapidly with the concentration than the attractive action of the anion upon the same particles of water.

It will be necessary to test this assumption by further experiments.

We have shown in the first paper that water particles diffuse through collodion membranes in the form of *positively* charged particles from pure solvent to solutions of electrolytes with monovalent or bivalent cation when the solution is neutral or alkaline in reaction. When, however, the solution is rendered sufficiently acid the water particles diffuse through the membrane as if they were *negatively* charged, being attracted by the cation and repelled by the anion of the electrolyte with a force increasing with the valency of the ions. We will now consider the influence of the concentration of electrolytes upon the rate of diffusion of *negatively* charged particles of water through the membrane.

We have stated in a former paper[2] that the collodion membranes were suspended for 1 night in a 1 per cent gelatin solution before being used; after this they were used sometimes for a week or more without any further gelatin treatment. The membranes were, of course, rinsed a large number of times in warm water after the gelatin treatment to remove all the gelatin that could be removed by rinsing. This gelatin treatment is not necessary to obtain the results with neutral solutions of electrolytes described in the preceding chapter. The gelatin treatment of the membrane is, however, necessary to obtain the results with negatively charged particles of water to be described in this chapter. We intend to return to this fact in a later paper.

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[2] Loeb, J., *J. Gen. Physiol.*, 1919–20, ii, 87.

Negatively charged particles of water are attracted powerfully by bivalent or polyvalent cations and repelled powerfully by bivalent or polyvalent anions. We may, therefore, expect that when we make a $CaCl_2$ solution sufficiently acid through the addition of HNO_3 or HCl the curves showing the influence of the concentration of the electrolyte on the rate of diffusion of water should be similar to the curves in Figs. 3, 4, and 6, representing the influence of different concentrations of neutral solutions of Na_2SO_4 upon the rate of diffusion of positively charged particles of water through the same membranes. Fig. 7 shows that this is correct. The two upper curves represent the influence of variations in the concentration of $CaCl_2$ or $Ca(NO_3)_2$ dissolved in M/1,024 or M/128 HNO_3 or HCl. These acid solutions of $CaCl_2$ or $Ca(NO_3)_2$ cause a negative electrification of the water particles diffusing through the membrane. The attraction of the negatively charged water particles by Ca ions increases with an increase in the concentration of the calcium salt up to M/64, when the curve falls until the concentration of the calcium salt is M/4 where a minimum is reached. After this the gas pressure effect makes itself felt and the curve rises rapidly with rising concentration. In this case the drop in the two curves for the acid solutions when the concentration of the calcium salt exceeds M/64 is due to the fact that beyond a certain concentration of the calcium salt the repelling effect of the anion (Cl and NO_3) upon the negatively charged particles of water increases more rapidly with increasing concentration than the attractive action of the Ca ion.

The fact that the curve for $Ca(NO_3)_2$ in M/128 HCl is slightly lower than the curve for $CaCl_2$ in M/1,024 HNO_3 is due to the "negative osmosis" caused by acid solutions of sufficient concentration, as will be shown in the next chapter.

The three lower curves of Fig. 7 represent the influence of various concentrations of $CaCl_2$ upon positively charged particles of water and these curves are similar to those given for the effect of neutral solutions of $CaCl_2$ in Figs. 5 and 6. When $CaCl_2$ is dissolved in M/128 KOH the rise and drop of the curve become a little more marked than when the solution of $CaCl_2$ is neutral. The reason for this will become clear through the discussion in the next chapter of the phenomenon of negative osmosis caused by $Ca(OH)_2$.

When we render Na_2SO_4 solutions acid (by dissolving the salt in M/128 or M/1,024 HNO_3) the negatively charged particles of water diffusing through the membrane will be repelled by the SO_4 ion and attracted by both the Na and H ions. Since the SO_4 ion carries two

