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The Influence of Wlectrolytes on the Electrification and the Rate of Diffusion of Water Through Collodion Membranes

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

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I. INTRODUCTION.

The direct measurements of the osmotic pressure of sugar solutions by Morse[1] and his fellow workers as well as by Lord Berkeley and Hartley[2] show so close an approximation to the values calculated on the basis of van't Hoff's theory that it is difficult to doubt the correctness of this theory. As Fick[3] pointed out as early as 1866, we can, on the assumption of the validity of the kinetic theory, treat a solution as a mixture of two gases, the solvent and the solute. When the solution is separated from the pure solvent by a semipermeable membrane more molecules of the solvent will impinge in the unit of time on the unit area of the membrane on the side of the pure solvent than on the side of the solution and hence the solvent will diffuse to the solution until the partial pressure of the solvent on the solution side becomes so great, that the number of molecules of solvent impinging on the unit of membrane on the solution side becomes equal to the number of molecules impinging on the unit of membrane on the side of the pure solvent.

There are, however, phenomena which suggest that in addition to the gas pressure other forces may enter into the problem of diffusion of water through a membrane. Such phenomena are the cases of

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[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.

[3] Fick, A., Die medizinische Physik., Braunschweig, 1866, 2nd edition, 36; *Z. physik. Chem.*, 1890, v, 526.

so called negative osmosis in which the solvent moves from a solution of higher to one of lower molecular concentration and which have been described and studied by Dutrochet, Thomas Graham, Girard, Flusin, Bartell, Bernstein, Freundlich,[4] and others.

Girard, Bernstein, and Bartell have reached the conclusion that potential differences caused by the electrolyte play a part in these phenomena of abnormal osmosis, and our results are in agreement with this view. We cannot agree, however, with the view of Girard and of Freundlich that the H and OH ions play the decisive part in the electrical phenomena which lead to abnormal osmosis. This view of a privileged position of the H and OH ions in these phenomena rests on the famous experiments of Perrin[5] on electric endosmose. It had been known that when a galvanic current is sent through a porous diaphragm bounded on both sides by water the latter migrates to one of the two electrodes. No reason could be assigned for the direction of the migration, until Perrin made the remarkable discovery that when a current is sent through a colloidal diaphragm (gelatin, silk, etc.) the direction of motion of the water can be altered at will; addition of acid causes the water to move to the anode, addition of alkali to the cathode. This phenomenon was explained by Perrin on the assumption that the H or OH ions of the water are adsorbed by the surface of the diaphragm transferring their charges to the latter. A double layer is formed, the molecules of water adjacent to the diaphragm assuming the opposite electrical charge. However, Perrin noticed and pointed out a serious difficulty in this assumption, namely that no other monovalent ions except the H and OH ions are capable of such an apparent transfer of their charges to the diaphragm.

The writer is under the impression that we must discriminate between two kinds of diaphragms, namely those which consist of material

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[4] Bernstein, J., Elektrobiologie, 1912. 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. Freundlich, H., *Kolloid-Z.*, 1916, xviii, 11. Girard, P., *Compt. rend. Acad.*, 1908, cxlvi, 927; 1909, cxlviii, 1047, 1186; 1910, cl, 1446; 1911, cliii, 401; La pression osmotique et le mêchanisme de l'osmose, Publications de la Société de Chimie-physique, Paris, 1912. Flusin, G., *Ann. chim. et phys.*, 1908, xiii, 480.

[5] Perrin, J., Notice sur les titres et travaux scientifiques de M. Jean Perrin, Paris, 1918.

which is an amphoteric electrolyte (*e.g.* gelatin or silk) and those which consist of non-amphoteric material. Both types are not necessarily influenced in the same way by acids and alkalies. Amphoteric electrolytes form salts with acids as well as with alkalies and this salt formation reverses the influence of the diaphragm on the sign of electric endosmose. HCl transforms gelatin into gelatin chloride, and NaOH transforms it into sodium gelatinate. In the case of gelatin chloride the gelatin ion is positive and in the case of sodium gelatinate it is negative. We assume that it is primarily the sign of the gelatin ion which determines the sense of the electrification of water and that the OH and H ions play only a secondary part. This would explain why Perrin could find no other monovalent ion except H or OH which was able to reverse the electrification of the gelatin diaphragm, since only acids and alkalies can transform a gelatin cation into a gelatin anion, or *vice versa*, while neutral salts cannot produce such an effect.[6]

We are, therefore, of the opinion that the experiments on electrical endosmose through diaphragms of colloidal substances like gelatin, pig's bladder, silk, or any other amphoteric electrolyte, do not warrant the assumption of a specific influence or predominant position of the H and OH ions in the electrification of a membrane bounded on both sides by water, except in so far as acids and alkalies are the only substances which can reverse the sense of ionization of an amphoteric electrolyte.

Girard, in accepting Perrin's idea of a direct electrification of the wall by H and OH ions, and of the specific action of these two ions, tried to ascribe the phenomena of abnormal osmosis he observed with membranes of pig's bladder to the acid or alkaline reaction of the solution. Thus neutral solutions, like those of NaCl and Na_2SO_4, should be without any other except a purely osmotic effect and he publishes data apparently supporting this conclusion.

The writer's results with collodion membranes do not agree with the conclusions of Girard, and we shall see that the solutions of neutral salts act as powerfully on the rate of diffusion of water through collodion membranes as the solutions of alkalies, acids, or acid salts. We

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[6] Loeb, J., *J. Gen. Physiol.*, 1918–19, i, 39, 237.

shall show that there is no difference between the osmotic effects of the hydroxides and of the chlorides or nitrates, *e.g.* M/128 NaCl and M/128 NaOH acting qualitatively and quantitatively practically alike in their influence on the rate of diffusion of water through collodion membranes.

