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ELECTRIFICATION OF WATER AND OSMOTIC PRESSURE.

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I. INTRODUCTION.

When a watery solution is separated from pure water by a strictly semipermeable membrane we call osmotic pressure the additional pressure upon the solution which is required to cause the migration of as many molecules of water from the side of the solution to the side of the pure solvent as migrate simultaneously from pure water to the solution. Van't Hoff's theory demands that this pressure should increase with the number of molecules in the solvent and that it should be equal to the gas pressure of the solute in the volume of the solution. The actual measurements of osmotic pressure of solutions of cane sugar made by Morse¹ and his collaborators as well as by the Earl of Berkeley² and his fellow workers show a rather close approximation to van't Hoff's theory.

When the solution is separated by a strictly semipermeable membrane, the difference in the rate of diffusion of water in opposite directions must be the greatest at the beginning of the experiment, and the difference must diminish steadily during the experiment as a consequence of the increase of hydrostatic pressure on the side of the solution. The value of the osmotic pressure of a solution as defined above must therefore vary with the difference in the rate of the diffusion of water molecules in the two opposite directions at the beginning of the experiment. When we double the concentration of the solute we also double the initial difference in the rate of diffusion of water molecules in opposite directions, and the additional pressure

¹ Morse, H. N., The osmotic pressure of aqueous solutions, *Carnegie Institution of Washington, Publication 198*, 1914.

² Earl of Berkeley, and Hartley, E. G. J., *Proc. Roy. Soc. London, Series A*, 1916, xcii, 477.

which is to be applied to the solution to make the rate of diffusion of water in both directions equal must also be doubled.

This influence of the concentration holds strictly only as long as the solute influences the rate of diffusion of water simply by the number of its molecules (*e.g.* in preventing a number of water molecules from impinging on the solution side of the membrane this number being equal to the number of molecules of solute impinging during the same time). Van't Hoff's law, however, must become inadequate if the molecules of the solute can modify the rate of the diffusion of water by other forces than mere gas pressure; *e.g.*, by electrical forces varying with the nature of the molecule. This is probably true for any solute but in a much smaller degree when the solute is a non-electrolyte than when it is an electrolyte; and in the case of electrolytes it holds in a smaller degree when the electrostatic field around the individual oppositely charged ions is nearly the same (*e.g.* in the case of NaCl) than when it is very different as in the case of $\text{Na}_4\text{Fe}(\text{CN})_6$ or LaCl_3 . This influence of the electrical field surrounding the ions upon the rate of diffusion is due to the electrification of the water molecules.

We use the term electrification of water merely as a short expression of the fact that electrostatic forces cause water to migrate in a definite sense through a membrane. Whether this electrification of water particles is due to a cluster formation of water molecules around an ion as a nucleus, or to some other cause, may for the present remain outside the discussion.

It is the purpose of this paper to show that the electrification of water molecules by ions in solution must in certain cases result in a deviation of the osmotic pressure of a solution from that to be expected on the basis of van't Hoff's theory; and that the sense and relative quantity of deviation can be predicted.

The writer has recently investigated the influence of various ions on the rate of diffusion of water through a collodion membrane separating pure water from a watery solution. Before being used for the experiment the collodion membranes were filled over night with a 1 per cent solution of gelatin and kept in water. The next day the gelatin solution was removed and the collodion flasks were rinsed a considerable number of times with warm water to remove

the remnants of the solution. The initial treatment of the membranes with gelatin apparently modified the collodion permanently since after weeks of daily use these membranes, treated once with gelatin, behaved differently from membranes not treated with gelatin. We shall return to this fact in another publication. An investigation of the influence of electrolytes on the rate of diffusion of water through such collodion membranes previously treated with gelatin has shown that all the phenomena observed can be explained on the basis of the following two rules.

"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 and diminishing inversely with a quantity which we will designate arbitrarily as the "radius" 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. Solutions of acids obey the same rule."³

These two rules allow us to predict in which sense the *nature* of the electrolyte in solution should modify the osmotic pressure of a solution calculated on the basis of van't Hoff's law. Suppose pure water is separated by a collodion membrane from a watery solution of an electrolyte. When the electrolyte is one of those mentioned in Rule 1, *i.e.* possessing a monovalent or bivalent cation, water is attracted by the solution and diffuses from the side of pure water into the solution, as if the particles of water were positively charged. They should therefore be attracted by the anion and repelled by the cation of the electrolyte and the more so the higher the valency of these ions. Hence water should diffuse more slowly into a solution of $M/192$ CaCl_2 than into a solution of $M/128$ NaCl , and more slowly into $M/128$ NaCl than into $M/192$ Na_2SO_4 , and considerably more slowly into $M/128$ NaCl than into $M/256$ Na_3PO_4 or $M/320$ $\text{Na}_4\text{Fe}(\text{CN})_6$. If, however, the water particles are negatively charged everything is reversed, the water diffusing more rapidly into $M/192$ CaCl_2 than

³ Loeb, J., *J. Gen. Physiol.*, 1918-19, i, 720.

into $M/128$ NaCl, and more rapidly into $M/128$ NaCl than into $M/192$ Na_2SO_4 .