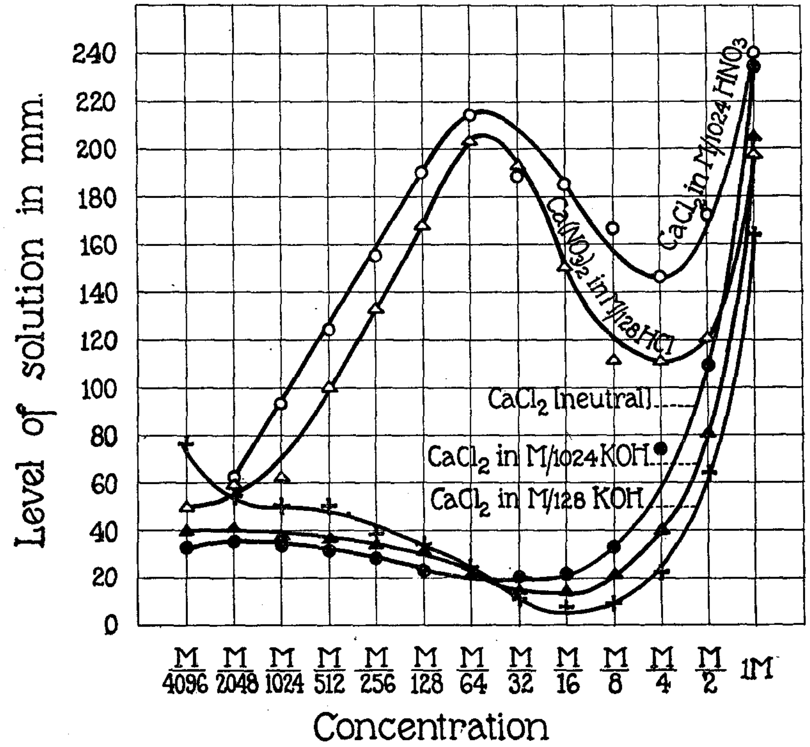

FIG. 7. Upper two curves representing influence of acid solutions of $CaCl_2$ or of $Ca(NO_3)_2$ upon negatively charged particles of water. At first there is a steep rise of the curve due to prevalence of attraction of Ca for the negatively charged particles of water, then beyond M/64 a drop in the curve due to prevalence of repelling action of NO_3 and Cl upon the negatively charged particles of water. No initial rise in the three lower curves, since in neutral and alkaline solutions of Ca water diffuses in the form of positively charged particles which are too strongly repelled by Ca to permit an initial rise in the level of the solution.

charges while the cations Na and H are monovalent the greater electrostatic action of the SO_4 ion should inhibit the electrostatic attraction of water by such solutions in the same way as is done by neutral solutions of $CaCl_2$ in the case of positively charged particles of water. Fig. 8 shows that this is the case. The two lower curves in Fig. 8 show the influence of concentrations of sufficiently acid solutions of Na_2SO_4 upon the rate of diffusion of water from distilled water into

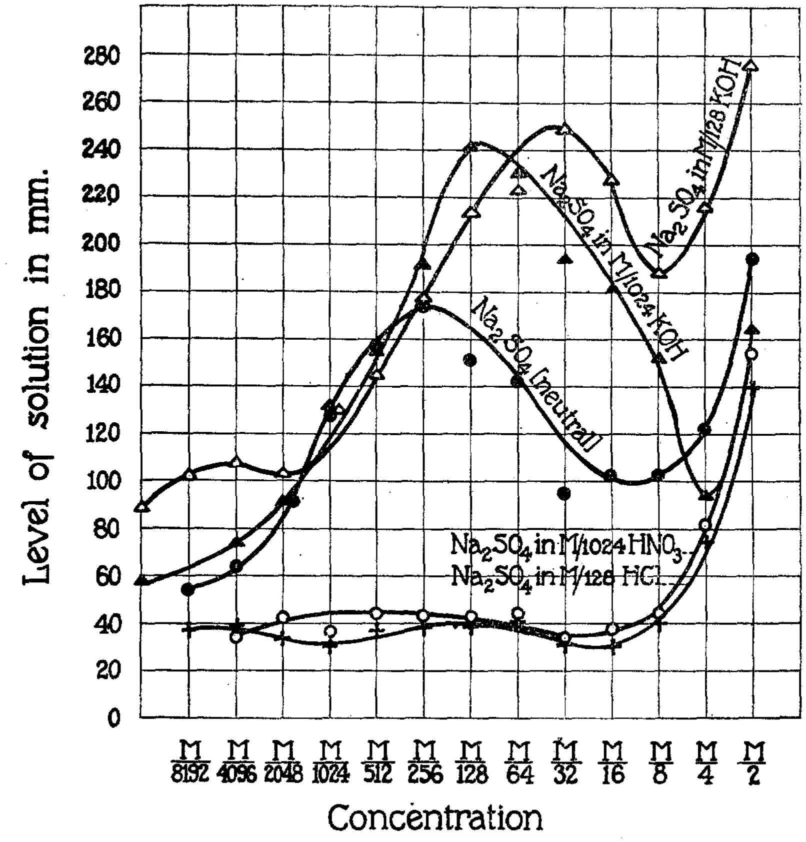

FIG. 8. The curves for solutions of Na_2SO_4 when sufficiently acid show no initial rise, since the negatively charged particles of water are too strongly repelled by the SO_4 ions.

solution. The curves resemble the curves for the effect of different concentrations of non-electrolytes, except for an intimation of a slight drop for concentrations of Na_2SO_4 between M/64 and M/8. The three upper curves represent the influence of concentrations of different neutral and alkaline solutions of Na_2SO_4 upon the rate of diffusion of positively charged water particles.

It was finally expected that the curves representing the influence of various concentrations of NaCl upon the rate of diffusion of water through collodion membranes should be similar in neutral, acid, and alkali solutions, for the reason that anion and cation of the salt are both monovalent (Fig. 9). In the presence of a sufficiently acid solution of NaCl the particles of water diffuse as negatively charged molecules through the membrane which are attracted by the Na ions and repelled by the Cl ions. The initial rise of the curve is due to the attractive action of the Na ion, and the drop in the curve is due to the increasing prevalence of the repelling action of the Cl ion. In neutral