The writer has carried out a series of experiments on the rate of diffusion of water through a collodion membrane separating the pure solvent from a solution. These experiments indicate that this process depends on two kinds of forces; namely, first, those of gas pressure which are clearly recognizable in the case of solutions of non-conductors like glucose or saccharose, and second, electrical forces which become predominant in the case of low concentrations of solutions of electrolytes. We shall deal in this paper with the electrical forces. They lead to the result that in the diffusion of water through a collodion membrane to a solution of an electrolyte the water molecules are either positively or negatively charged according to the nature of the electrolyte in the solution and that these charges are a factor in the rate of diffusion. The laws or rules controlling this factor can be expressed in the following way.

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, the high electrostatic effect of the hydrogen ion being probably due to its small "ionic radius."

We shall show first that the assumption of a difference in the sign of the charge of water molecules (according to the two rules just mentioned) explains all the phenomena that can be observed; and we shall show later that the correctness of the assumption concerning the sign of the charge of the molecules of water can be proved directly by experiments on electric endosmose.

II. Observations on the Rate of Filtration.

Collodion bags in the form of Erlenmeyer flasks of a content of about 50 cc. were prepared in as uniform a way as possible and were used after several days testing. Fresh bags were usually too permeable to serve for our purpose. The mouth of the collodion bag was closed with a perforated rubber stopper and the mouth of the bag was fitted tightly to the stopper with the aid of rubber bands. Through the hole in the stopper a glass tube with a bore of about 2 mm. in diameter was pushed into the bag. The collodion bag was filled with distilled water which reached into the glass tube to a height of about 110 mm. above the level of the distilled water of a beaker into which the bag was dipped. This pressure head of about 110 mm. of water inside the bag increases the number of particles impinging during the unit of time on the unit of area of the inside of the collodion bag and as a consequence more water diffuses in the unit of time from the bag into the beaker than diffuses in the opposite direction. Consequently water diffuses out and the pressure head on the water in the bag diminishes constantly. By measuring the level of the water in the glass tubes at definite intervals and plotting the values of the level as ordinates over the time as abscissæ we get a picture of the rate of diffusion of water out of the bag (Fig. 1).

When the outside solution is not distilled water but a solution of a non-conductor, *e.g.* cane sugar, the rate of diffusion of water is accelerated owing to the fact that the presence of sugar particles diminishes the number of water particles which in the unit of time impinge on the unit of area on the outside of the collodion membrane. Hence if the inside of the bag contains water and if the pressure head of the water inside the bag is at the beginning again about 110 mm. of water, the difference in the number of particles of water impinging on the inside remains the same as before while the number of water molecules impinging on the outside is diminished through the presence of the sugar particles. This diminution must be in proportion to the concentration of the sugar solution.

Fig. 1 gives the curves for the rate of fall in the pressure head of water in the glass tube when the beaker contains distilled water or different molecular concentrations of cane sugar. The curves show that the accelerating influence of a M/64 solution of cane sugar on the rate of outflow of water is still very slight under the conditions of these experiments but that the influence of the sugar solution increases with a further increase in its concentration. These curves may serve as standards of comparison for the curves obtained with electrolytes. The influence of solutions of lower concentration of cane sugar than M/64 is not noticeable by this method.

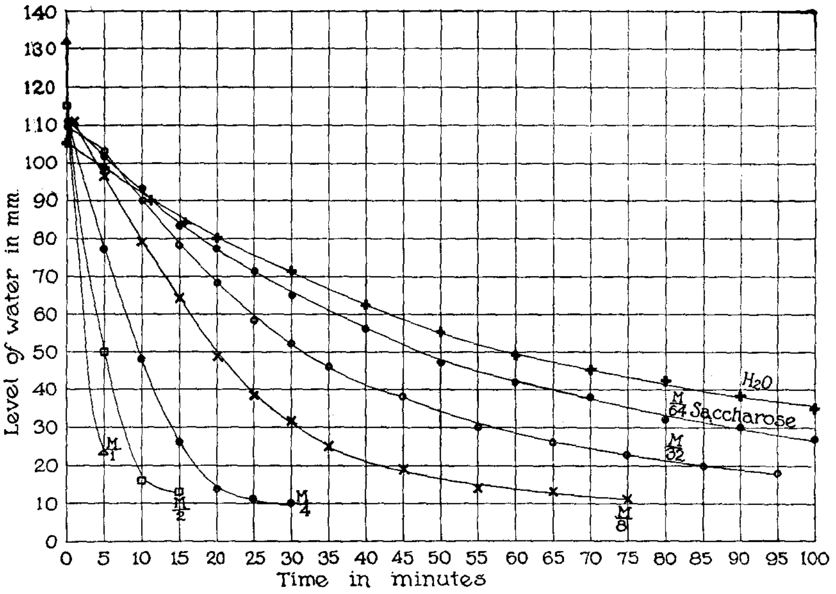


FIG. 1. Curves of fall of level of water diffusing against distilled water and cane sugar solutions of various concentrations.

When we replace the sugar solutions in the beaker with solutions of electrolytes of approximately the same osmotic pressure we notice considerable variations in the rate of outflow of water (or rather the fall of the pressure head in the glass tube) with the nature of the electrolyte, and these variations find their expression—as far as the writer's present observations go—in the two rules mentioned above.

Although in these experiments water not only diffuses from the collodion bag into the beaker but electrolyte diffuses also from the beaker into the collodion bag, we shall show in Chapter IV that the differences in our curves are not due to differences in the rate of the diffusion of the electrolytes but to differences in the rate of diffusion of water from the collodion bag into the beaker. Equilibrium will be reached when the solutions inside and outside of the beaker are identical, but our experiments deal only with the initial rate of diffusion of water leading to this condition of equilibrium and not with the condition of equilibrium itself.

