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INFLUENCE OF THE CONCENTRATION OF ELECTROLYTES ON SOME PHYSICAL PROPERTIES OF COLLOIDS AND OF CRYSTALLOIDS.

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I. INTRODUCTION.

When we separate neutral solutions of salts with monovalent cation from pure water by a collodion membrane, water will diffuse into the solution. The writer has shown in a preceding publication¹ that the initial rate of diffusion will at first increase with the concentration of the electrolyte, but as soon as the concentration of the latter is about $M/256$, the initial rate of diffusion of water into the solution will in the case of many electrolytes diminish with a further increase in the concentration of the electrolyte until at a concentration varying between $M/32$ and $M/8$ (according to the nature of the electrolyte) a minimum is reached. This phenomenon is due to the influence of the ions on the electrification and rate of diffusion of water through the collodion membrane. In the presence of neutral solutions of salts with monovalent or bivalent cation, water diffuses through the collodion membrane as if its particles were positively charged and as if they were attracted by the anion and repelled by the cation of the electrolyte with a force increasing with the valency of the ion. With low concentrations of electrolytes the attractive action of the anion upon the positively charged particles of water prevails over the repulsive force of the cation, while, when the concentration exceeds a certain value, which for a number of salts is about $M/256$, the repelling force of the cations of the electrolyte upon the positively charged particles of the water increases more rapidly than the attractive force of the anions. This idea is supported by the fact that the addition of salts with

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

bivalent cation causes a more rapid drop than the addition of a salt with monovalent cation. These phenomena bear so striking a resemblance to the action of the concentration of electrolytes upon the osmotic pressure, the swelling, and other properties of colloids that a discussion of the similarity may seem of interest.

It was found by Pauli² that the addition of a little acid to blood albumin which had been dialyzed for weeks (and which was therefore approximately isoelectric) caused an increase in the viscosity of the protein, which at first was the greater the more acid was added. Very soon, however, a point was reached where the addition of more acid caused again a diminution in the viscosity. The same phenomenon occurs when acid is added to isoelectric gelatin. The addition of a slight amount of acid causes an increase in the osmotic pressure until finally a point is reached where the further addition causes a diminution (Fig. 1). The increase in the osmotic pressure of isoelectric gelatin when a slight quantity of HCl is added, is due to the formation of gelatin chloride, but the depressing effect of the addition of an excess of acid is not so easy to explain. According to Pauli we should ascribe it to the diminution of the degree of electrolytic dissociation of protein chloride due to the increase in the concentration of the common anion Cl. The writer's measurements of conductivity do not support this idea.³ Another suggestion made by colloid chemists is that the addition of more acid causes an aggregate formation of the gelatin particles and therefore a diminution of osmotic pressure. This suggestion rests only on the phenomenon which it is supposed to explain, but it may, nevertheless, be correct. If so, it remains to be explained why an increase in the concentration of electrolytes causes a formation of aggregates.

In a preceding publication⁴ the writer has shown that a 1 per cent solution of gelatin-acid salt, *e.g.* gelatin chloride or gelatin citrate, etc., has its maximal osmotic pressure when the pH is about 3.4 or 3.3. When to gelatin chloride of this pH acid or neutral salt is added, the osmotic pressure (as well as the swelling, viscosity, etc.) falls and the more so the more acid or salt has been added. When we add

² Pauli, W., *Fortschr. naturwiss. Forschung*, 1912, iv, 223.

³ Loeb, J., *J. Gen. Physiol.*, 1918-19, i, 483, 559.

⁴ Loeb, J., *J. Gen. Physiol.*, 1918-19, i, 559.

alkali, the osmotic pressure falls also, but in this case a complication arises, since the addition of NaOH to a gelatin-acid salt causes a neutralization of the acid and the gradual transformation of the gelatin-acid salt into isoelectric gelatin which has a minimal osmotic pressure.

A 1 per cent solution of metal gelatinate, *e.g.* Na gelatinate, has its maximal osmotic pressure at a pH of about 8.4. When to a 1 per cent solution of metal gelatinate of this pH alkali or neutral salt is added, the osmotic pressure (as well as the swelling and the viscosity) is diminished. When acid is added the same phenomenon occurs but for another reason since the addition of acid lowers the pH and transforms gelatin salt into isoelectric gelatin. We will first discuss the action of electrolytes on the osmotic pressure of metal gelatinate.

II. Water Charged Positively.

Doses of 1 gm. each of commercial, finely powdered gelatin are rendered isoelectric, melted, and made up into 1 per cent solutions of gelatin by adding enough NaOH and water to make the volume 100 cc. The amount of NaOH contained in 100 cc. of each solution varied and it was for different solutions 0, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 cc. of $M/4$ NaOH. Part of this NaOH combined with the gelatin, forming Na gelatinate; the rest remained free. As shown in a preceding paper, there exists a definite chemical equilibrium between the Na gelatinate formed, the isoelectric gelatin, and the hydrogen ion concentration. If the alkali of such a solution is neutralized by an acid (*e.g.* CO_2) or if it is allowed to diffuse out from the solution, the equilibrium is disturbed and some of the metal gelatinate will be transformed into non-ionogenic (isoelectric) gelatin.

These gelatin solutions containing different amounts of NaOH were put into collodion bags. The latter were closed with a rubber stopper which was perforated by a glass tube with a bore of 2 mm. in diameter which served as a manometer to measure the osmotic pressure of the solutions. These bags were put into beakers containing 350 cc. of a solution of NaOH which in each case had the same amount of NaOH in 100 cc. solution as was originally added to the gelatin solution which it surrounded. Thus the 1 per cent solution of Na

gelatinate which had 6.4 cc. of $M/4$ NaOH in 100 cc. was dipped into a beaker with water which had 6.4 cc. of $M/4$ NaOH per 100 cc. of H_2O . Since a small part of the NaOH inside the collodion bag had combined with the gelatin, the concentration of NaOH in the outside solution was at first slightly greater than that inside, and as a consequence some NaOH diffused from the outside into the bags. Part of the NaOH in the outside solution was gradually neutralized by