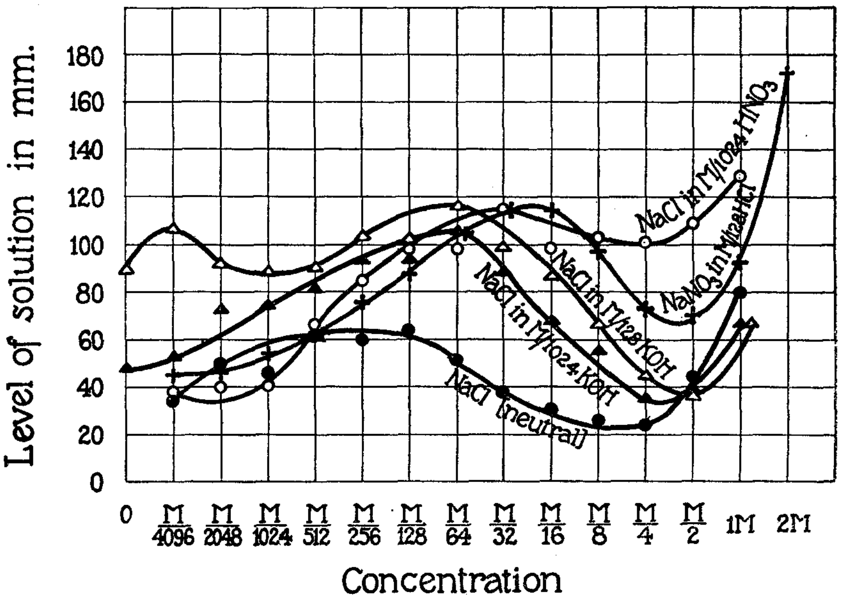

FIG. 9. Salts with monovalent anion and cation, like NaCl, show both rise and drop in alkaline, neutral, and acid solutions. In neutral and alkaline solutions the first rise is due to the attractive action of the Cl ion and the drop to the repelling action of the Na ion upon the positively charged particles of water. In acid solution the first rise in the curve is due to the attractive action of the Na ion and the drop to the repelling action of the Cl ion upon the negatively charged particles of water.

and alkaline solutions of NaCl the Cl ion attracts the water (which is charged positively) and the fall of the curve is due to the Na ion. The complete suppression of the rise which is caused in $CaCl_2$ when the solution is neutral or alkaline, and in Na_2SO_4 when the solution is acid, is due to the fact that in these cases the attracting ion is monovalent and the repelling ion bivalent. Fig. 9 shows that the curves representing the influence of the concentration of NaCl solutions upon the rate of diffusion of water are similar for neutral, alkaline, and acid solutions of NaCl. The drop is more considerable for $NaNO_3$ solu-

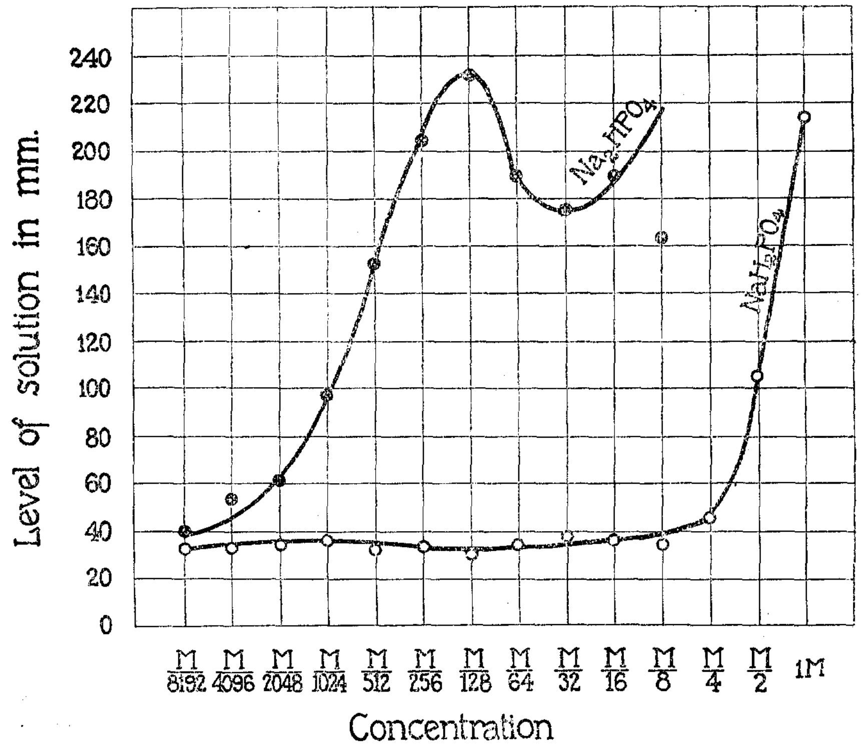

FIG. 10. The Na_2HPO_4 curve shows the initial rise and drop since the water diffuses in the presence of this salt in the form of positively charged particles which are attracted by the trivalent PO_4 ion and repelled by the monovalent Na and H ions. The NaH_2PO_4 curve shows no initial rise, since in the presence of this salt water diffuses in the form of negatively charged particles which are repelled by the trivalent PO_4 ion and attracted by the monovalent Na and H ion.

tions in M/128 HCl than in M/1,024 acid, on account of the negative osmosis caused by solutions of acids, as the next chapter will show.

Fig. 10 shows the difference in the influence of concentration upon the rate of diffusion of water in the case of Na_2HPO_4 and NaH_2PO_4. In the presence of the latter solution the water diffusing through the membrane is negatively charged and the curve does not show the initial rise and drop but shows only the gas pressure effect of the solution. In the case of Na_2HPO_4 water diffuses in the form of positively charged particles and the curve shows the rise and drop as described for neutral and alkaline salts in which the anion has a higher valency than the cation.