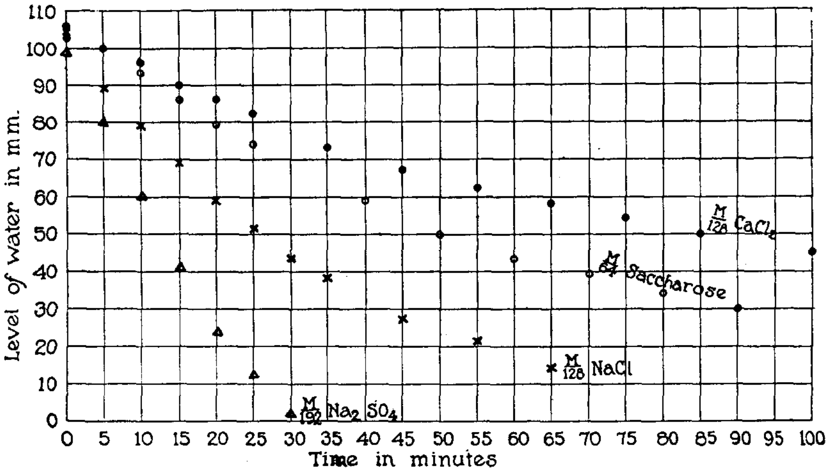


FIG. 2. Curves of fall of level of water when diffusing against solutions of M/64 cane sugar, M/128 $CaCl_2$, M/128 NaCl, and M/192 Na_2SO_4, showing the opposite effect of increase in valency of anion and cation on the rate of diffusion of water.

Fig. 2 illustrates the influence of solutions of three neutral salts, NaCl, $CaCl_2$, and Na_2SO_4, on the rate of diffusion of distilled water from the bag into the beaker containing the salt solution. The water in the bag had an initial pressure head of about 110 mm. of water. Water diffuses more rapidly against a M/128 solution of NaCl and still more rapidly against a M/192 Na_2SO_4 solution than against a M/64 solution of cane sugar. This difference cannot be ascribed to a difference in osmotic pressure of the three solutions since their osmotic pressure was approximately the same and we shall see later that the phenomenon in question is widely independent of differences in the osmotic pressure of electrolytes. On the other hand, water diffuses more slowly against a M/128 solution of $CaCl_2$ than against a M/64 sugar solution.

These facts may serve as an illustration of our statement that in the case of electrolytes with univalent and bivalent cation water behaves as if it were positively charged and attracted by the anion and repelled by the cation of the salt, and that both attraction and repulsion increase with the number of charges of an ion. In the case of NaCl the attractive action of Cl is for some reason greater than the repelling action of Na, hence the water diffuses more rapidly towards M/128 NaCl than against M/64 cane sugar. It diffuses still more rapidly against M/192 Na_2SO_4 than against M/128 NaCl because the SO_4 ion has two charges united in one ion. In the case of $CaCl_2$ the two positive charges united in the one Ca ion suffice to annihilate practically completely the attractive action of the two negative Cl ions. As a consequence M/128 solutions of $CaCl_2$ act almost like distilled water on the rate of diffusion of water. Solutions of $MgCl_2$, $SrCl_2$, $BaCl_2$, $CoCl_2$, and $MnCl_2$ act similarly to solutions of $CaCl_2$. Fig. 3 shows that the rate of diffusion of distilled water under a pressure head of about 110 mm. towards M/192 $MgCl_2$ is practically identical with the rate of diffusion of water under the same pressure head against distilled water and that a M/4 solution of $MgCl_2$ is required to accelerate the diffusion of water through the collodion membrane to approximately the same amount as is done by a M/128 solution of NaCl.

Fig. 4 shows that the attractive action of anions of salts with univalent cations (Na and K) increases with the valency of the anion. Very dilute solutions of oxalates, phosphates, citrates, and the tetravalent anion $Fe(CN)_6$ attract water so violently that it diffuses extremely rapidly through the membrane. Hence an increase in the number of charges of a cation lowers the attraction of the electrolyte for water, while an increase in the number of charges in an anion increases the attraction. All this agrees with the assumption that the molecules of water possess a positive charge.

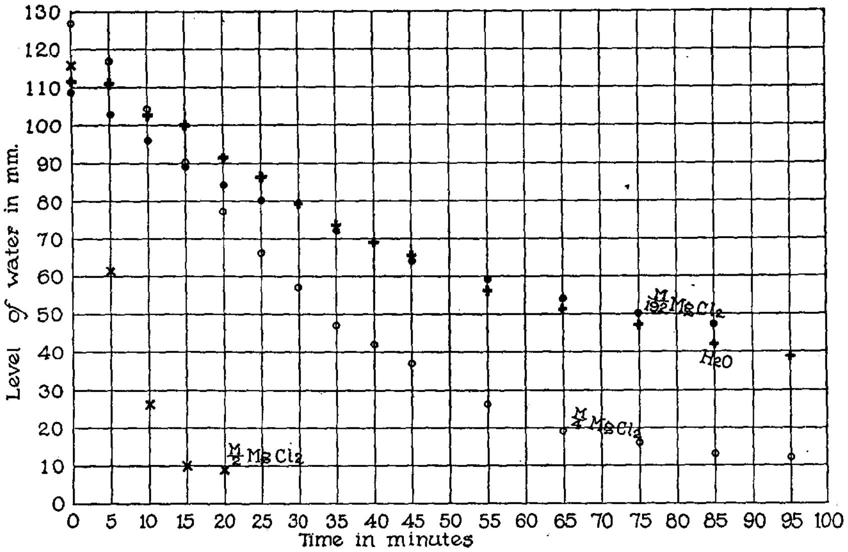


FIG. 3. Curves of fall of level of water when diffusing against solutions of $MgCl_2$ of different concentrations.

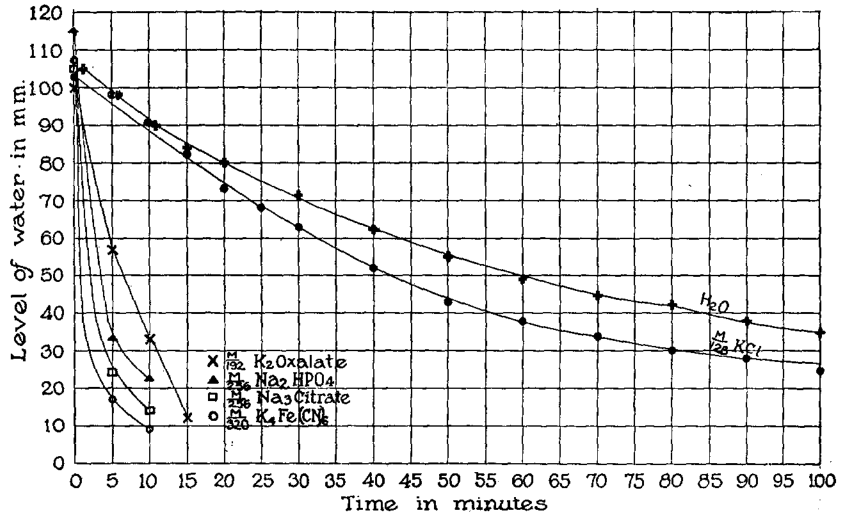


FIG. 4. Curves of fall of level of water when diffusing against solutions of different salts of sodium and potassium, showing the increase in rate with increase in valency of anion.