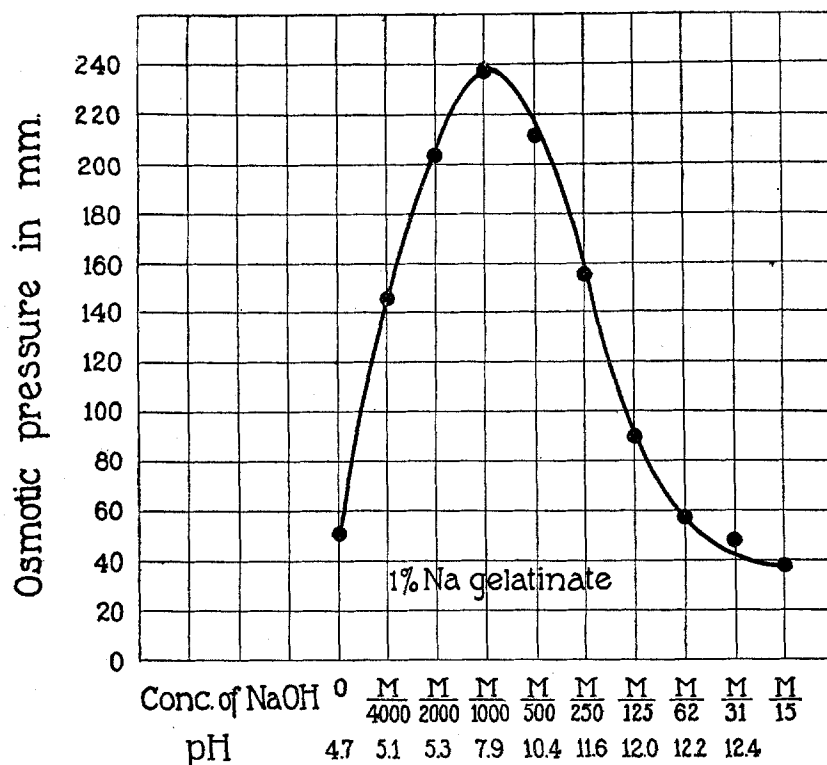


FIG. 1. Curve of osmotic pressure of 1 per cent Na gelatinate solutions contained in collodion bags and surrounded by solutions of NaOH of the same concentration as that in which the isoelectric gelatin was dissolved. Abscissæ are the logarithms of concentration of NaOH in which the isoelectric gelatin was dissolved; below is given the pH of the gelatin solution at the conclusion of the experiment ($4\frac{1}{2}$ hours after beginning). The osmotic pressure rises steeply at first until the pH is about 8.4, and then when more NaOH is contained in solution the osmotic pressure falls again equally steeply with a further increase in concentration of NaOH added.

the absorption of CO_2 from the air and this diminished the concentration of NaOH in the outside and, as a consequence, also in the inside solution.

Fig. 1 represents the osmotic pressure reached after about 5 hours in the various solutions. (At this time the permanent osmotic pressure is generally attained when the solution undergoes no further chemical changes.) The abscissæ of Fig. 1 are the logarithms of the concentration of the NaOH . The row of figures below the figures for the concentration of NaOH is the pH as found in each gelatin solution at the end of the experiment. The ordinates are the osmotic

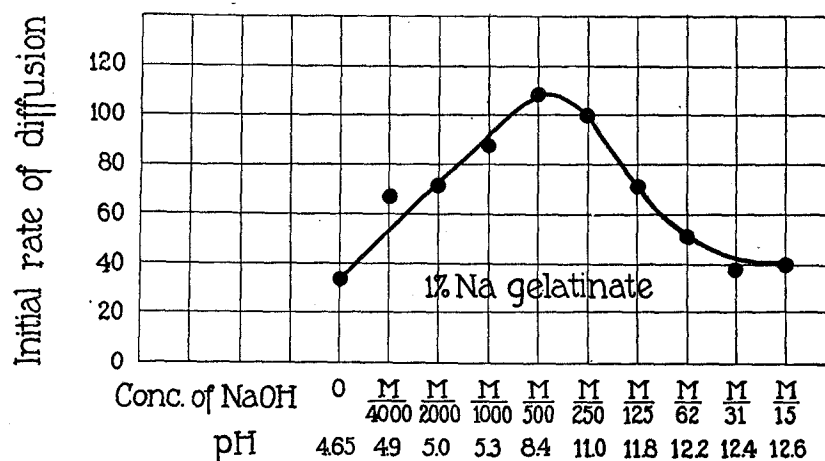


FIG. 2. Curve of initial rate of diffusion of water into 1 per cent gelatin dissolved in the same concentrations of NaOH as those used in Fig. 1, measured by rise of level of liquid in manometer 30 minutes after beginning of experiment. Abscissæ are the concentrations of NaOH , ordinates are the rise of level of liquid in manometer after 30 minutes. The curve is similar to the curve of osmotic pressure. Maximum at $\text{pH} = 8.4$.

pressures expressed in mm. of a column of 1 per cent gelatin solution. The maximum should have been at a pH of about 8.4 (between $\frac{M}{1,000}$ and $\frac{M}{500}$). The figure shows that the osmotic pressure rises first rapidly with an increase in the pH and falls equally rapidly beyond a pH which (from other experiments) we judge to be about 8.4. At a pH of 12.2 the curve is almost as low as it is for isoelectric gelatin.

Fig. 2 shows the influence of the concentration of NaOH upon the initial rate of diffusion of water into the solutions of Na gelatinate. The ordinates represent the height to which the liquid had risen in the manometer 30 minutes after commencement of the experiment. The abscissæ are again the logarithms of the concentration of the NaOH and the pH is that found after 30 minutes. The reader will notice that the critical points in this curve coincide with the critical points in Fig. 1. The curve rises steeply until $\text{pH} = 8.4$ when the maximum is reached, and falls equally steeply until a $\text{pH} = 12.2$ is reached. We have given the reason for this coincidence of the critical points in the curves of Figs. 1 and 2 in a preceding paper.⁵

The question arises, what causes the drop of the two curves when the pH exceeds 8.4? This drop seems to be the same as the drop in the initial rate of diffusion of water into a solution of Na_2SO_4 which occurs when the concentration exceeds $\text{m}/256$. When we separate metal gelatinates from distilled water by a collodion membrane, water diffuses into the gelatin solution as if its particles were positively charged; being attracted by the gelatin anion and repelled by the metal ion. Metal gelatinates behave therefore towards the electrification and rate of diffusion of water through collodion membranes like neutral or alkaline solutions of Na_2SO_4 or $\text{Na}_4\text{Fe}(\text{CN})_6$. The analogy can be carried further, since the addition of little salt depresses both the rate at which water will diffuse into the gelatin solution through the membrane as well as the permanent osmotic pressure of the solution.

Fig. 3 shows the rapid fall in the permanent osmotic pressure of a 1 per cent solution of Na gelatinate with a pH of about 8.4 to which various concentrations of a salt, KCl, K_2SO_4 , K_3 citrate, and CaCl_2 , are added. The amounts of salts contained in 100 cc. of gelatin solution were 0, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 cc. of $\text{m}/4$. These solutions were put into the collodion bags described, and the collodion bags were put into beakers containing the same salt in the same concentration which had been added to the gelatin solution. Fig. 3 gives the rise in the manometer after 30 minutes and Fig. 4 the osmotic pressure after 6 hours. The curves show the rapid drop

⁵ Loeb, J., *J. Gen. Physiol.*, 1919-20, ii, 87.

of the initial rate of diffusion, as well as of the permanent osmotic pressure with the increase in the concentration of the salt added. The drop is more rapid when Ca is added than when K is added, as it should be on account of the fact that the particles of water diffusing through the membrane are positively charged.