We can therefore state that for the diffusion of negatively as well as positively electrified particles of water the law of van't Hoff is reversed within a certain range of concentrations of electrolyte—in the extreme between about M/256 and M/4—inasmuch as in this range the attraction of a solution of an electrolyte for pure water diminishes with increasing concentration.

III. Negative Osmosis.

Dutrochet,[3] Graham,[4] and Flusin[5] have observed a striking phenomenon of negative osmosis in certain acids; namely, that the stream of liquid diffuses through pig's bladder from acid to pure water, instead of in the opposite direction. This was observed for tartaric and oxalic acids. Flusin tries to explain the phenomenon on the basis of a difference in degree of imbibition or swelling of the two sides of pig's bladder, one side being in contact with pure water where the swelling is slight, the other being in contact with acid where the swelling is great. Bartell, and Bartell and Hocker[6] have observed negative osmosis through porcelain even in the case of some neutral

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[3] Dutrochet, H., *Ann. chim. et. phys.* 1835, lx, 337.

[4] Graham, T., *Phil. Tr.*, 1854, cxliv, 177.

[5] Flusin, G., *Ann. chim. et phys.*, 1908, xiii, 480. For a discussion of the literature see Höber, R., Physikalische Chemie der Zelle und der Gewebe, Leipsic, 4th edition, 1914, 248.

[6] Bartell, F. E., *J. Am. Chem. Soc.*, 1914, xxxvi, 646. Bartell, F. E., and Hocker, C. D., *J. Am. Chem. Soc.*, 1916, xxxviii, 1029, 1036.

salts. The writer has never observed negative osmosis when solutions of neutral salts were separated from pure solvent by collodion membranes.

The writer has recently investigated the influence of the concentration in acids and alkalies on the rate of diffusion of water through collodion membranes (previously treated with gelatin), with the result that the phenomenon of negative osmosis described for tartaric and oxalic acids is very common in acids and alkalies, that it *occurs in exactly the same range of concentration where the drop in the curves of the neutral salt solutions occurs, namely within a range between* M*/256 to about* M*/4, and that the phenomenon is in reality nothing else but this drop.* The difference between the nature of the drop in the case of solutions of neutral salts on the one hand and of solutions of acids and alkalies on the other is that in the case of alkalies and acids the drop is not only relative but absolute. Titration experiments show that acid diffuses from the acid solution into distilled water and that the concentration of acid in the solution is considerably less after 20 minutes than at the beginning. Since at the same time the total volume of solution diminishes—this being the nature of negative osmosis—we must conclude that the diminution of the volume of the solution is due to the fact that the combined volume of acid and water diffusing out from the solution is slightly larger than the volume of water diffusing simultaneously into the solution. We shall return to this problem in a subsequent paper. Since acids as well as bases diffuse into the pure solvent the phenomenon of negative osmosis can only be observed during a short period at the beginning of the experiment.

In all the experiments described in the preceding pages it was necessary to put the solution into the collodion flask and to dip the latter into distilled water in order to observe the influence of the solution on the initial rate of diffusion of water. More water diffuses into the solution than diffuses simultaneously in the opposite direction and as a consequence the level of the water in the glass tube rises. When we put solutions of certain acids or alkalies into the collodion flasks and dip these flasks into distilled water the level of the liquid in the manometer falls instead of rising. If, however, we put the solution of the same acids or alkalies outside, filling the collodion flask with distilled water, we observe an initial rise of liquid in the manometer. For these experiments with acids, the collodion membranes must be bathed once over night in a 1 per cent gelatin solution. Fig. 11 shows the influence of the nature and concentration of acid upon the phenomenon. Since we are dealing here with a loss of volume on the part of the solution, we must plot the rise observed in the manometer as a negative quantity below the zero line. The curves show that the drop is confined to the same range of concentrations where a similar drop occurs in the case of the neutral salts. The level of the water in the manometer tube was at the beginning of the experiment about 30 mm. When the flasks thus filled with distilled water were put

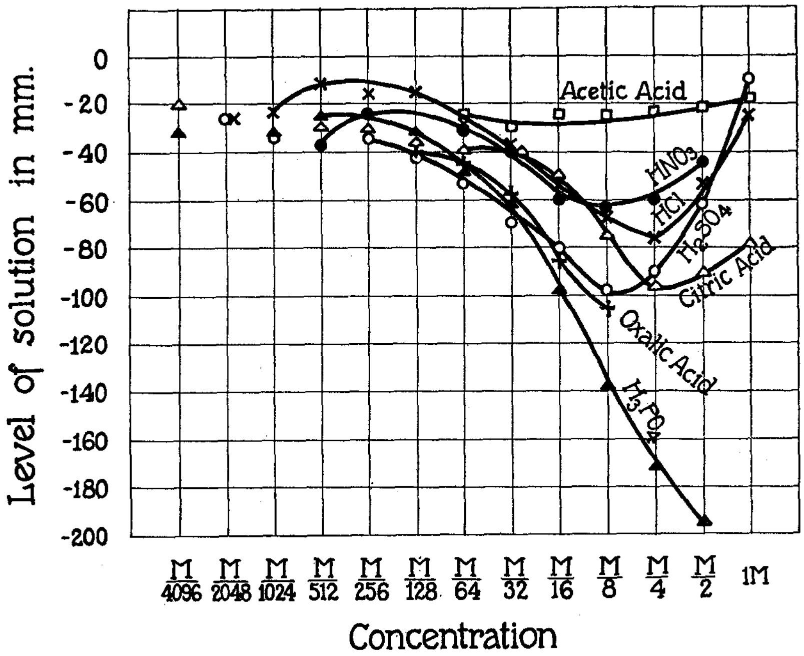

FIG. 11. Negative osmosis in acids, showing that the drop occurs here as in all other cases in a range of concentrations between M/256 and M/8 or M/4. The drop is greater for acids with bivalent or trivalent anion than for acids with monovalent anion, showing that the drop is due to the repelling action of the anion upon the negatively charged particles of water.