But this is only true as long as we deal with neutral salts with univalent and bivalent cation. When we deal with neutral salts with trivalent or tetravalent cations the rule is suddenly reversed. Chlorides or nitrates of salts with trivalent or tetravalent cations attract water considerably more than the salts with bivalent or even with monovalent cation. This discontinuity of effect with increase of the number of charges of the cation led the writer to the conclusion that water behaves towards salts with trivalent and tetravalent cations as if its molecules were negatively charged. On account of the high charge of the trivalent and tetravalent cations the attraction for water should be very powerful, as it indeed is. Of course, many of these solutions are strongly acid on account of the hydrolytic dissociation, but this is true only to a slight degree for Ce_2Cl_6 or La_2Cl_6. Yet a M/512 solution of these two salts attracts water almost as powerfully as does M/192 Na_2SO_4 of the same hydrogen ion concentration.

That water is attracted by salts with trivalent and tetravalent cations as if its molecules were negatively charged becomes obvious from a comparison of the effects of the chlorides and sulfates of these salts. Since the anion of a salt should repel negatively charged water —and the more so the greater the valency of the anion—the attractive power of a trivalent cation for water should be less in the case of a sulfate than of a chloride. Hence M/512 Cr_2Cl_6 should have a greater attraction for water than M/320 $Cr_2(SO_4)_3$. This is indeed the case. It was found that water in the bag diffused under a pressure head of about 110 mm. of water more rapidly towards M/512 Al_2Cl_6 or Cr_2Cl_6 than towards M/320 $Al_2(SO_4)_3$ or $Cr_2(SO_4)_3$. In a M/2048 solution of Al_2Cl_6 it took only 20 minutes for the water in the manometer to fall from a pressure head of 105 to that of 10 mm.; while a M/32 to M/16 solution of $Al_2(SO_4)_3$ was required to bring about the same rate of filtration.

It required about 40 minutes for the water to fall from the pressure head of 105 mm. to that of 20 mm. when the outside solution consisted of a M/2048 solution of Cr_2Cl_6. When $Cr_2(SO_4)_3$ was used in the beaker, even a M/16 solution of the sulfate did not act as strongly as a M/2048 solution of the chloride, although the latter was at least partly in suspension. The nitrates of these salts behaved like the chlorides. It is, therefore, obvious that in the case of trivalent cations

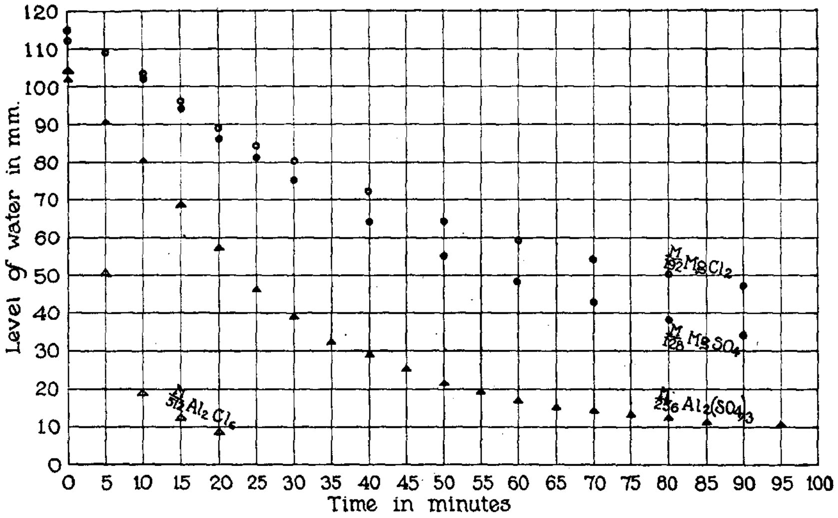
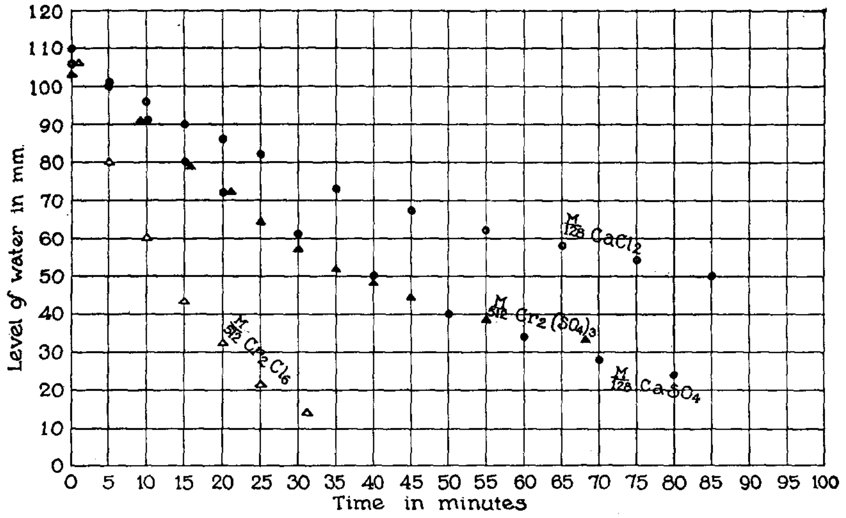


FIG. 5.