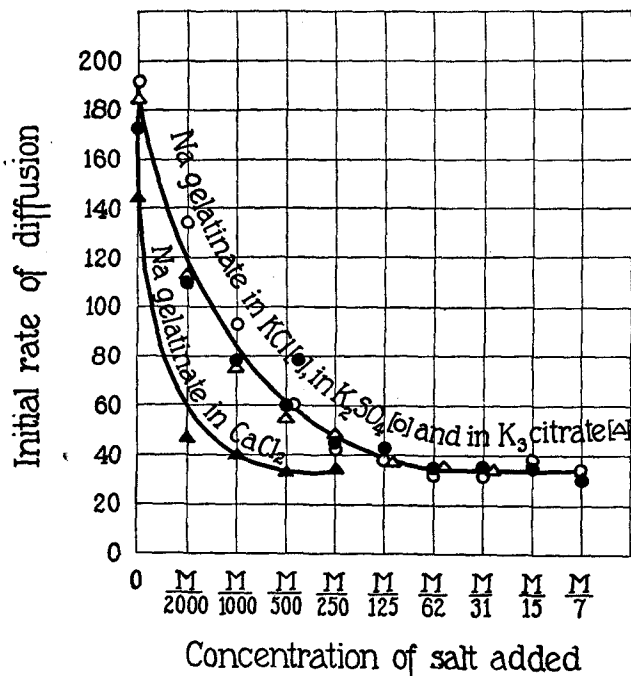


FIG. 3. Depressing effect of the addition of neutral salt to a 1 per cent solution of Na gelatin of pH about 8.4 upon the initial rate of diffusion of water into the solution during 30 minutes. Abscissæ are the concentration of salt added, ordinates the height of level of liquid in manometer after 30 minutes. The depressing effect of Ca is greater than that of K.

Figs. 5 and 6 show that the depressing effect of the addition of alkali is the same as that of the addition of neutral salt with the same cation, $Ca(OH)_2$ causing a greater depression than KOH. This contradicts the statement current in the literature of colloid chemistry that salts lower and that alkalies raise the osmotic pressure of gelatin solutions.

The influence of the concentration of electrolytes upon the electrification and rate of diffusion of water into gelatin solutions is similar

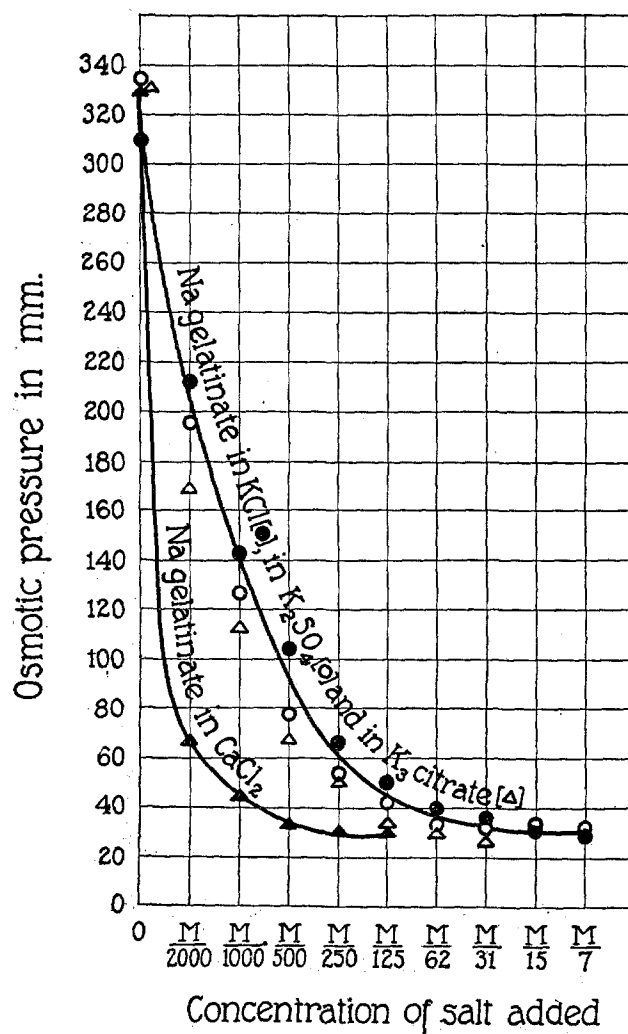


FIG. 4. Depressing effect of the addition of salts to 1 per cent Na gelatinate of pH = 8.4 upon osmotic pressure of solution. Ca depresses more than K.

to the influence of the concentration of electrolytes when we substitute a neutral salt like Na₂SO₄ or Na₄Fe(CN)₆ for the solution of metal

gelatinate. It may be well to point out this analogy by making the experimental methods in both cases as much alike as possible.

To solutions of $M/256$ Na_2SO_4 were added the same concentrations of salt as in the gelatin experiments; namely, 0, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 cc. of $M/4$ salt in 100 cc. of solution. These solutions were put into collodion bags and the latter were put into the solutions of the same salts as those in which the Na_2SO_4 was made

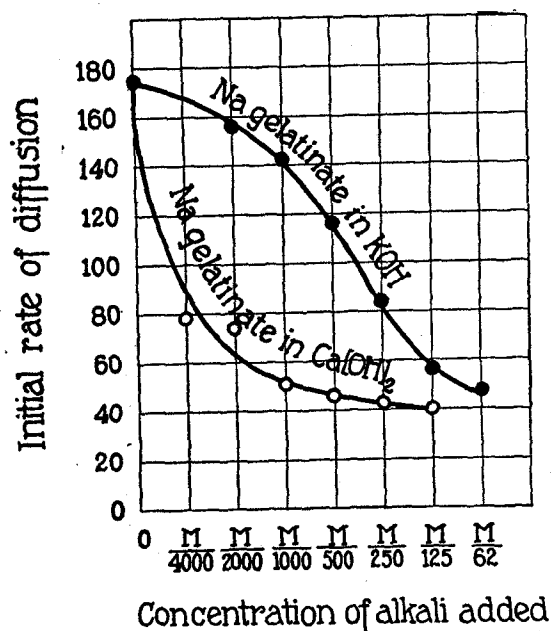


FIG. 5. Depressing effect of the addition of alkali to 1 per cent Na gelatinate of $\text{pH} = 8.4$ upon the initial rate of diffusion of water into the gelatin solution. $\text{Ca}(\text{OH})_2$ depresses more than KOH.

up. This means, that when 100 cc. of the solution in the collodion bag were a mixture of $M/256$ Na_2SO_4 in $M/2,000$ KCl, the outside solution was $M/2,000$ KCl (without Na_2SO_4), and so on. This was done to make the experiments in every point like the gelatin experiments, in which the outside solution also contained the same concentration of salt which was added to the gelatin solution. It was found that the addition of salts and of alkali depresses the initial rate of

diffusion of water into a $M/256$ solution of Na_2SO_4 in the same way as it depresses the initial rate of diffusion of water into a solution of Na gelatinate.