into beakers containing solutions of acid the level of the pure water in the flask rose during the first 20 minutes or more whenever the concentration of the acid was M/256 and the rise increased with an increase in the concentration until the concentration was about M/4. Then the level of the water inside the flask fell again.

In the presence of acids water diffuses through the membrane in the form of negatively charged particles. We have assumed that the drop is due to the repelling action of that ion of the electrolyte which has the same charge as the water particles; *i.e.*, the anion in the case of acids. Our assumption is supported by the fact that aside from the degree of electrolytic dissociation the drop increases with the increase of valency of the anion of the acid as we should expect. The drop is least in the case of the acids with monovalent anion (NO_3 and Cl), is greater in the case of SO_4 and oxalate anion, and still greater in the case of PO_4. The drop in citric acid is a little less than in oxalic acid, as is to be expected from the fact that citric acid is a weak acid. In the case of acetic acid no rise and drop in the curve is noticeable except the rise due to the gas pressure effect of the solution.

In the case of alkalies we are restricted to low concentrations by the fact that they dissolve the collodion membranes when the concentration becomes moderately strong. As Fig. 12 shows, we observe absolute negative osmosis in the case of $Ca(OH)_2$ and $Ba(OH)_2$ when the concentration of the solution exceeds M/256. In the case of alkalies with monovalent cation the usual drop in the curves—*i.e.* relative negative osmosis—was observed, but not an absolute negative osmosis; *i.e.*, an absolute diminution of the volume of the solution.

The negative osmosis in the case of acids and alkalies becomes absolute for the reason that the initial rise in the curve due to the attractive action of the ion with the opposite sign of charge from that of the water is too slight or entirely lacking in the case of the acids or alkalies.

The writer was interested in finding out whether aluminium salts with bivalent or trivalent anion induce negative osmosis. In Fig. 13 are plotted the curves representing the influence of different concentrations of Al_2Cl_6, $Al_2(SO_4)_3$, and aluminium citrate on the rate of diffusion of water through a collodion membrane. All the solutions had about the same hydrogen ion concentration and the water diffused through the membrane in the form of negatively charged molecules, which according to our theory are attracted by the Al ion and repelled by the anion, the repelling action increasing with the valency of the anion. The curves show that Al_2Cl_6 attracts water very violently, $Al_2(SO_4)_3$ much less, and that aluminium citrate acts like a solution of a non-electrolyte, the attractive and repelling action of the two trivalent ions, Al and citrate, balancing each other. But no negative osmosis was noticed. This shows that the electrostatic effect of the H ion upon the rate of diffusion of water is considerably smaller than

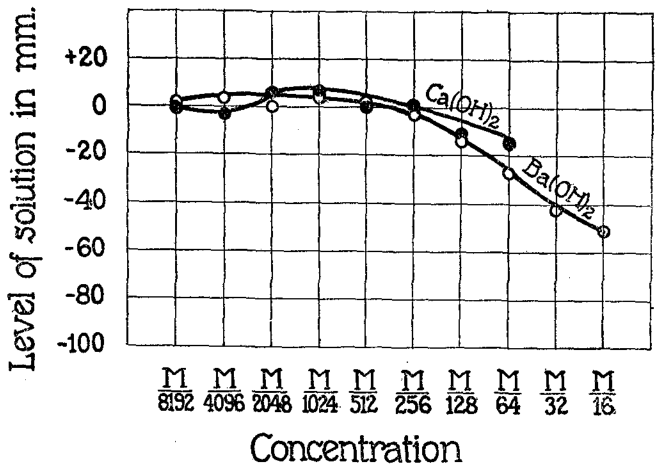

FIG. 12. Curves showing negative osmosis in the case of $Ca(OH)_2$ and $Ba(OH)_2$ occurring in that range of concentrations where the drop in Fig. 3 occurs.

the electrostatic action of trivalent cations like Al, while the electrifying effect of the H ion upon the water seems to be more nearly equal to the electrifying effect of the trivalent cation upon water. This suggests that the electrifying effect of ions upon water and their electrostatic effect upon the rate of diffusion of water are due to different qualities of the ion.

The curves for aluminium salts in Fig. 13 show no drop. As a matter of fact, a slight drop can be demonstrated in the $AlCl_3$ curves but in concentrations higher than those in Fig. 13, namely about M/32 or M/16, a phenomenon which finds its explanation perhaps in the fact that the cation is trivalent and the anion only monovalent.