From the theoretical connection between the relative rate of diffusion of water from pure water to the solution through a semipermeable membrane discussed before, it follows that the osmotic pressure of a solution should be modified by the *nature* of the ions it contains in the same sense as the initial rate of diffusion of water is modified. This idea can be put to a test by the choice of electrolytes for which the collodion membrane is strictly semipermeable; *e.g.*, gelatin salts. Gelatin solutions attain in bags of collodion an osmotic pressure which is permanent, provided the hydrogen ion concentration of the solution does not undergo any change during the experiment.

II. Analogies between Solutions of Gelatin and Aluminium Salts.

Gelatin is an amphoteric electrolyte which when the hydrogen ion concentration of its solution exceeds the critical value $2 \times 10^{-5} N$ forms only salts of the type of gelatin chloride, gelatin sulfate, etc., while when its hydrogen ion concentration falls below this value it can form only salts of the form of metal gelatinates; *e.g.*, Na gelatinate, Ca gelatinate, and so on. At the critical hydrogen ion concentration $2 \times 10^{-5} N$ —the isoelectric point for gelatin—it can exist only in the form of pure, *i.e.* non-ionogenic, gelatin.⁴ In this condition gelatin is practically insoluble, practically non-ionized, and is practically incapable of producing any osmotic pressure. Both types of gelatin salts, metal gelatinates as well as gelatin chloride, etc., are very soluble, are strongly ionized, and are capable of producing osmotic pressure. The writer's experiments, which are not yet all published, have shown that for each given hydrogen ion concentration there exists a definite equilibrium between non-ionogenic gelatin, gelatin salt, and free acid. If we have 1 per cent solutions of isoelectric gelatin the ionized or salt portion of the gelatin is practically zero. When we add increasing quantities of an acid, *e.g.* HCl, an increasing portion of the gelatin is transformed into gelatin chloride, while the portion of non-ionogenic gelatin is correspondingly dimin-

⁴Loeb, J., *J. Gen. Physiol.*, 1918-19, i, 39, 237, 363, 483, 559.

ished. The relative proportion of gelatin salt and non-ionogenic gelatin depends therefore upon the hydrogen ion concentration of the solution and increases in a characteristic way with this concentration. This hydrogen ion concentration of the solution is, of course, not identical with the concentration of the acid added to the solution, since part of this acid is in combination with the gelatin forming the gelatin salt. Since practically only that fraction of the 1 per cent gelatin solution which is transformed into a gelatin salt produces an osmotic pressure it is obvious that the osmotic pressure of a 1 per cent solution of gelatin must change in a definite way with the hydrogen ion concentration of the solution. If we use different acids we find that different quantities of acid are required to bring a 1 per cent gelatin solution to the same pH.

When the hydrogen ion concentration is below the critical value 2×10^{-5} (or to use Sørensen's logarithmic symbol, when pH is > 4.7) a part of the non-ionogenic gelatin is transformed into metal gelatinates and this part is the greater the more the hydrogen ion concentration falls below 2×10^{-5} . There is again a definite equilibrium between hydrogen ion concentration, gelatin salt, and non-ionogenic gelatin.

Hence if we wish to compare the osmotic behavior of different gelatin salts we must see that the solutions have not only the same concentration of gelatin but also the same hydrogen ion concentration.⁵

The influence of solutions of gelatin on the electrification of water is the same as that of any other electrolyte and follows the two rules mentioned above. In solutions of metal gelatinates with monovalent or bivalent cations, water migrates through a collodion membrane as if the molecules of water were positively charged; in solutions of gelatin acid salts water migrates as if its particles were negatively charged. The turning point for the sense of migration seems to be near (or identical with) the isoelectric point of gelatin; *i.e.*, pH = 4.7.

⁵ This latter point has been overlooked by the majority of colloid chemists who refuse to admit the chemical nature of the equilibrium between colloid and crystalloid, and who consequently ignore the rôle of the hydrogen ion concentration of the solution. Instead they compare the effect of the addition of equal quantities of different acids, overlooking the fact that they are thus comparing solutions in which the proportion of non-ionogenic gelatin and gelatin salt is different in the case of each acid.

It is perhaps not without interest that the behavior of gelatin is paralleled by the behavior of amphoteric electrolytes of a crystalloid character; *e.g.*, aluminium salts. Thus aluminium chloride exists only when the hydrogen ion concentration exceeds a certain critical value which seems to lie near that of the point of neutrality. When the solution becomes alkaline metal aluminates are formed. Na aluminate as well as AlCl_3 is very soluble. At the isoelectric point neither salt can exist and the insoluble $\text{Al}(\text{OH})_3$ is formed.⁶ The insoluble $\text{Al}(\text{OH})_3$ has no osmotic pressure (or does not attract water) while solutions of both AlCl_3 as well as NaAlO_2 attract water powerfully. In the presence of AlCl_3 water molecules are apparently negatively electrified and in the presence of NaAlO_2 water shows positive electrification. The turning point for the sense of migration of water molecules seems to lie near or at the isoelectric point of aluminium; namely, pH about 7.0. It would be very important if we could measure the permanent osmotic pressure of aluminium salts in collodion bags, but this is impossible since aluminium salts (with the exception of the insoluble $\text{Al}(\text{OH})_3$) diffuse through collodion membranes. It is, however, possible to determine the influence of different aluminium salts upon the rate of diffusion of water through a collodion membrane and it is found that this influence obeys the two rules.