FIGS. 5 and 6. Curves showing that in comparison with Cl, SO_4 increases the rate of outflow in the case of bivalent cation and diminishes it in the case of trivalent anion.

the presence of SO_4 ions retards the rate of diffusion of water in comparison with Cl or NO_3 ions and this supports our conclusion that H_2O acts towards the solution of salts of trivalent cations as if its molecules were negatively charged.

The reverse is true when the cation of a salt is bivalent. When the outside solution was M/128 $MgSO_4$ or M/128 $CaSO_4$ it required about 75 minutes for the pressure head of H_2O inside the bag to fall from 120 mm. to about 30 mm. When the sulfates were replaced by the chlorides it required much higher concentrations to produce the same rate of diffusion. In the case of $MgCl_2$ and $CaCl_2$ it required a concentration of approximately M/8. This is to be expected when the molecules of water are positively charged since in this case the attractive power of SO_4 should be superior to that of the chlorides. These statements are supported by Figs. 5 and 6 illustrating the difference here discussed.

III. Modification of the Method.

We had measured in the preceding experiments the rate of diffusion of distilled water under an initial pressure head of about 110 mm. of water against solutions of various electrolytes. When we reverse the procedure, putting the solution of electrolyte inside of the bag and the distilled water outside, the latter will diffuse into the bag and at the same time the solution will commence to diffuse outside. Since, however, the concentration of the solute is at the beginning greater inside than outside, water will at first diffuse into the bag and the liquid in the manometer tube will rise. After 1 hour or more the maximum height in the glass tube is reached and the level of liquid in the glass tube commences to fall again. By comparing the height to which the liquid in the tubes rises in about 70 minutes we shall get not a quantitative measure, but a qualitative indication of the relative influence of the various types of ions on the rate of diffusion of water; for we shall show in the next chapter that the differences observed are the expression of differences in the rate of diffusion of water into the solution and not the expression of differences in the rate of diffusion of the solute into the distilled water. We used M/128 solutions, since we found that M/64 and even M/32 solutions of cane sugar or dextrose caused only a slight rise in the level of liquid. This excludes the possibility that the rise in liquid observed could be ascribed to the gas pressure of the solute.

A comparison of the relative rise of the liquid in the tube in Table I leads to a verification of the two rules. M/128 solutions of the chlorides of the alkaline metals cause a considerable rise, the rise increasing with an increase in the "radius" of the cation in the order Li, Na, K, Rb (Li having the smallest ionic radius). This agrees with the assumption that water behaves towards these solutions as if its molecules were positively charged and attracted by the anion and repelled by the cation, the repulsion being the greater the smaller the "ionic radius" of the cation.

The most striking fact is that the M/128 solutions of the neutral salts of bivalent metals cause no rise. In fact the water fell constantly in the glass tube containing the solutions, since the initial pressure head in the tube was always about 25 mm. of the column of solution. Hence solutions of M/128 $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, $CoCl_2$, and $MnCl_2$ possess actually no attraction for water (beyond that caused by the laws of gas pressure). This was to be expected since the positively charged water molecules are repelled more powerfully by the bivalent than by the univalent cations. This difference between the salts with univalent and bivalent cations exists not only in the case of chlorides but also of nitrates and of sulfates (Table I), and, as we shall see later, the hydroxides. The concentration of all solutions except two used in the table was M/128. The slight differences in the osmotic pressure of the various solutions do not influence the result, as we shall show in a later chapter.

Table II shows that the attractive action of sodium salts increases with the valency of the anion, as our rule demands. Table I also shows that in the case of neutral salts with univalent and bivalent cations the sulfates attract water more powerfully than the chlorides.

Table I shows, moreover, that the salts with trivalent and tetravalent cations have a very powerful attraction for water, which we should expect if water molecules behave like negatively charged bodies towards solutions of these salts.

TABLE I.

A. Solutions which attract water as if its molecules were positively charged.

Chlorides.	Level of solution after 70 min.	Nitrates.	Level of solution after 70 min.	Sulfates.	Level of solution after 70 min.
	mm.		*mm.*		*mm.*
LiCl	96	$LiNO_3$	64	Li_2SO_4	356
NaCl	106	$NaNO_3$	112	Na_2SO_4	410
KBr	131				
RbCl	154				
CsCl	143				
$MgCl_2$	12	$Mg(NO_3)_2$	10	$MgSO_4$	74
$CaCl_2$	18	$Ca(NO_3)_2$	22	$CaSO_4$	45
$SrCl_2$	13	$Sr(NO_3)_2$	19		
$BaCl_2$	16	$Ba(NO_3)_2$	15		
$CoCl_2$	15				

B. Solutions which attract water as if its molecules were negatively charged.

Ce_2Cl_6	260	$Ce_2(NO_3)_6$	531		
Al_2Cl_6	376				
Fe_2Cl_6	663				
M/320 $ThCl_4$	630	M/320 $Th(NO_3)_4$	535		

TABLE II.

Solutions which attract water as if its molecules were positively charged.

	Osmotic pressure in mm. of height of solution after 70 min.
	mm.
NaCl	106
$NaNO_3$	112
Na_2SO_4	410
Na_2 succinate	601
Na_2 tartrate	497
$NaHCO_3$	294
Na_2CO_3	520
Na_2HPO_4	484
Na_3 citrate	846
$K_4Fe(CN)_6$	930

IV. The Rate of Diffusion of Electrolytes through the Collodion Membranes.

We therefore see that no rise in the manometer occurs when a collodion bag filled with a M/128 solution of $MgCl_2$ or $CaCl_2$ is dipped into a beaker with distilled water, while a considerable rise occurs when the bag is filled with a M/128 solution of NaCl or Na_2 oxalate. The writer was at first inclined to assume that salts of the type of $MgCl_2$ diffused so rapidly through the collodion membrane that no osmotic effect had time to occur, while the diffusion of NaCl or Na_2 oxalate was supposed to be much slower. In order to test this idea the following experiments were made.