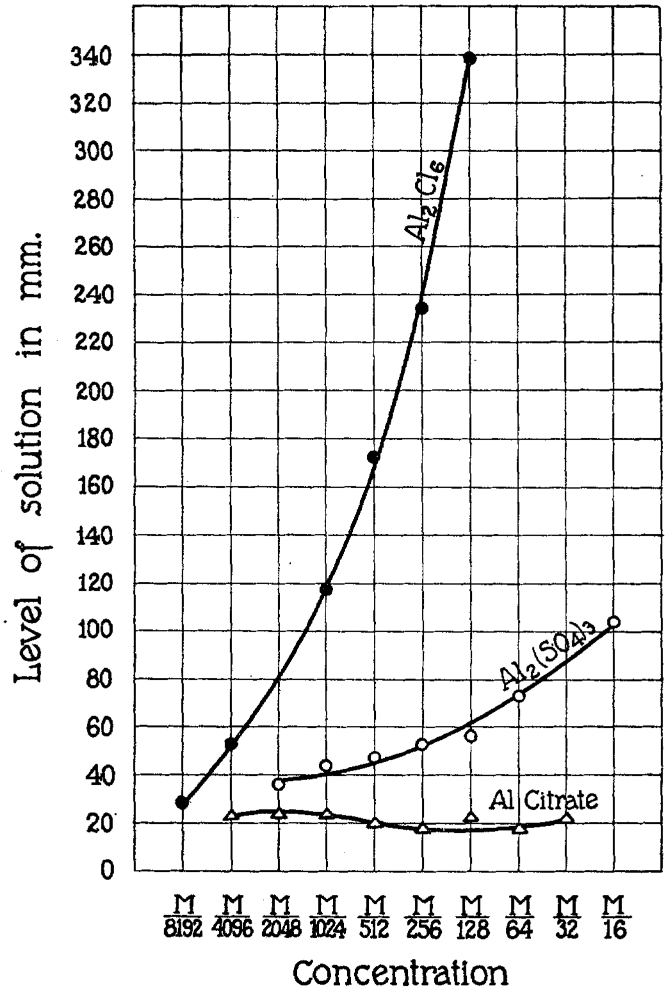

FIG. 13. Curves representing the attraction of different aluminium salts for negatively charged particles of water. The attraction is a maximum in the case of Al_2Cl_6, is less in the case of $Al_2(SO_4)_3$, and is practically lacking in the case of aluminium citrate, showing the increase in the repelling effect of the anion upon the negatively charged particles of water with increasing valency of the anion.

IV. Further Proof that the Negative Osmosis Is Due to the Repelling Action of the Ion with the Same Sign of Charge as that of the Electrified Water Particles.

When we fill the collodion flask with a M/256 solution of Na_2SO_4 (made neutral or slightly alkaline) and dip the flask into distilled water, we notice a rather high initial rate of diffusion of water into the flask caused by the fact that the attraction of the SO_4 ion with its two charges upon the positively charged particles of water is greater than the sum of the repelling action of the two Na ions. In higher concentrations of Na_2SO_4 this difference becomes less (Fig. 4), as we assume through the fact that for some reason the repelling action of the Na ions on the positively charged water particles increases more rapidly with further increase in concentration than the attractive action of SO_4. If this assumption is correct the addition of a salt of the type $MgCl_2$ to a M/256 solution of Na_2SO_4 should lower the rate of diffusion of water into the M/256 solution of Na_2SO_4 more than the addition of the same concentration of KCl; since the repelling effect of the bivalent Mg ion upon the positively charged water particles is greater than the repelling effect of the monovalent K ions. The addition of LiCl should lower the rate of diffusion of water more than the addition of KCl but less than $MgCl_2$, since the electrostatic effect of Li is greater than that of the K ion but less than that of the Mg ion. Fig. 14 shows that this is actually true. 100 cc. of M/256 Na_2SO_4 (pH about 6.0) contained 0, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 cc. of M/4 KCl, LiCl, or $MgCl_2$. The addition of KCl caused only a slight diminution in the rate of diffusion when 12.8 to 25.6 cc. of M/4 KCl were added. LiCl caused more of a drop, but a slight addition of $MgCl_2$ caused a considerable drop, as our theory demands.

When, however, a salt with polyvalent anion and monovalent cation like $K_4Fe(CN)_6$ is added to M/256 Na_2SO_4 the attraction of the ferrocyanide ion for water counteracts to a large extent the drop caused by the weak repelling action of the K ions added. Fig. 3 shows that the attraction of the $Fe(CN)_6$ ion for water is greater than that of the sulfate ion. Hence the addition of slight quantities of $K_4Fe(CN)_6$ to M/256 Na_2SO_4 increases the initial rate of diffusion of water into the solution but as soon as the concentration of $K_4Fe(CN)_6$ added reaches