We have mentioned this analogy between an amphoteric crystalloid, AlCl_3 and NaAlO_2 on the one hand, and an amphoteric colloid, gelatin chloride and sodium gelatinate, on the other to show that the fact of diffusibility or non-diffusibility through a collodion membrane does not force us to assume that the gelatin salts form no true solutions.

III. Osmotic Pressure of Different Metal Gelatinates.

Only the metal gelatinates with monovalent and bivalent cations need to be considered since the gelatin salts with trivalent cation seem to be insoluble. Different metal gelatinates were prepared

⁶ The sparingly soluble $\text{Al}(\text{OH})_3$ may be called a colloid since it does not diffuse through parchment paper. Sodium aluminate and AlCl_3 are crystalloids since they diffuse rapidly through such a membrane.

from gelatin rendered isoelectric (in the way described in former papers) by adding LiOH, NaOH, etc., to the gelatin. About 18 cc. of 0.01 *N* NaOH or Ca(OH)₂ must be contained in 100 cc. of a 1 per cent solution of isoelectric gelatin to obtain a metal gelatinate with a pH of 7.0; *i.e.*, with neutral reaction. We shall call a solution containing 1 gm. of isoelectric gelatin in 100 cc. a 1 per cent gelatin solution notwithstanding the fact that the gelatin is caused to combine with an acid or base.

We will first show that the gelatin salts with monovalent and bivalent cations influence the rate of diffusion of water in the same sense as is done by common crystalloid salts with monovalent and bivalent cations. Since in the presence of such metal gelatinate water diffuses through a collodion membrane as if its particles were positively charged (as ascertained by experiments with a constant current) we should expect that water should diffuse more rapidly into 1 per cent solution of metal gelatinate with monovalent cations, Li, Na, K, NH₄, than with bivalent cations, Mg, Ca, Sr, Ba, etc. This is indeed the case. We proceeded in the same way as in our previous experiments. Collodion bags,⁷ in the shape of Erlenmeyer flasks with about 50 cc. contents, and all with the same surface, were prepared in as uniform a way as possible. The flasks were closed with a perforated rubber stopper through the opening of which a glass tube (with bore of about 2 mm. diameter) serving as a manometer was pushed. These collodion flasks were filled with water distilled in a tin still and having a pH of about 5.2. The collodion bag was put into a beaker filled with a 1 per cent solution of a metal gelatinate and the pressure head of the water in the manometer tube was at the beginning of the experiment about 120 mm. of H₂O. The fall of the level of the water in the glass tube was measured in definite intervals. In Figs. 1 and 2 the levels are plotted as ordinates over the time elapsed since the beginning of the experiment. The experi-

⁷ The permeability of the collodion bags was tested before each experiment by filling them with *m*/4 cane sugar and measuring the rate at which water diffused into them. When the water rose in the glass tube with a bore of 2 mm. in diameter to a height of about 110 mm. in 20 minutes the membranes were considered serviceable.

ments were made at a constant temperature of 24°. The two figures show that water diffuses more rapidly into Li and K gelatinate than into Ba and Ca gelatinate. Na and NH₄ gelatinate behaved like Li and K gelatinate. The pH of the gelatin solutions was 8.2 in this experiment.

A second method of testing the influence of different metal gelatinates upon the rate of diffusion consisted in determining that concentration which a cane sugar solution must have in order to balance

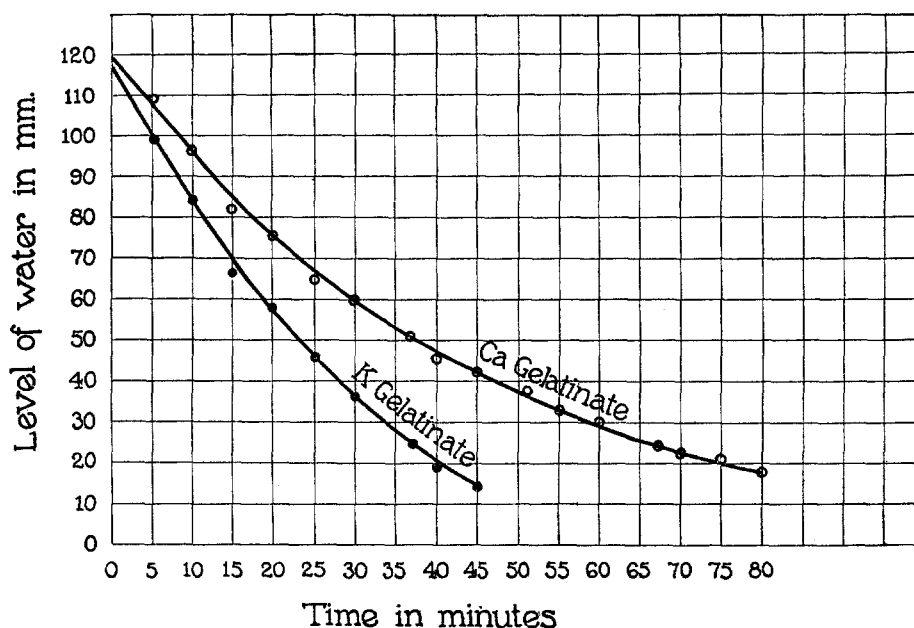


FIG. 1. Curves of fall of level of water when diffusing under an initial pressure head of about 120 mm. of H₂O against 1 per cent solutions of Ca and K gelatinate (pH = 8.2).