Various concentrations of LiCl, NaCl, KCl, $MgCl_2$, and $CaBr_2$ were put inside of the collodion bag and the latter was surrounded by a beaker containing 350 cc. of H_2O. Every half hour the amount of Cl or Br contained in 20 cc. of the liquid in the beaker was ascertained by titration after Volhard's method. (Table III.)

TABLE III.

Quantity of 0.1 N Cl (or Br) found in 20 cc. of the outside solution.

After 30 minutes.

	M/1	M/2	M/4	M/8	M/16	M/32	M/64
	cc.	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
LiCl		5.4	2.5	1.28	0.585	0.265	0.140
NaCl		5.5	2.7	1.15	0.635	0.25	0.125
KCl	12.8	5.4	3.2	1.45	0.59	0.32	0.20
$MgCl_2$		10.7	5.7	2.3	1.3	0.7	
$CaBr_2$	23.9	11.8	5.5	2.7	1.05	0.52	
After 60 minutes.							
LiCl		8.1	4.1	1.9	0.90	0.425	0.22
NaCl		7.55	4.2	1.75	0.94	0.38	0.195
KCl	15.0	7.6	4.7	2.2	0.95	0.53	0.28
$MgCl_2$	30.4	17.4	9.25	3.6	1.9	1.0	
$CaBr_2$	28.4	14.3	7.3	3.7	1.5	0.8	

These experiments show first that the rate of diffusion of these five salts occurs in proportion to their concentration and second that in the same time almost equal numbers of molecules of LiCl, NaCl, KCl, $MgCl_2$, and $CaBr_2$ diffuse from equally concentrated solutions into the distilled water. (The diffusion velocity of KCl may possibly be slightly larger than that of LiCl or NaCl.)

Hence the fact that the liquid does not rise when the collodion bag is filled with solutions of salts with a bivalent cation while it rises when it is filled with salts with univalent cation of the same osmotic pressure cannot be explained on the assumption that the salts like $MgCl_2$ or $CaCl_2$ diffuse out more rapidly into distilled water than do salts of the type NaCl. The only other possible explanation is that water diffuses more rapidly into a collodion bag filled with a solution of a salt like NaCl than into a bag filled with a salt like $CaCl_2$ of the same osmotic pressure.

TABLE IV.

Quantity of 0.1 N HCl and H_2SO_4 found in 20 cc. of the surrounding H_2O.

After 30 minutes.

	N/1	N/2	N/4	N/8	N/16	N/32	N/64	N/128	N/256	N/512	N/1024
	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
HCl.............	14.9	8.4	4.1	1.76	0.795	0.405	0.175	0.09	0.04	0.02	0.01
H_2SO_4...........	15.3	7.1	3.3	1.4	0.77	0.33	0.15	0.06	0.02	0.01	0.01
After 60 minutes.											
HCl.............	20.1	11.1	5.5	2.5	1.2	0.54	0.25	0.13	0.07	0.03	0.02
H_2SO_4...........	18.2	9.4	4.2	2.0	0.99	0.44	0.21	0.10	0.04	0.02	0.01

A similar experiment was carried out with the rate of diffusion of HCl and H_2SO_4. The results are given in Table IV.

The quantities of acid diffusing out are again for each acid approximately in proportion to the concentration of the acid, and almost equal numbers of molecules diffuse out from the same molecular concentrations of the two acids though the rate of diffusion seems to be a trifle less for H_2SO_4 than for HCl. (The reader will notice that the equal concentrations in Table IV mean equal normality and not equimolecular concentration as in Table III for the neutral salts.)

In order to compare two salts with univalent and bivalent anions, M/128 NaCl and M/128 Na_2 oxalate were chosen, since they vary considerably in their attraction for water. In the M/128 Na_2 oxalate solution the liquid in the manometer rose in 30 minutes to a height of 420 mm. and in the M/128 solution of NaCl to a height of 60 mm. It might again be argued that this difference was due not to a more rapid diffusion of water into the Na_2 oxalate solution but to a more rapid diffusion of the NaCl into the distilled water. Titration showed that after 30 minutes the NaCl solution inside the bag had been diminished by 3.6 cc. M/100 NaCl per 20 cc. solution, while the Na_2 oxalate solution had been diminished by 3.8 cc. M/100 Na_2 oxalate. Again the difference in the rate of diffusion of the two salts is small and cannot explain the large difference in the osmotic behavior of the two salts. We are therefore compelled to ascribe this difference to a difference in the influence of the ions on the rate of the diffusion of water into these solutions, as the rules expressed at the end of Chapter I demand.

While this is correct for solutions of electrolytes above a molecular concentration of M/128, it is possible that for solutions of electrolytes of a concentration below a certain limit the nature of the electrolyte may modify the result. We intend to deal with this possibility in a later paper.

V. Measurements of the Approximate Value of the Electric Force Influencing Diffusion.

These experiments show that aside from the gas pressure of water a second type of forces, namely electrical forces, influence the rate of diffusion of water from solvent to solution of electrolyte through a collodion membrane. If we denote these two types of forces by p and by e (for the osmotic pressure and the electrical attraction respectively), the question arises whether we cannot arrive at an approximate determination of the value of e. This can be done in a simple way. When we fill the collodion bag with a solution, *e.g.* of M/128 KCl, this solution has approximately the same osmotic pressure as a M/64 solution of cane sugar. If we surround the bag containing the M/128 solution of KCl with a solution of M/64 cane sugar approximately equal numbers of molecules of water should impinge on both sides of the collodion membrane and no change in the level of the two liquids should occur, if only the osmotic pressure p were active. As a matter of fact the water will diffuse from the M/64 sugar solution into the M/128 solution of KCl owing to the electrical force e due to the electrolyte. By using higher concentrations of cane sugar we arrive at finding one concentration which balances the combined osmotic pressure and electrical force of a M/128 solution of NaCl. The concentration of cane sugar which balances the combined osmotic and electric attraction of M/128 NaCl for water was found to be approximately M/8. Assuming that the osmotic attraction p of M/128 NaCl for water is equal to the osmotic pressure of a M/64 solution of cane sugar, the force e of the M/128 KCl solution must be equal to the osmotic pressure M/8 − M/64 = 7 M/64, or $\frac{7 \times 22.4}{64} = 2.4$ atmospheres. In this way we have determined the value of e for a number of electrolytes by selecting as the balancing concentration that concentration of a cane sugar solution in which the level of liquid does not rise when a beaker filled with the cane sugar solution is dipped into a solution of the electrolyte. This method has the advantage that the concentration of the balancing solution of cane sugar can be roughly estimated in about 5 minutes, although in fact most of our experiments were continued for half an hour or an hour. We used the same set of membranes for a large number of experiments and two sets were used in all; occasionally a membrane began to leak and we had to replace it by another membrane. Measurements of the height of the column of solution inside the tube were taken at first every 5 and later every 10 minutes. The sugar solutions were in the bag and 350 cc. of the M/128 NaCl solution were outside. The initial level of the liquid in the manometer tube was about 25 mm. above the level of the sugar solution. Table V gives the results of our measurements. The balancing solution is always that concentration of cane sugar in which the level of liquid in the manometer tube falls slightly in the first 10 minutes, while in the next higher concentration of cane sugar a marked rise occurs. It should, however, be stated that this sharp line of demarcation was not found to exist in all solutions. As a consequence the figures of this table serve mainly the purpose of confirming the two rules.