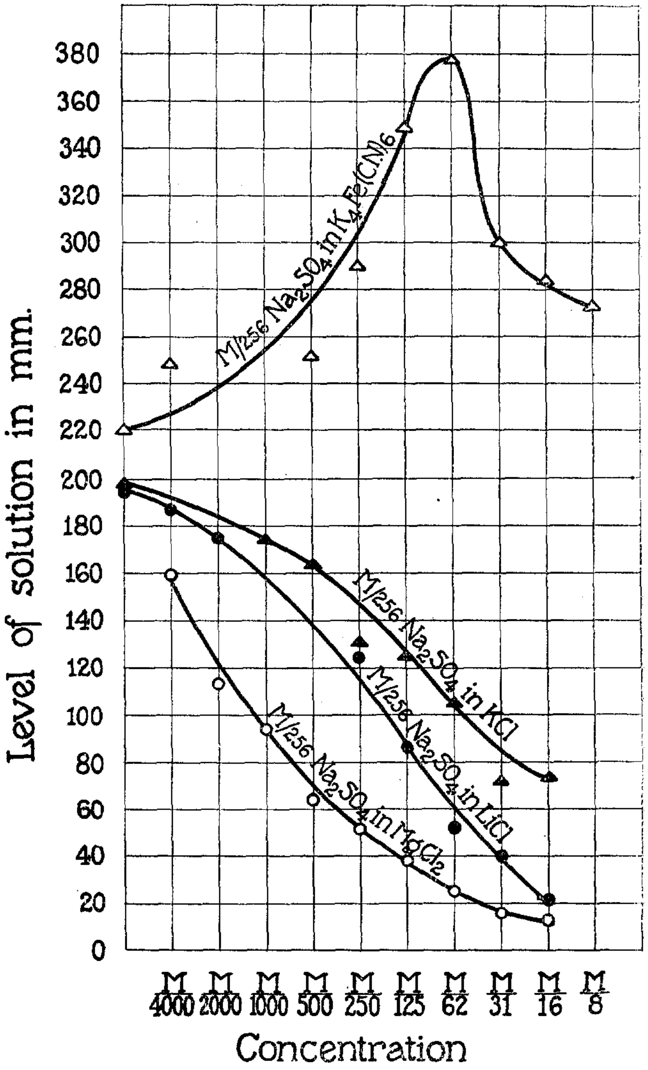

FIG. 14. Curves showing that when we add increasing concentrations of neutral salts with monovalent anion to a neutral M/256 solution of Na_2SO_4 the attraction of the Na_2SO_4 solution for water is diminished. Since this diminution increases in the order K, Li, Mg, the latter being the most depressing ion, it supports the idea that the drop observed in curves of Fig. 3 is due to the repelling action of the cation upon the positively charged particles of water.

the concentration of M/62 a further addition of $K_4Fe(CN)_6$ lowers the rate of diffusion of water into the solution. From this concentration on the repelling action of the K and Na ions upon water prevails over the attractive action of the anion.

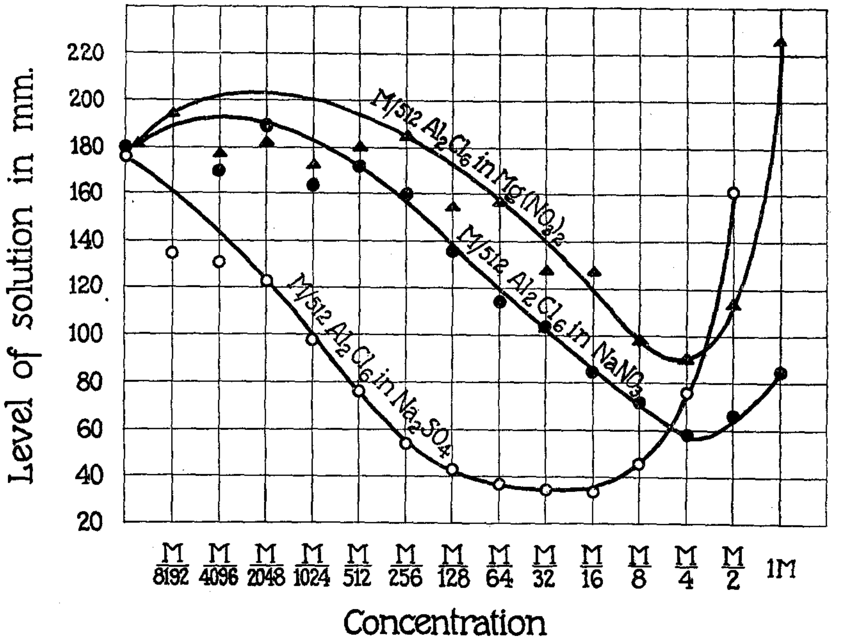

FIG. 15. Curves showing that when we add increasing concentrations of $NaNO_3$, $Mg(NO_3)_2$, and Na_2SO_4 to M/512 solutions of Al_2Cl_6 the depressing effect is greater for SO_4 than for NO_3. Since the water diffuses in this case in the form of negatively charged particles the curves support the idea that the depressing effect of the salt added is due to the repelling action of the anion upon the negatively charged particles of water.

When the collodion flask (previously bathed in gelatin) is filled with M/512 Al_2Cl_6 and dipped into a beaker with distilled water, water diffuses at first very rapidly into the flask. The water is in this case negatively charged and attracted by the Al ion and repelled by the anion. When we add small quantities of a salt with bivalent anion, *e.g.* Na_2SO_4, to the Al_2Cl_6 solution the attraction of the Al_2Cl_6 solution for water is diminished more rapidly than when we add a salt with a monovalent anion like $NaNO_3$ or $Mg(NO_3)_2$ (Fig. 15). The Mg ion attracts negatively charged water more powerfully than the $NaNO_3$ and hence the depressing effect of $Mg(NO_3)_2$ is smaller than the depressing effect of $NaNO_3$. Fig. 16 shows that the depressing effect of the addition of H_2SO_4 upon M/512 Al_2Cl_6 is greater than the addition of HNO_3, both acids acting similarly to the potassium salts with the same anion.