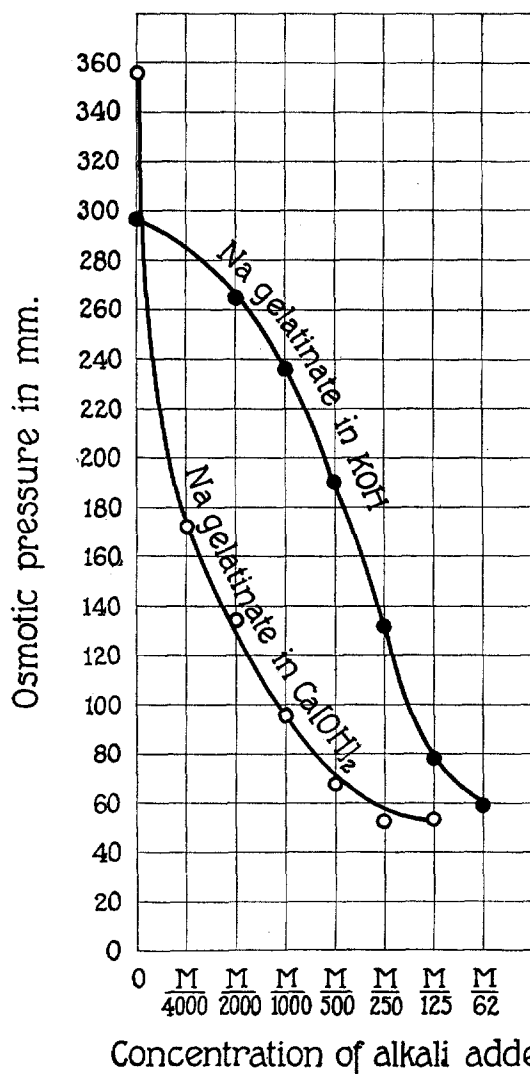


FIG. 6. Depressing effect of the addition of alkali to 1 per cent Na gelatinate of $\text{pH} = 8.4$ upon osmotic pressure of gelatin solution. $\text{Ca}(\text{OH})_2$ depresses more than KOH . The effect is similar to that of addition of neutral salt.

This is illustrated by the experiments represented in Fig. 7. The abscissæ are the concentration of the salt added to the $m/256$ Na_2SO_4 solutions. The electrolytes added were KOH, KCl, and MgCl_2 .

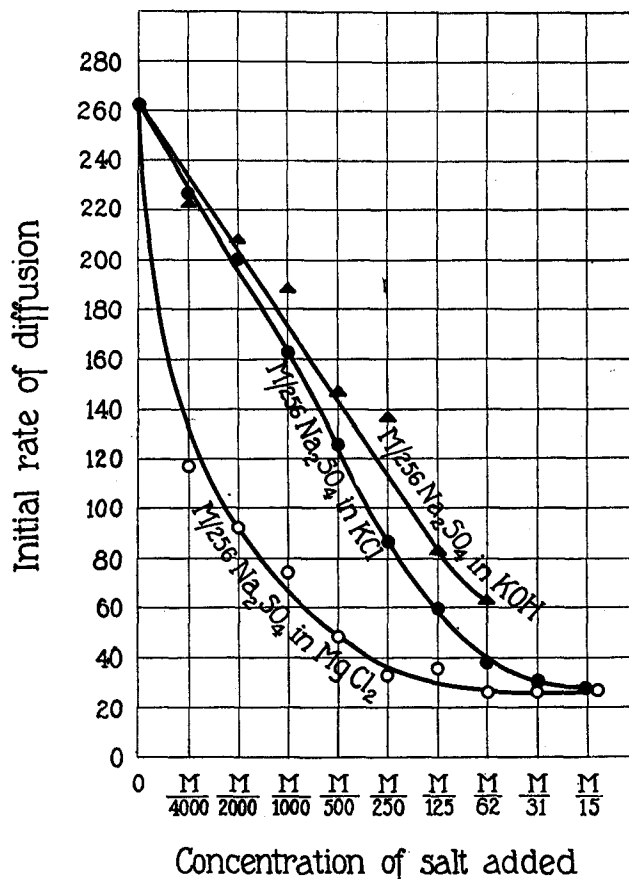


FIG. 7. $m/256$ Na_2SO_4 solutions separated from water by a collodion membrane, showing that the addition of salt or alkali to $m/256$ Na_2SO_4 causes a similar depression upon the initial rate of diffusion of water into the solution of $m/256$ Na_2SO_4 as the addition of salt to a solution of Na gelatin. Mg depresses more than K.

There was little difference in the effect of KOH and of KCl, while the depressing effect of MgCl_2 was considerably greater. *It should be stated that the collodion membranes used in these experiments had not been treated with gelatin.*

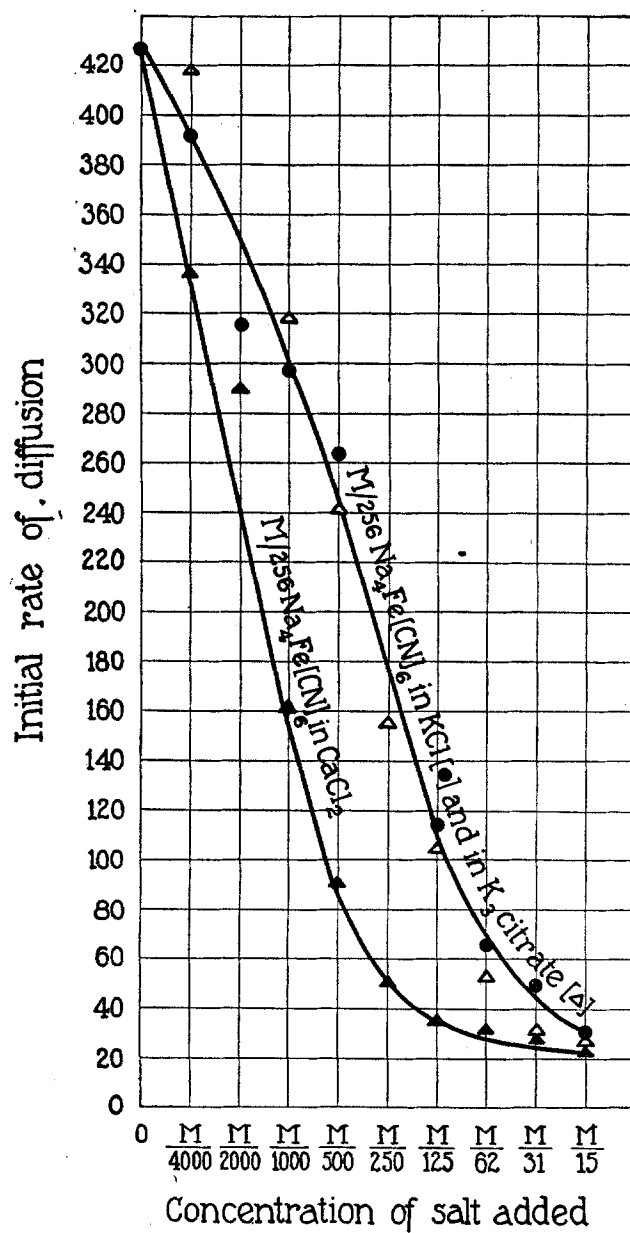


FIG. 8. $\frac{M}{256} \text{Na}_4\text{Fe(CN)}_6$ separated from water by a collodion membrane, showing the depressing effect of the addition of salt to the solution upon the initial rate of diffusion of water into the solution.