The first vertical column gives the molecular concentration of the solution of the electrolyte which was in every case selected so that on the assumption of complete electrolytic dissociation the solution was isosmotic to a M/64 solution of cane sugar. These solutions were, of course, not strictly isosmotic but we shall see in Chapter VIII that such small differences in osmotic pressure as occurred in these experiments cannot influence the result, on account of the fact that the maximal value of the electric force is generally reached in concentrations of the electrolytes lower than those used in this table and that a further rise in concentration of the electrolyte does not materially affect the value of *e*. For this reason we must not deduct $\frac{1}{64}$ from the concentration of the balancing solution in order to get the value of *e*, but a much smaller figure which will fall within the limits of the exactness of our methods. Therefore, the concentration of the balancing solution of cane sugar can be considered as a rough approximation of the value of *e*.

The second vertical column gives the nature of the electrolyte, the third the pH of the solution, and the fourth the approximate molecular concentration of the *balancing* sugar solution. The fifth column gives the value *e* in terms of atmospheres of the balancing solution. All the values of the balancing concentration are only rough approximations.

These data find their full explanation on the basis of the two rules expressed at the end of Chapter I.

First we notice that the electrolytes of the first group (*A*, in Table V) possessing univalent or bivalent cations attract water as if the molecules of the water were positively charged bodies. Thus the concentration of the balancing solution (and the value of *e*) increases with the increase in the number of charges of the anion and diminishes with an increase in the number of charges of the cation—the latter acting as if it repelled the positively charged water molecules.

We also notice that in Group *A* the repelling action of the cation increases inversely with its "atomic radius," the lithium salts having a lower balancing concentration and a lower value of *e* than the sodium or potassium salts with the same anion.

It is especially worth mentioning that the hydroxides act exactly like the chlorides or nitrates, thus disposing of the possibility that the hydroxyl ions occupy a privileged position in the electrification of water.

TABLE V.

Approximate Concentration of Balancing Solution of Cane Sugar for Various Solutions of Electrolytes.

A. Electrolytes towards which water acts as if it were positively charged.

Molecular concentration.	Nature of electrolyte.	pH	Approximate molecular concentration of balancing solution of cane sugar.	Approximate value of *e* in atmospheres.
M/128	$LiCl$	5.4	Slightly above M/32	Slightly above 0.7
M/128	$NaCl$	5.4	M/8	2.8
M/128	KCl	5.3	M/8	2.8
M/128	$RbCl$	5.5	M/4	5.6
M/192	$MgCl_2$	5.4	M/64	About 0
M/192	$Mg(NO_3)_2$	5.6	Below M/64	" 0
M/192	$CaCl_2$	5.5	" M/64	" 0
M/192	$SrCl_2$	5.4	" M/64	" 0
M/192	$BaCl_2$	5.4	M/64	" 0
M/192	$CoCl_2$	5.0	Below M/64	" 0
M/192	$MnCl_2$	5.3	" M/64	" 0
M/128	$LiOH$		M/16	1.4
M/128	$NaOH$		3M/32	2.1
M/128	KOH		M/4	5.6
M/192	$Ca(OH)_2$		Less than M/64	About 0
M/192	$Ba(OH)_2$		" " M/64	" 0
M/128	NH_4OH	10.2	M/32	0.7
M/192	Li_2SO_4	5.4	M/4	5.6
M/192	Na_2SO_4	5.4	Slightly above M/4	Slightly above 5.6
M/192	K_2SO_4	5.4	Less than M/2	" below 11.2
M/128	$MgSO_4$	5.4	M/32	0.7
M/128	$CaSO_4$	5.4	M/16	1.4
M/128	$MnSO_4$	5.4	Slightly less than M/32	Slightly below 0.7
M/128	$KCNS$	5.5	M/8	2.8
M/128	K acetate	6.3	Slightly above M/4	Slightly above 5.6
M/192	K_2 tartrate	6.4	" " M/2	" " 11.2
M/192	K_2 oxalate	5.9	M/2	11.2
M/256	K_2HPO_4	8.2	Slightly above M/2	Slightly above 11.2
M/256	K_3 citrate	7.8	" " 3M/4	" " 16.8
M/320	$K_4Fe(CN)_6$	6.2	" below 3M/4	" below 16.8