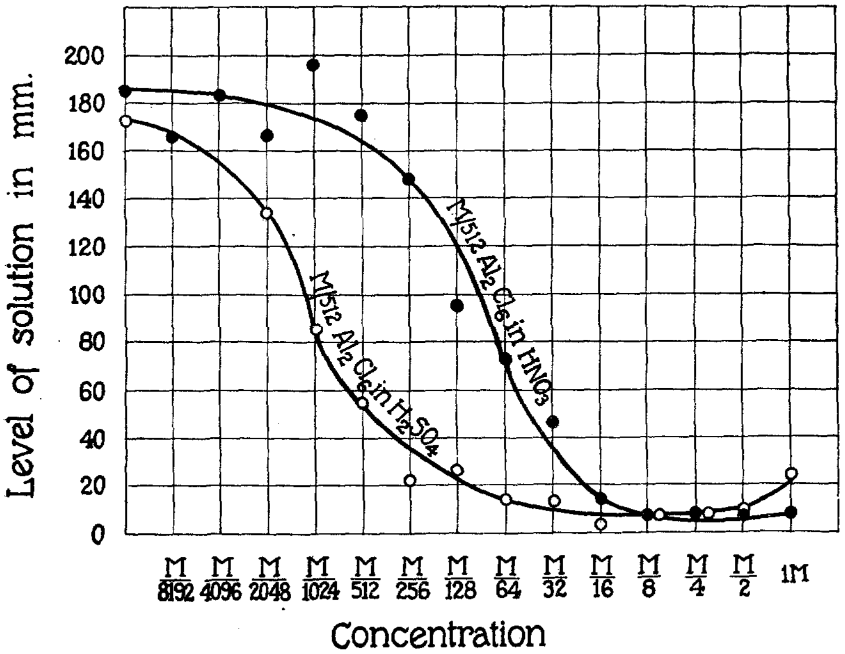

FIG. 16. Curves showing that the depressing effect of HNO_3 and H_2SO_4 is similar to the depressing effect of $NaNO_3$ and Na_2SO_4 when added to M/512 Al_2Cl_6.

All these facts support our assumption that the drop in the curves representing the influence of the concentration of the electrolyte upon the rate of diffusion of water through collodion membranes is due to the fact that beyond a certain concentration the repelling action of the ion with the same sign of charge as that of water increases more rapidly with a further increase in concentration than the attractive action of the ion with the opposite charge upon the water.

SUMMARY.

1. When a watery solution is separated from pure water by a collodion membrane, the initial rate of diffusion of water into the solution is influenced in an entirely different way by solutions of electrolytes and of non-electrolytes. Solutions of non-electrolytes, *e.g.* sugars, influence the initial rate of diffusion of water through the membrane approximately in direct proportion to their concentration, and this influence begins to show itself under the conditions of our experiments when the concentration of the sugar solution is above M/64 or M/32. We call this effect of the concentration of the solute on the initial rate of diffusion of water into the solution the gas pressure effect.

2. Solutions of electrolytes show the gas pressure effect upon the initial rate of diffusion also, but it commences at a somewhat higher concentration than M/64; namely, at M/16 or more (according to the nature of the electrolyte).

3. Solutions of electrolytes of a lower concentration than M/16 or M/8 have a specific influence on the initial rate of diffusion of water through a collodion membrane from pure solvent into solution which is not found in the case of the solutions of non-electrolytes and which is due to the fact that the particles of water diffuse in this case through the membrane in an electrified condition, the sign of the charge depending upon the nature of the electrolyte in solution, according to two rules given in a preceding paper.[1]

4. In these lower concentrations the curves representing the influence of the concentration of the electrolyte on the initial rate of diffusion of water into the solution rise at first steeply with an increase in the concentration, until a maximum is reached at a concentration of M/256 or above. A further increase in concentration causes a drop in the curve and this drop increases with a further increase of concentration until that concentration of the solute is reached in which the gas pressure effect begins to prevail; *i.e.*, above M/16. Within a range of concentrations between M/256 and M/16 or more (according to the nature of the electrolyte) we notice the reverse of what we should expect on the basis of van't Hoff's law; namely, that the attraction of a solution of an electrolyte for water diminishes with an increase in concentration.

5. We wish to make no definite assumption concerning the origin of the electrification of water and concerning the mechanism whereby ions influence the rate of diffusion of water particles through collodion membranes from pure solvent to solution. It will facilitate, however, the presentation of our results if it be permitted to present them in terms of attraction and repulsion of the charged particles of water by the ions. With this reservation we may say that in the lowest concentrations attraction of the electrified water particles by the ions with the opposite charge prevails over the repulsion of the electrified water particles by the ions with the same sign of charge as that of the water; while beyond a certain critical concentration the repelling action of the ion with the same sign of charge as that of the water particles upon the latter increases more rapidly with increasing concentration of the solute than the attractive action of the ion with the opposite charge.

6. It is shown that negative osmosis, *i.e.* the diminution of the volume of the solution of acids and of alkalies when separated by collodion membranes from pure water, occurs in the same range of concentrations in which the drop in the curves of neutral salts occurs, and that it is due to the same cause; namely, the repulsion of the electrified particles of water by the ion with the same sign of charge as that of the water. This conclusion is supported by the fact that negative osmosis becomes pronounced when the ion with the same sign of charge as that of the electrified particles of water carries more than one charge.