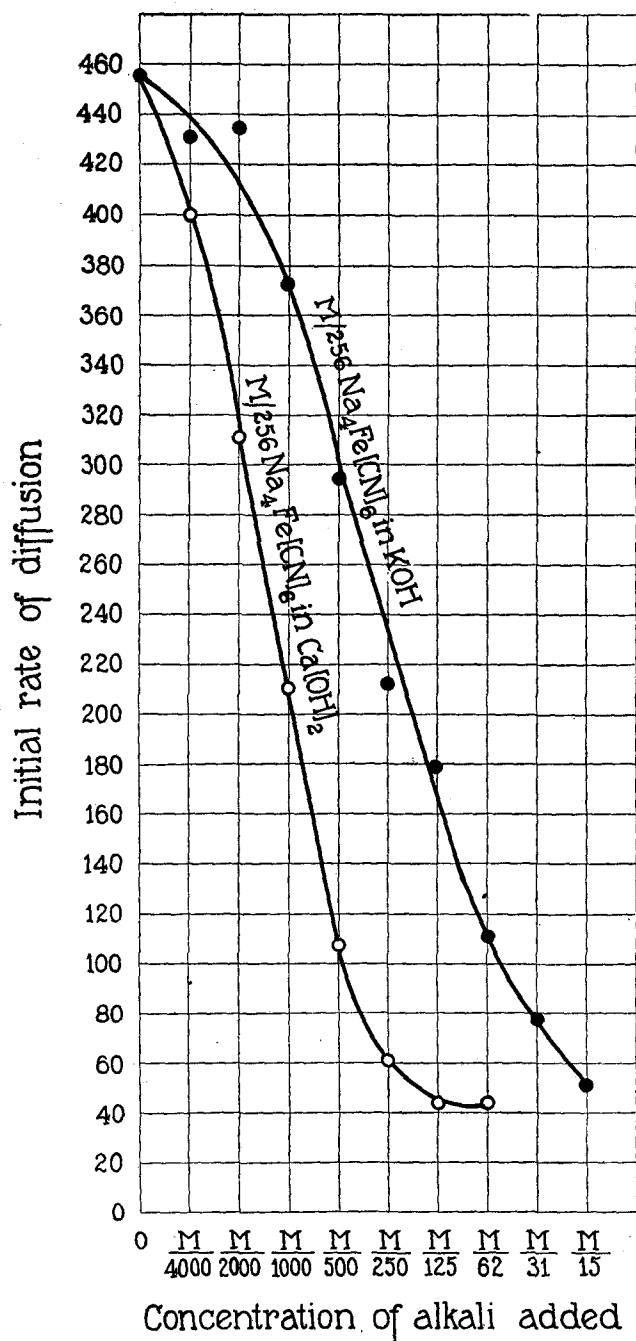


FIG. 9. Showing the same depressing effect of the addition of alkali to $m/256 \text{ Na}_4\text{Fe(CN)}_6$.

These experiments can be repeated with any other neutral or alkaline salt with univalent cation. Figs. 8 and 9 show the depressing effect of the addition of neutral salts (Fig. 8) or of alkalies (Fig. 9) to a solution of $m/256 \text{ Na}_4\text{Fe}(\text{CN})_6$. Again the influence of the valency of the cation and the identity of the effects of alkalies and neutral salts with the same cation are manifest.

In all these experiments in which the particles of water were positively charged the depressing effect of the addition of salt was greater when the cation of the salt was bivalent than when it was monovalent.

Such experiments have been made with a large number of salts, all yielding the same result; namely, that the depressing effect of the addition of increasing concentrations of alkalies and neutral salts upon the attraction of water by gelatin solutions is paralleled by the influence of the addition of increasing concentrations of salts upon the attraction of water by solutions of salts, in the presence of which water is positively charged. This raises the question whether or not the depressing influence of high concentrations of electrolytes upon the osmotic pressure of gelatin is necessarily connected with the colloidal character of gelatin or whether it is based upon a much more general property of matter; namely, the influence of electrolytes upon the electrification and the rate of diffusion of water through membranes. We only wish to point out this possibility without deciding definitely.

It may suffice to point out that the influence of the concentration and the valency of electrolytes on the osmotic pressure of gelatin solutions can be demonstrated equally well for the phenomenon of swelling and the curves representing this influence are similar to those given in this paper for the influence on the osmotic pressure.

III. Negatively Charged Particles of Water.

When we separate solutions of gelatin-acid salts from pure water by a collodion membrane, the particles of water diffusing through the membrane act as if they were negatively charged. That this is so can be demonstrated by experiments on electrical endosmose.

When acid, *e.g.* HCl, is added to isoelectric gelatin, part of the acid combines with gelatin to form gelatin chloride and part of the acid remains free. There is a chemical equilibrium between isoelectric gelatin, gelatin chloride, and free hydrochloric acid. As long as the pH of the gelatin chloride solution does not exceed 3.3 (*i.e.* as long as the pH varies between 4.7 and 3.3) the osmotic pressure of gelatin chloride increases with an increase in the concentration of the acid. As soon, however, as the pH reaches 3.3, the osmotic pressure of gelatin chloride diminishes again with increasing concentration of acid.

Fig. 10 may serve as an illustration. To each of a series of doses of 1 gm. of isoelectric gelatin were added 0, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 cc. of $M/4$ HCl, water was added, the gelatin melted by heating to about 40°C ., and enough water was added to make the volume of the solution 100 cc., so that each solution contained 1 per cent gelatin. This solution was put into collodion bags closed by a rubber stopper perforated with a glass tube serving as a manometer. The collodion bag was put into a beaker containing 350 cc. of the same concentration of acid in water as that originally added to the gelatin. Thus the gelatin solution to which 0.2 cc. of $M/4$ HCl was added per 100 cc. of solution was immersed in a HCl solution containing 0.2 cc. of $M/4$ HCl in 100 cc. of water. This outside solution was a little more concentrated than the concentration of the free acid inside, since part of the acid added to the gelatin entered into combination with the latter. This difference was equalized by the diffusion of some of the outside acid into the gelatin solution, thus slightly lowering the original pH.

The upper curve (Fig. 10) shows that the osmotic pressure of the solution (measured after 20 hours) rises with an increase of the hydrogen ion concentration until it reaches a maximum at pH about 3.4 or 3.3, and that with a further rise in the amount of free acid the osmotic pressure of the solution falls until at pH 1.75 the osmotic pressure of the gelatin solution is almost as low as it is near the isoelectric point.