the attraction of a 1 per cent solution of metal gelatinate for water. The procedure was as follows. 350 cc. of a 1 per cent solution of a metal gelatinate, *e.g.* Na gelatinate, of pH 7.0 were put into each of a series of beakers and into each beaker was put one of the collodion flasks filled with a different concentration of cane sugar varying from

M/1 to M/64. It was useless to go below a concentration of M/64 of cane sugar since this was about the lowest concentration at which cane sugar influenced the rate of diffusion of water. The level of the cane sugar solution in the manometer tube was about 25 mm. at the beginning of the experiment. When the water diffused more rapidly from gelatin to cane sugar than in the opposite direction, the level in the manometer rose, when the water diffused more rapidly

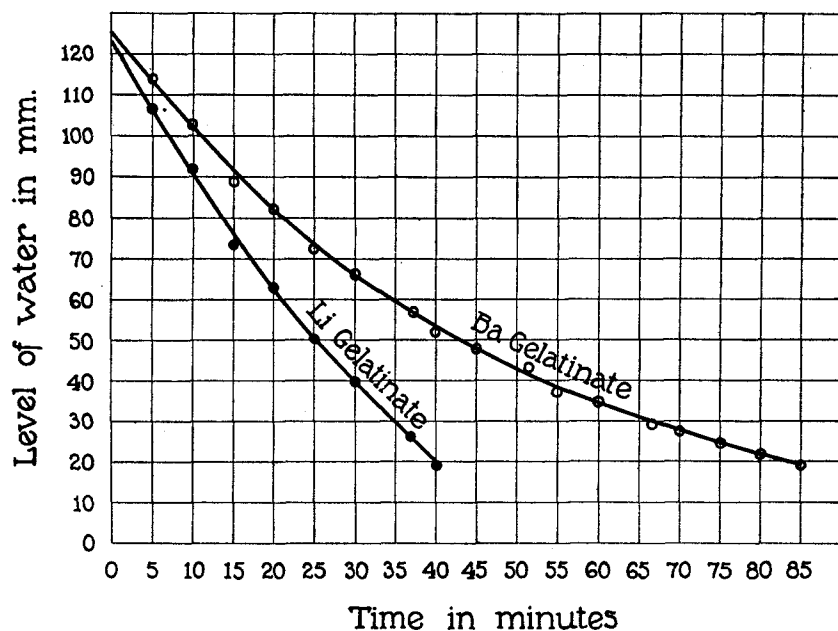


FIG. 2. Curves of fall of level of water when diffusing under an initial pressure head of about 120 mm. of H₂O against 1 per cent solution of Ba and Li gelatinate (pH = 8.2).

from cane sugar into gelatin than in the opposite direction the level in the manometer tube fell. Between the two was a concentration where the rate of diffusion in both directions was the same and this concentration of cane sugar we called the balancing concentration of cane sugar. Such experiments are only of value when of short duration on account of the fact that the sugar diffuses out into the gelatin

solution. In Table I the level of the water in the manometer tube after 30 minutes is given for the different 1 per cent gelatin solutions. The plus sign means a rise in the level of water in the cane sugar solution above the original level of 25 mm., the minus sign means a fall of the level of the sugar solution in the manometer tube.

We notice that the concentration which a cane sugar solution must have to balance osmotically 1 per cent solutions of gelatin salts with monovalent cations of a pH of about 7.0 lies between $M/8$ and $3M/32$, while for Ca gelatinate of the same concentration and pH the balancing concentration of cane sugar has a value between $M/32$ and $M/16$,

TABLE I.

Nature of gelatin salt used.	Change of level of liquid in the manometer tube of different concentrations of cane sugar solution when immersed in 1 per cent solutions of different metal gelatinates of pH 7.0, after 30 min.										
	Concentration of cane sugar solution.										
	$M/1$	$3M/4$	$M/2$	$3M/8$	$M/4$	$3M/16$	$M/8$	$3M/32$	$M/16$	$M/32$	$M/64$
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
Li gelatinate.....	358	294	195	109	+60	+24	-4	-11	-16	-21	-16
Na "	397	289	251	120	+97	+22	-3	-11	-20	-19	-17
K "	379	285	186	102	+62	+22	-3	-7	-15	-18	-22
NH ₄ "	390	323	222	127	+96	+35	+4	-4	-16	-19	-20
Ca "	397	300	241	172	+99	+69	+33	+16	+2	-2	-18
Ba "	376	310	225	145	+97	+77	+36	+29	+12	0	-15

and for Ba gelatinate a slightly lower value. We may, therefore, state that the balancing concentration of cane sugar is roughly over twice as great when the metal gelatinate has a monovalent cation as when it has a bivalent cation. Since water diffuses towards a cane sugar solution with a velocity which in the beginning of the experiment increases in proportion with the concentration of the sugar, we can say that the rate of diffusion of water into 1 per cent solutions of gelatin salts of the type Na gelatinate is between two and three times as great as the rate of diffusion of water into a solution of Ca or Ba gelatinate of the same concentration and pH.