The lower curve in Fig. 10 represents the velocity of diffusion of water into the gelatin solution measured by the height of the column of liquid in the manometer after 30 minutes. The maximum and the two minima of the curve coincide with those of the upper curve

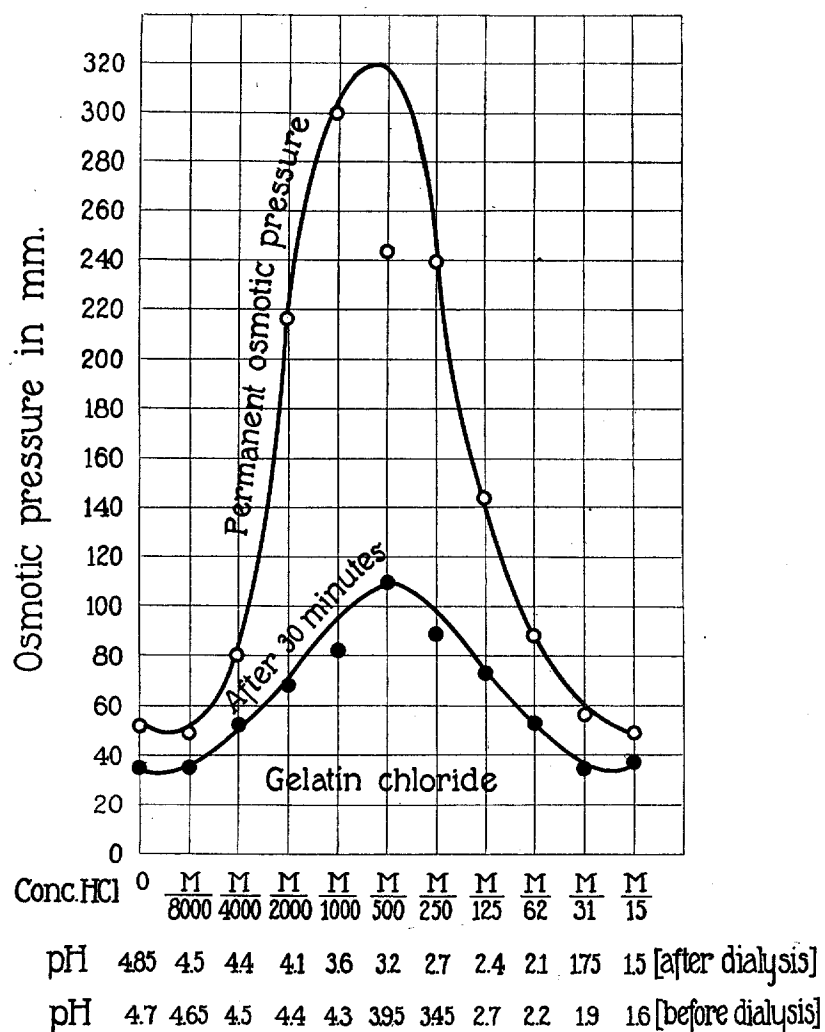


FIG. 10. 1 per cent isoelectric gelatin solutions dissolved in increasing concentrations of HCl. Abscissæ are the concentrations of HCl in which the gelatin is dissolved, with the pH at the end and at the beginning of experiment. Ordinates of upper curve represent the final osmotic pressure (after 20 hours); ordinates of lower curve represent the initial rate of diffusion of water into solution. Maximum in both cases at pH 3.3. Showing the depressing effect of the further addition of HCl when pH 3.3 is reached.

representing the permanent osmotic pressures of the various gelatin solutions.

When we select gelatin chloride with about the maximal osmotic pressure, *i.e.* gelatin chloride with a pH of 3.5, and add various

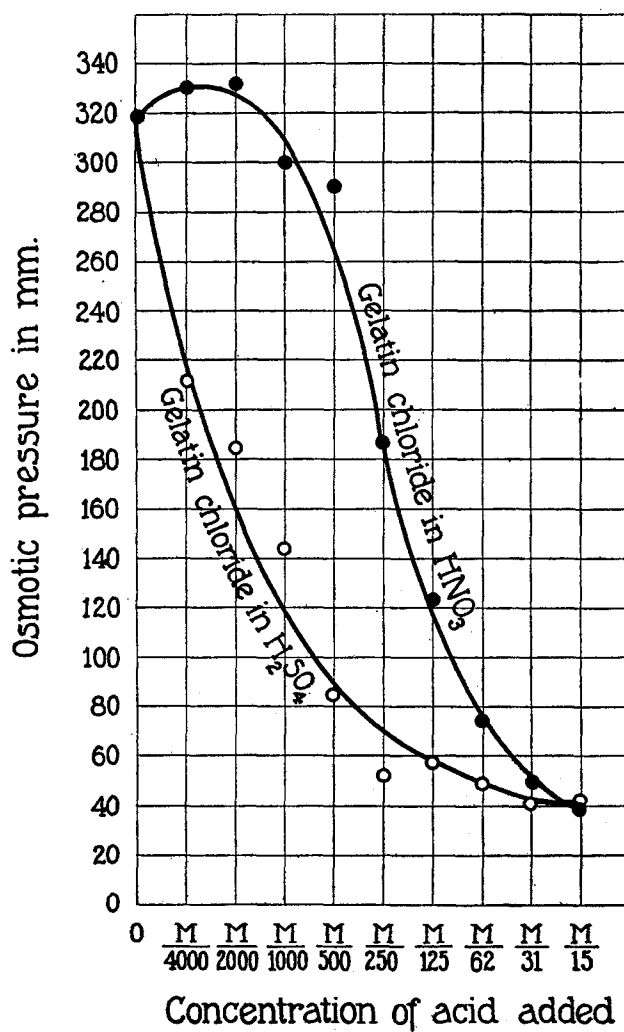


FIG. 11. Showing depressing effect of addition of HNO_3 and H_2SO_4 to 1 per cent gelatin chloride upon osmotic pressure. Depressing effect of SO_4 greater than that of HNO_3 .

concentrations of another acid to it, we notice a similar depression. Fig. 11 gives the effect of the addition of different quantities of HNO_3 and of H_2SO_4 to 1 gm. of gelatin of pH 3.3; 0, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 cc. of $\text{M}/4$ acid were contained in 100 cc. of gelatin solution of pH 3.5. The outside solution contained the same concentration of acid. The depressing effect of HNO_3 was like that of HCl , and the depressing effect of H_2SO_4 was greater. Fig. 12 shows that the depressing influence of the addition of acid is manifested in a similar way in the influence of the concentration of acid upon the initial diffusion of water into the gelatin solution.

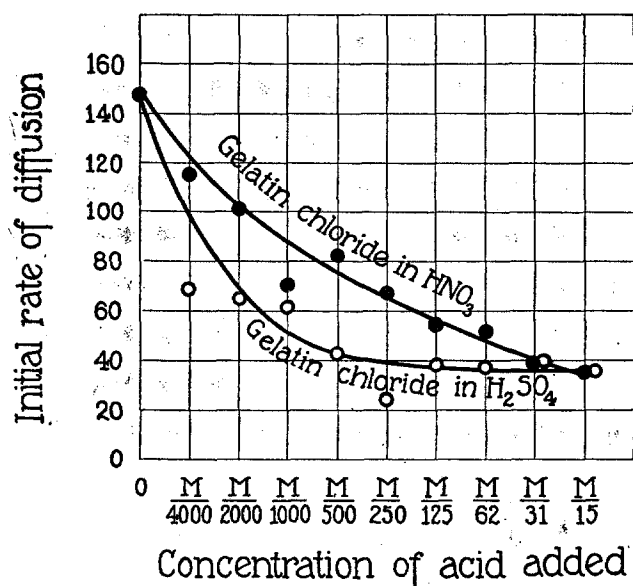
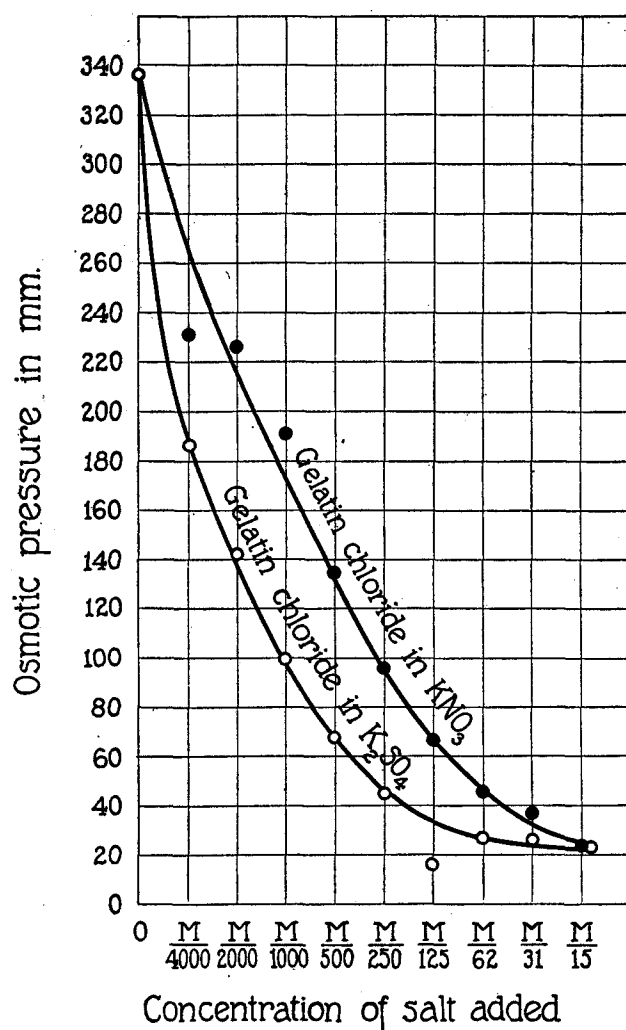


FIG. 12. The same effect of the addition of acid upon the initial rate of diffusion of water into the gelatin chloride solution.

If we add neutral salt, *e.g.* KNO_3 or K_2SO_4 , to a 1 per cent gelatin solution with a $\text{pH} = 3.5$, taking care that the pH of the solution is not altered by the addition of salt, the depressing effect is about the same as when we add acid. To doses of 1 gm. isoelectric gelatin of $\text{pH} 3.5$ were added 0, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 cc. of $\text{M}/4$ KNO_3 or K_2SO_4 , and enough water was added to make the volume 100 cc. The pH remained the same in all solutions.

The outside solutions had the same pH as the solution in the colloid bag and contained also the same concentration of potassium



FIGS. 13 and 14. Depressing effect of addition of salt to 1 per cent gelatin chloride pH = 3.3. SO₄ depresses more than NO₃.

salt as was added to the gelatin. The curves in Figs. 13 and 14 show that the depressing effect of an addition of KNO₃ is about the same as the addition of an equal amount of HNO₃, and that the addition

of K_2SO_4 has about the same depressing effect as the addition of H_2SO_4 .

When gelatin-acid salts, *e.g.* gelatin chloride, are separated from distilled water or a salt solution of the same pH by a collodion bag, water diffuses through the membrane in the form of negatively charged particles which are attracted by the gelatin cation and repelled by the anion. When we wish to replace the gelatin solution by a crystalloidal electrolyte in the presence of which water diffuses

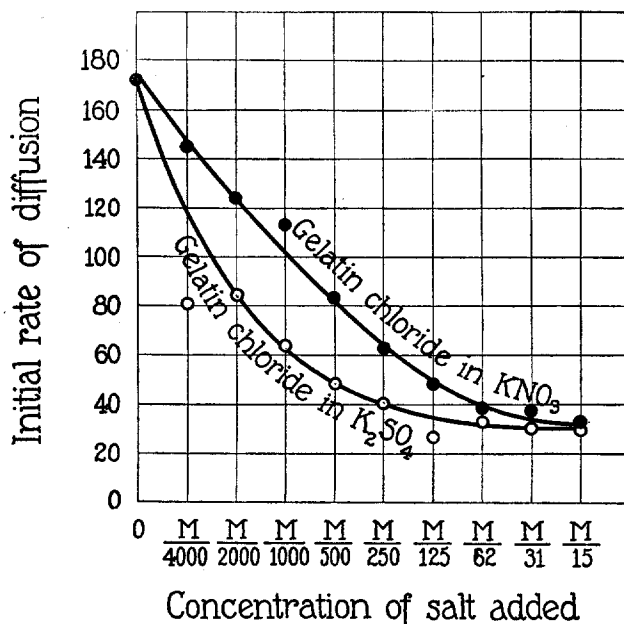


FIG. 14.

through the membrane in the form of negatively charged particles, we have to fulfill two conditions. First, we must use as electrolytes salts with trivalent (or tetravalent) cation, *e.g.* $CeCl_3$ or $AlCl_3$, or if we wish to use salts with monovalent or bivalent cation the salts must be rendered sufficiently acid; *e.g.*, pH = 4.0 or less. Second, the collodion membrane must previously receive a treatment with gelatin. The gelatin will be rinsed out, but some gelatin obviously adheres to the wall. As I shall show in another paper this treatment

of the collodion membrane with a protein is necessary since otherwise water will diffuse through the collodion membrane in the form of positively charged particles and then the case is no longer comparable with that of gelatin-acid salts. This gelatin treatment of the collodion membrane is not required when we wish to experiment with positively charged particles of water, since water assumes practically always a positive charge when in contact with a collodion membrane free from gelatin, even in comparatively high concentrations of acid.

If we use membranes which had contained a 1 per cent gelatin solution over night but were then freed from the gelatin by a number of washings with warm water, and if we substitute for the gelatin-acid salt a crystalloidal salt which causes water to be charged negatively in such gelatin-treated membranes, *e.g.* $m/512 \text{ Al}_2\text{Cl}_6$, we notice the same depressing effect of an increase of the concentration of electrolytes on the initial rate of diffusion of water into the solution as was described in the case of the solutions of gelatin-acid salts. When we separate a collodion bag filled with $m/512 \text{ Al}_2\text{Cl}_6$ (which causes water to be charged negatively) and put it into H_2O , the level of liquid in the manometer will rise to a height of about 300 mm. in 20 minutes. When we add varying quantities of a neutral salt to the $m/512$ solution of Al_2Cl_6 , and put the same concentration of salt into the outside beaker containing the water—in order to eliminate the direct effect of the salt added upon the rate of diffusion—we notice that the rate of diffusion of water will diminish the more rapidly the more salt we add. This is illustrated in Fig. 15. NaNO_3 and CaCl_2 have about the same depressing effect, showing that the depression is not due to the influence of the cation; while SO_4 and still more citrate depress much more powerfully than the chlorides, showing that the depression is due to the influence of the increasing concentration of the anion upon the negatively charged particles of water.