The question now arises; Is there a similar difference between the

permanent osmotic pressure of 1 per cent solution of metal gelatinates when the cation is monovalent and bivalent? We have already published such measurements before we were aware of the fact that the electrification of water might play a rôle in osmotic pressure. In a paper published in this *Journal*⁸ we have shown that when 1 per cent solutions of gelatin salts with monovalent cation—Li, Na, K, and NH₄ gelatinates—are separated by collodion membranes from distilled water they may reach a maximal osmotic pressure of from 300 to 325 mm. of gelatin solution, while the 1 per cent gelatin solutions with bivalent cation—Ca and Ba gelatinates—never reach an osmotic pressure higher than 130 mm.; *i.e.*, a little more than one-third the value of the highest osmotic pressure of 1 per cent solutions of gelatin salts with monovalent cation.

It seemed desirable to get the time curve for the rise in pressure, since such a curve permits a comparison between the influence of the cation on both the velocity of the diffusion of water from water into solution as well as on the pressure when osmotic equilibrium is reached. The experiment was as follows. The gelatin was rendered isoelectric in a way described in a previous paper. To 1 gm. of isoelectric gelatin were added 20 cc. of 0.01 N of an alkali (LiOH, NaOH, etc.) and then enough distilled water to bring the solution of the gelatin (which was melted) to 100 cc. The pH of these solutions in the experiment under discussion turned out to be about 8.8. The solutions were put into the collodion flasks and the latter were put into beakers containing 350 cc. of H₂O, the pH of which was raised at the beginning to about 9.0 by adding 0.2 cc. of 0.01 N NaOH to 350 cc. of H₂O, in order to prevent a rapid lowering of the pH of the gelatin solution through the CO₂ absorbed from the air by the distilled water of the outside solution. The temperature was 24°C. The pH decreased slowly in the beaker and as a consequence also in the gelatin solution, and in 20 hours the pH had fallen to about 7.0 in the gelatin solutions with monovalent cations, while it had fallen less in the gelatin solutions with bivalent cations. When the pH fell, the osmotic pressure also began to diminish on account of the shifting of

⁸ Loeb, J., *J. Gen. Physiol.*, 1918-19, i, 483.

the equilibrium between non-ionogenic gelatin and the metal gelatinate formed.⁹

Fig. 3 gives the rise of level of liquid in the manometer during the first 12 hours for a 1 per cent NH_4 gelatinate and a 1 per cent Ba gelatinate solution. Equilibrium was reached after about 6 hours. The slight diminution of osmotic pressure due to the fall of pH on

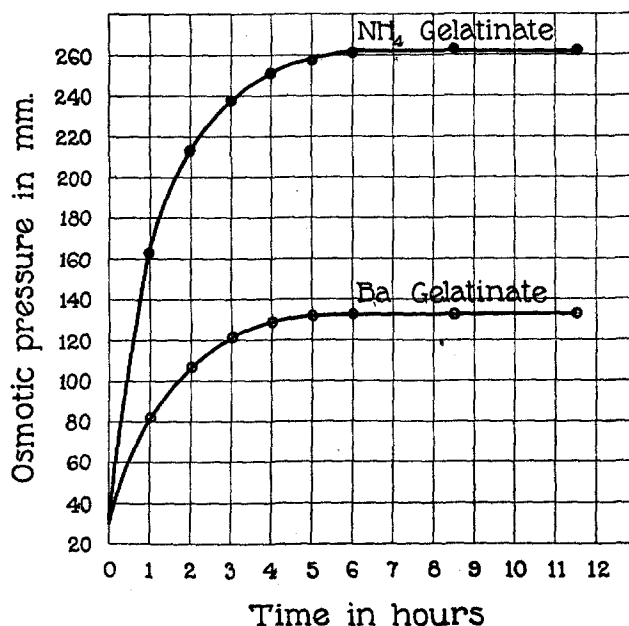


FIG. 3. Curves of rise of osmotic pressure of 1 per cent solutions of NH_4 and Ba gelatinate ($\text{pH} = 8.8$). Pressure in mm. of column of gelatin solution.

account of CO_2 action did not commence until later. The osmotic pressure of the 1 per cent solution of NH_4 gelatinate is in this experi-

⁹ In order to make sure that the osmotic pressure reached is permanent, the experiments with metal gelatinates should be made with the exclusion of CO_2 . Since, however, this source of error does not exist in the case of gelatin acid salts where the permanency of the final pressure reached can be made sure of, and since the results in that case are the same, as we shall presently see, and since the error was less for Ca and Ba gelatinate than for Na gelatinate, we need not dwell upon this point.

ment about twice as high as that of the 1 per cent solution of Ba gelatinate of about the same pH. During the first hour the relative rise of level in the solutions is also approximately as 1:2. Fig. 4 gives the curves for Na gelatinate and Ca gelatinate. The curve for Na gelatinate in Fig. 4 is identical with the curve for NH_4 gelatinate in Fig. 3 and the curve for Ca gelatinate in Fig. 4 is identical with the curve for Ba gelatinate in Fig. 3. The curves for Li and K gelatinate were identical with the curves for NH_4 and Na gelatinate in Figs. 3 and 4. Such results are always obtainable when both the

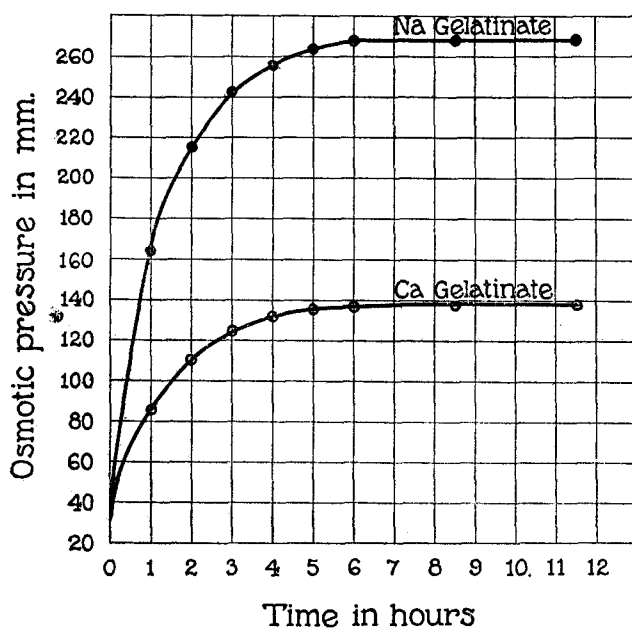


FIG. 4. Curves of osmotic pressure of 1 per cent solutions of Na and Ca gelatinate (pH = 8.8). Pressure in mm. of column of gelatin solution.

concentration and the pH of the solutions are identical. We therefore reach the conclusion that the different metal ions influence the osmotic pressure of gelatin solutions in the same sense as they influence the rate of migration of water into the solution. This supports the idea that the electrification of the water particles plays a rôle in the magnitude of the osmotic pressure as obtained by the use of semipermeable membranes.

IV. The Gelatin Cation.

When the hydrogen ion concentration of the gelatin solution is higher than 2×10^{-5} the gelatin can exist only in the form of gelatin chloride, sulfate, citrate, etc. Water is electrified negatively by such gelatin solutions and hence when pure water is separated by a collodion membrane from a 1 per cent solution of gelatin chloride or sulfate, etc., the water should diffuse more rapidly into the gelatin solution when the anion is monovalent than when it is bivalent. We have shown in a former paper¹⁰ that all dibasic and tribasic acids (thus far tried by us), with the exception of sulfuric acid, combine in molecular and not equivalent proportions with gelatin. Thus gelatin forms with phosphoric acid a monogelatin phosphate, with tartaric acid a monogelatin tartrate; only with sulfuric acid does it form a digelatin sulfate. In the case of gelatin oxalate it is possible that we have a mixture of both the monogelatin and the digelatin oxalate, the former prevailing.

This fact is of great importance for our problem. In the case of monogelatin phosphate the anion is not trivalent PO_4 , but essentially the monovalent anion H_2PO_4 . The same is true for monogelatin citrate and in the case of monogelatin oxalate the anion is not a bivalent oxalate ion but a monovalent oxalate ion with one hydrogen attached. Only in the case of gelatin sulfate is the anion divalent. We have shown in our preceding paper that in the case of NaH_2PO_4 the attraction of the salt for water is of the order of magnitude of a salt with monovalent anion like NaCl , showing that the presence of the two H ions weakens the influence of the trivalent PO_4 ions considerably. We therefore should expect that in the case of salts like monogelatin citrate, monogelatin phosphate, monogelatin oxalate, and monogelatin tartrate the influence of anion on the rate of the diffusion of water should be of the same order of magnitude as in the case of gelatin chloride or nitrate; while in the case of digelatin sulfate the SO_4 ion should act as a divalent anion producing a stronger repelling effect on the negatively charged water than is done by gelatin chloride. This turns out as expected (Fig. 5).

¹⁰ Loeb, J., *J. Gen. Physiol.*, 1918-19, i, 559.

When we fill the collodion bags as described with distilled water and put the bags into 1 per cent solutions of different gelatin acid salts of the same pH, giving the water inside the bag an initial pressure head of about 125 mm. of H_2O , the water will diffuse out more slowly against the gelatin sulfate than against any of the solutions of the other gelatin salts. This is demonstrated by Fig. 5. The abscissæ are the time in minutes, the ordinates the level of water in

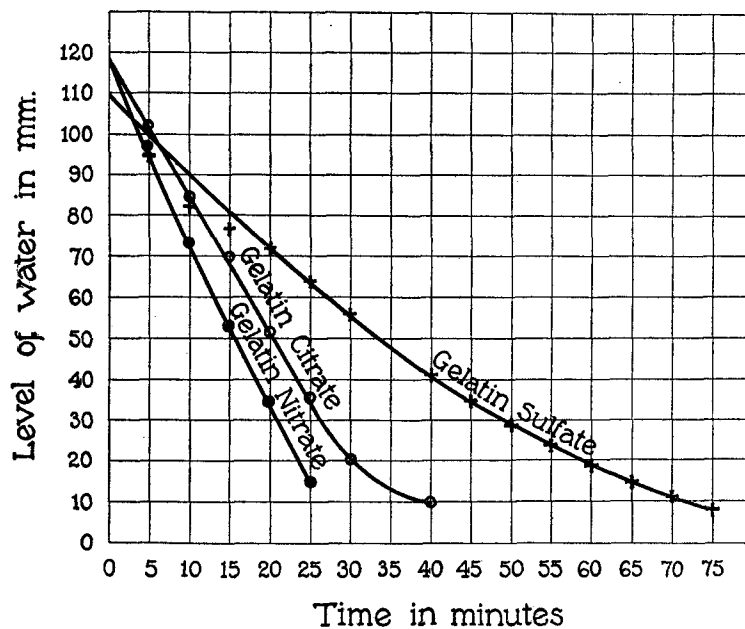


FIG. 5. Curves of fall of level of water when diffusing under an initial pressure head of about 120 mm. of H_2O against 1 per cent solutions of gelatin sulfate, gelatin citrate, and gelatin nitrate (pH = 3.5).

the manometer of the collodion flask. The initial pressure head was 125 mm. It required about 25 or 30 minutes for the pressure head of distilled water to fall from 120 mm. to about 20 mm. when it diffused into gelatin nitrate and monogelatin citrate, and 60 minutes when the distilled water diffused into gelatin sulfate.