Similar experiments were made with solutions of CaCl_2 which were rendered sufficiently acid in order to cause the water to be charged negatively. If we select $m/128$ solutions of such acidulated CaCl_2 as a substitute for gelatin-acid solutions, we find that the addition of acid as well as of neutral salt causes a depression of the influence of

the acidulated CaCl_2 solution upon the initial rate of diffusion of water into the solution.

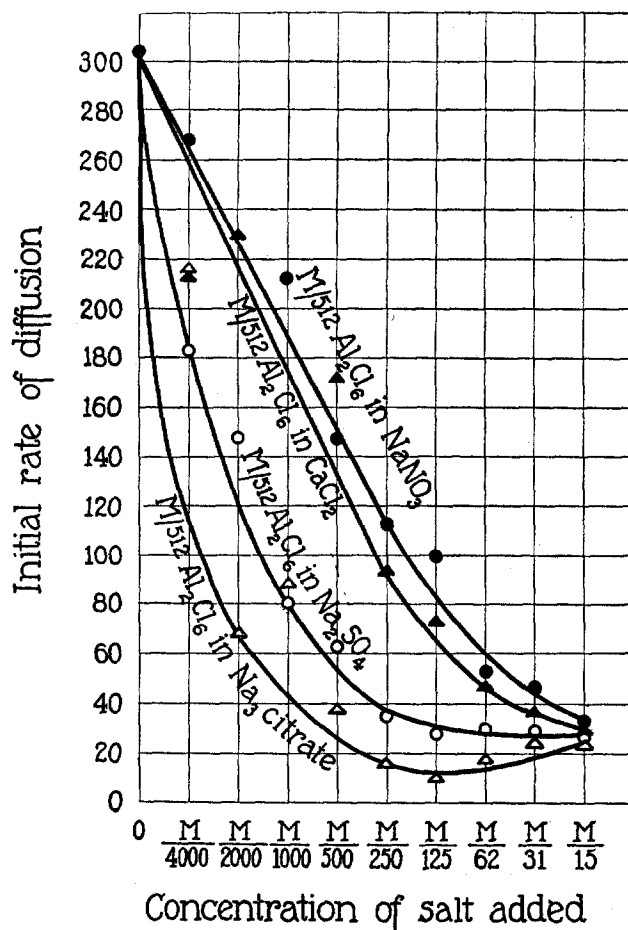


FIG. 15. $\text{M}/512 \text{ Al}_2\text{Cl}_6$ separated from water by collodion bag. Depressing effect of addition of salt to $\text{M}/512 \text{ Al}_2\text{Cl}_6$ upon the initial rate of diffusion of water into the bag. SO_4 depresses more than NO_3 or Cl .

In all the experiments mentioned the electrolyte was added not only to the inside but also to the outside solution. It is hardly necessary to state that the depressing effect is also well marked if the electrolyte is added only to the solution inside the collodion bag, while on the outside is distilled water.

These facts, then, show that the depressing effect of the addition of electrolyte upon the osmotic pressure of gelatin solutions (or colloidal solutions in general) is paralleled by the effect the addition of electrolyte has upon the initial rate of diffusion from water into solution through a collodion membrane, when we substitute a crystalloidal electrolyte for the gelatin salt.

SUMMARY.

1. When a 1 per cent solution of a metal gelatinate, *e.g.* Na gelatinate, of pH = 8.4 is separated from distilled water by a collodion membrane, water will diffuse into the solution with a certain rate which can be measured by the rise of the level of the liquid in a manometer. When to such a solution alkali or neutral salt is added the initial rate with which water will diffuse into the solution is diminished and the more so the more alkali or salt is added. This depressing effect of the addition of alkali and neutral salt is greater when the cation of the electrolyte added is bivalent than when it is monovalent. This seems to indicate that the depressing effect is due to the cation of the electrolyte added.

2. When a neutral $m/256$ solution of a salt with monovalent cation (*e.g.* Na_2SO_4 or $\text{K}_4\text{Fe}(\text{CN})_6$, etc.) is separated from distilled water by a collodion membrane, water will diffuse into the solution with a certain initial rate. When to such a solution alkali or neutral salt is added, the initial rate with which water will diffuse into the solution is diminished and the more so the more alkali or salt is added. The depressing effect of the addition of alkali or neutral salt is greater when the cation of the electrolyte added is bivalent than when it is monovalent. This seems to indicate that the depressing effect is due to the cation of the electrolyte added. The membranes used in these experiments were not treated with gelatin.

3. It can be shown that water diffuses through the collodion membrane in the form of positively charged particles under the conditions mentioned in (1) and (2). In the case of diffusion of water into a neutral solution of a salt with monovalent or bivalent cation the effect of the addition of electrolyte on the rate of diffusion can be explained on the basis of the influence of the ions on the electrifica-

tion and the rate of diffusion of electrified particles of water. Since the influence of the addition of electrolyte seems to be the same in the case of solutions of metal gelatinates, the question arises whether this influence of the addition of electrolyte cannot also be explained in the same way, and, if this be true, the further question can be raised whether this depressing effect necessarily depends upon the colloidal character of the gelatin solution, or whether we are not dealing in both cases with the same property of matter; namely, the influence of ions on the electrification and rate of diffusion of water through a membrane.

4. It can be shown that the curve representing the influence of the concentration of electrolyte on the initial rate of diffusion of water from solvent into the solution through the membrane is similar to the curve representing the permanent osmotic pressure of the gelatin solution. The question which has been raised in (3) should then apply also to the influence of the concentration of ions upon the osmotic pressure and perhaps other physical properties of gelatin which depend in a similar way upon the concentration of electrolyte added; *e.g.*, swelling.

5. When a 1 per cent solution of a gelatin-acid salt, *e.g.* gelatin chloride, of pH 3.4 is separated from distilled water by a collodion membrane, water will diffuse into the solution with a certain rate. When to such a solution acid or neutral salt is added—taking care in the latter case that the pH is not altered—the initial rate with which water will diffuse into the solution is diminished and the more so the more acid or salt is added. Water diffuses into a gelatin chloride solution through a collodion membrane in the form of negatively charged particles.

6. When we replace the gelatin-acid salt by a crystalloidal salt, which causes the water to diffuse through the collodion membrane in the form of negatively charged particles, *e.g.* $\text{M}/512 \text{ Al}_2\text{Cl}_6$, we find that the addition of acid or of neutral salt will diminish the initial rate with which water diffuses into the $\text{M}/512$ solution of Al_2Cl_6 , in a similar way as it does in the case of a solution of a gelatin-acid salt.