The second method of testing the influence of the anion on the rate of diffusion of water consisted in determining the balancing

concentration of cane sugar for each of these salts in the way described. Table II gives the values observed after 30 minutes. The gelatin solutions had a pH of 3.5.

Using the same criterion as before we find that the balancing concentration of cane sugar lies for gelatin sulfate between $3M/32$ and $M/8$ and for all the others between $3M/16$ and $M/4$. In other words, the balancing concentration possesses for gelatin sulfate about one-half the value found for the other salts.

The writer has already published measurements of the osmotic pressure of 1 per cent solution of different gelatin salts. The osmotic

TABLE II.

Nature of gelatin salt used.	Change of level of liquid in the manometer tube of different concentrations of cane sugar solution when immersed in 1 per cent solutions of gelatin acid salts of pH 3.5, after 30 min.										
	Concentration of cane sugar solution.										
	$M/1$	$3M/4$	$M/2$	$3M/8$	$M/4$	$3M/16$	$M/8$	$3M/32$	$M/16$	$M/32$	$M/64$
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
Gelatin chloride.....	265	198	110	+15	+6	-18	-12	-22	-22	-19	-19
“ nitrate.....	262	200	98	+25	+8	-11	-10	-19	-18	-19	-16
Monogelatin oxalate.....	273	203	146	+75	+33	0	-4	-12	-17	-15	-20
“ tartrate.....	288	215	159	+47	+30	-4	-6	-20	-14	-16	-19
“ phosphate.....	290	196	125	+45	+18	-8	-14	-19	-14	-13	-16
“ citrate.....	335	244	115	+53	+30	0	-5	-9	-16	-24	-11
Digelatin sulfate.....	278	215	143	+74	+35	+10	+2	-8	-14	-14	-19

pressure varies for the same concentration of a gelatin salt with the pH of the solution and is a maximum at a pH of about 3.4. It was found that the maximum osmotic pressure of a 1 per cent solution of gelatin chloride, gelatin bromide, gelatin nitrate, gelatin acetate, monogelatin oxalate, monogelatin tartrate, monogelatin phosphate, and monogelatin citrate is about 320 mm. of the gelatin solution; while for a 1 per cent solution of gelatin sulfate the highest pressure obtainable is about 130 mm. This is in satisfactory agreement with the ratio we should expect on the basis of the influence of the anions on the rate of diffusion of the negatively electrified particles of water.

We considered it necessary to obtain also the curves for the increase

in the height of the level of water in the manometer with time until the equilibrium is reached. 1 per cent solutions of gelatin chloride, nitrate, oxalate, tartrate, citrate, and sulfate were prepared by making up the solution with the addition of as much of these acids to 1 gm. isoelectric gelatin as was required to produce a pH of 3.5. These 1 per cent gelatin solutions were put into collodion flasks containing the glass tube as described and each flask was put into a beaker with 350 cc. of distilled water the pH of which was made 3.0 by adding in each case the same acid as that of the gelatin. In Fig. 6 is plotted the rise and the final osmotic pressure of these solutions. The osmotic pressure reached in the case of gelatin sulfate was about 159 mm. while for the other salts it was almost twice as high (between 260 and 310 mm.). It is also noticeable from the curves that the relative velocity of rise during the 1st hour of the experiment also showed about the same ratio of almost 1:2 as the final equilibrium. The results thus confirm our expectation that on account of the electrification of the water molecules both the rate of diffusion as well as the final osmotic equilibrium are affected in the same sense.

If we wish to explain the differences between the observed osmotic pressure of solutions of calcium and sodium gelatinate or of gelatin chloride and gelatin sulfate, exclusively on the basis of van't Hoff's law, we are compelled to seek refuge in the assumption of the formation of aggregates of gelatin ions by which the number of these particles is diminished without diminution of the number of their charges.¹¹ This suggestion was first offered by Bayliss¹² when he found that the osmotic pressure of the colloid Congo red was considerably lower than was to be expected according to the molecular concentration and the conductivity of the solution. This assumption, however, which the writer had also tentatively accepted to explain the difference between the osmotic pressure of calcium and sodium gelatinate of the same concentration rests only on the facts which the assumption is supposed to explain, while the connection between rate of diffusion of water and osmotic pressure of a solution holds generally in all

¹¹ The writer has shown that the conductivity of 1 per cent Na gelatinate and of 1 per cent Ca gelatinate at the same pH is identical.

¹² Bayliss, W. M., *Proc. Roy. Soc. London, Series B*, 1911-12, lxxxiv, 229.

cases of dynamical equilibrium between two processes which occur simultaneously in opposite directions; *e.g.*, chemical equilibrium between reversible reactions.

Procter¹³ and his collaborators have developed a theory of swelling of colloids based on the assumption that swelling is a purely osmotic phenomenon. On the basis of this theory we may consider the

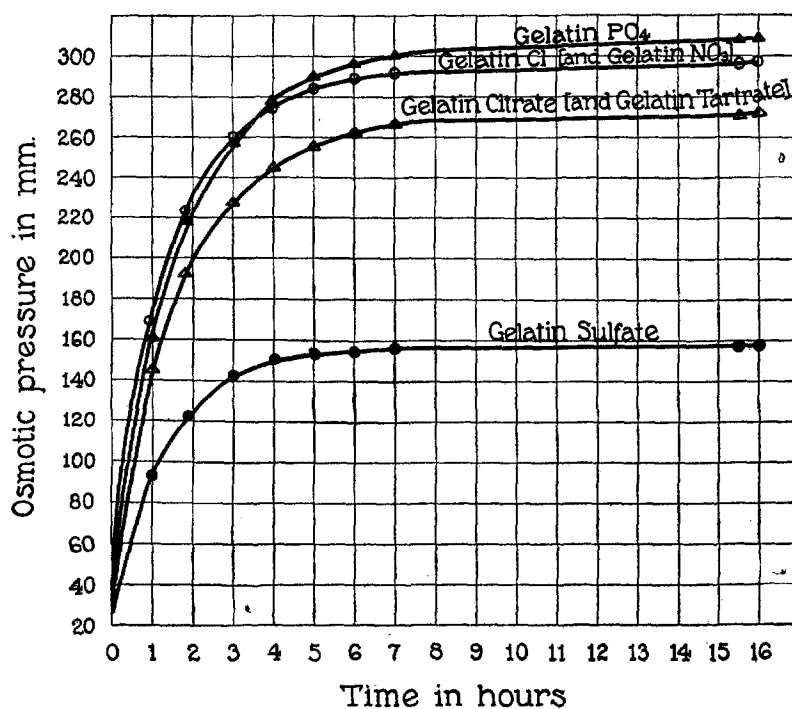


FIG. 6. Curves of osmotic pressure of 1 per cent solutions of gelatin phosphate, gelatin chloride (nitrate), gelatin citrate (tartrate), and gelatin sulfate (pH = 3.5). Pressure in mm. of column of gelatin solution.

surface and all the other solid parts of a block of gelatin to act as membranes permeable for water and crystalloids but not for gelatin. The osmotic conditions inside a solid block of gelatin which is

¹³ Procter, H. R., and Wilson, J. A., *J. Chem. Soc.*, 1916, cix, 307. Procter, H. R., and Burton, D., *J. Soc. Chem. Ind.*, 1916, xxxv, 404.

submersed in water are therefore comparable to those in our experiments except that we substitute a collodion membrane for the gelatin membrane.

The writer has shown that metal gelatinates of the same concentration of gelatin and of hydrogen ions swell much more when the metal in combination with the gelatin is monovalent (*e.g.* Li, Na, K, or NH_4) than when it is bivalent (*e.g.* Ca or Ba).⁸ When gelatin is a cation the swelling is greater when the anion in combination with gelatin is monovalent (*e.g.* Cl, NO_3 , or H_2PO_4) than when it is bivalent (*e.g.* SO_4).¹⁰ The curves representing the influence of different acids and alkalies on the swelling of gelatin are similar to the curves representing the influence of the same acids and alkalies on the osmotic pressure of gelatin solutions. This similarity becomes clear if we adopt Procter's osmotic theory of swelling, adding to it our theory of the rôle of the electrification of particles of water in the phenomena of osmosis. In these experiments the solution surrounding the block of gelatin salt must have a low concentration of electrolyte since the presence of an excess of electrolyte suppresses the swelling, as pointed out in previous publications.

SUMMARY.

1. Amphoteric electrolytes form salts with both acids and alkalies. It is shown for two amphoteric electrolytes, $\text{Al}(\text{OH})_3$ and gelatin, that in the presence of an acid salt water diffuses through a collodion membrane into a solution of these substances as if its particles were negatively charged, while water diffuses into solutions of these electrolytes, when they exist as monovalent or bivalent metal salts, as if the particles of water were positively charged. The turning point for the sign of the electrification of water seems to be near or to coincide with the isoelectric point of these two ampholytes which is a hydrogen ion concentration of about 2×10^{-5} N for gelatin and about 10^{-7} N for $\text{Al}(\text{OH})_3$.

2. In conformity with the rules given in a preceding paper the apparently positively charged water diffuses with less rapidity through a collodion membrane into a solution of Ca and Ba gelatinate than into a solution of Li, Na, K, or NH_4 gelatinate of the same concentra-

tion of gelatin and of hydrogen ions. Apparently negatively charged water diffuses also with less rapidity through a collodion membrane into a solution of gelatin sulfate than into a solution of gelatin chloride or nitrate of the same concentration of gelatin and of hydrogen ions.

3. If we define osmotic pressure as that additional pressure upon the solution required to cause as many molecules of water to diffuse from solution to the pure water as diffuse simultaneously in the opposite direction through the membrane, it follows that the osmotic pressure cannot depend only on the concentration of the solute but must depend also on the electrostatic effects of the ions present and that the influence of ions on the osmotic pressure must be the same as that on the initial velocity of diffusion. This assumption was put to a test in experiments with gelatin salts for which a collodion membrane is strictly semipermeable and the tests confirmed the expectation.