TABLE V—*Concluded.*

B. Electrolytes towards which water acts as if it were negatively charged.

Molecular concentration.	Nature of electrolyte.	pH	Approximate molecular concentration of balancing solution of cane sugar.	Approximate value of *e* in atmospheres.
M/192	$BeCl_2$	4.5	M/8	2.8
M/512	Ce_2Cl_6	5.1	M/4	5.6
M/512	La_2Cl_6	5.2	Slightly above 3M/8	Slightly above 8.4
M/512	Al_2Cl_6	3.8	" " M/2	" " 11.2
M/512	$Cr_2(NO_3)_6$		" less than M/2	" below 11.2
M/320	$ThCl_4$	3.2	" above 3M/8	" above 8.4
M/128	$BeSO_4$	3.5	M/64	0.3
M/320	$Al_2(SO_4)_3$	3.8	M/8	2.8
M/320	$Cr_2(SO_4)_3$		M/32	0.7
M/128	HCl		M/32	0.7
M/128	HNO_3	2.1	M/64	0.3
M/128	Acetic acid	3.3	Less than M/64	About 0
M/192	H_2SO_4		" " M/64	" 0
M/192	Oxalic acid	2.2	" " M/64	" 0
M/192	Tartaric acid	2.6	" " M/64	" 0
M/256	Citric acid	3.0	" " M/64	" 0
M/256	H_3PO_4	2.4	" " M/64	" 0

The electrolytes of Group *B*, including all salts with trivalent and tetravalent cations, influence the rate of diffusion of water as if the water molecules were negatively charged, being attracted by the cation and repelled by the anion. The correctness of this assumption lies in the fact that the attraction of this group for water is greater when the anion is univalent than when it is bivalent, the repelling action being greater in the latter case. Thus the value for *e* is in Group *B* greater when the anion is a chloride than when it is a sulfate, while in the preceding group of electrolytes towards which water was positively charged the sulfates acted more strongly than the chlorides or nitrates or hydroxides.

The acids belong to Group *B*, although the hydrogen ion carries only one charge. But the latter fact is compensated by the smallness of the "ionic radius" of hydrogen which is the smallest of all elements. This smallness of the "ionic radius" makes the electrostatic action of the positively charged nucleus comparatively strong. Li comes next among the univalent cations in smallness of "ionic radius" and this explains why the lithium salts attract water less actively than the sodium salts with the same anion.

Since the solutions of some of the salts with trivalent and tetravalent cations are acid (due to hydrolysis), it might be argued that it is only the presence of free acid which makes the salts of Group *B* behave differently from those of Group *A*. This assumption is disproved by the fact that La_2Cl_6 and Ce_2Cl_6 which belong to Group *B* are neutral salts; *i.e.*, the hydrogen ion concentration of their solution has a pH of the order of that of the solution of neutral salts of Group *A*.

Since, however, the idea of a specific rôle of hydrogen and hydroxyl ions is so general in the colloid literature it seemed of importance to make sure that the differences we have established between the salts of Groups *A* and *B* remain valid when the salts have an identical hydrogen ion concentration. The pH of M/512 La_2Cl_6 was found to be 5.2, that of M/512 Ce_2Cl_6 5.1 (due to the presence of CO_2).[7] We prepared solutions of M/128 KCl, M/192 $MgCl_2$, M/192 K_2SO_4, and M/128 $MgSO_4$ of the same or even a slightly lower pH, namely 5.0 to 5.1. Table VI gives the balancing concentration of cane sugar for the six solutions.

TABLE VI.

Nature of solution.	pH	Concentration of balancing cane sugar solution.
M/512 La_2Cl_6	5.2	Slightly above 3M/8
M/512 Ce_2Cl_6	5.15	" below 3M/8
M/192 $MgCl_2$	5.1	Less than M/64
M/128 $MgSO_4$	5.05	M/64
M/128 KCl	5.0	M/16
M/192 K_2SO_4	5.0	3M/16

We notice, first, that for the same pH of about 5.1 the salts with bivalent cation show the characteristic low value for *e*, their attraction for water being less than that of the salts of K as well as of La or Ce.

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[7] The pH of the distilled water used varied between 5.1 and 5.3 and this accounts for the pH found in our solutions of neutral salts.

We notice, second, that the attraction for water is greater in the case of $MgSO_4$ than in the case of $MgCl_2$, and greater in the case of K_2SO_4 than in the case of KCl, showing that up to pH = 5.0 or 5.1 these salts attract positively charged water molecules. Hence the action of the salts of Group *B* is due to the trivalent or tetravalent cation and the H ion owes its effect not to any specific "adsorption" but to the smallness of its "atomic radius," which gives it a high electrostatic effect.

On the other hand, a high degree of acidity of a solution of a salt with a bivalent cation induces a negative charge in the water molecule. This is true for beryllium salts. In this case the action of H ions is simply added to that of the Be ions (which have a small "ionic radius"), and the combined effect of both ions exceeds the effect of the Cl ions. We also notice that $BeSO_4$ acts less powerfully than $BeCl_2$, as it should if in the presence of these salts water is negatively charged. The Be salts therefore belong in Group *B*. We shall come back to the effects of a mixture of two electrolytes in another paper.

TABLE VII.

Nature of solution.	pH	Concentration of balancing cane sugar solution.
M/192 Na_2CO_3	9.2	Slightly above M/2
M/192 $NaHCO_3$	11.0	" " 3M/8
M/256 Na_3PO_4	12.0	" " M/2
M/256 Na_2HPO_4	8.6	" " M/2
M/256 NaH_2PO_4	4.2	M/16
M/256 H_3PO_4	2.4	Less than M/64

From what has been said it is to be expected that the substitution of an H for an Na ion in the carbonates or phosphates increases the cation effect owing to the fact that H has a smaller "ionic radius" than Na (Table VII).

It is obvious that in the two carbonates and the first three phosphates toward which (as we shall see in the next chapter) water is positively charged, the attraction of the CO_3 or PO_4 for water diminishes the more the more H ions replace the Na ions, as our theory demands.

VII. Direct Proof of the Influence of the Valency and Radius of Ions on the Sign of the Charge of Water.

Experiments on the migration of water through a collodion membrane under the influence of a constant current (electric endosmose) furnish the direct proof that our assumption is correct.

It is known that if a current is sent through the walls of a porous cell bounded on both sides by the same liquid conductor, water migrates either to the cathode or the anode. This migration is indicated by a rise in the level of the water on the side of that electrode towards which the water migrates. Helmholtz explained this phenomenon by the formation of an electrical double layer at the boundary of the diaphragm and the water particles. When a current is sent through the liquid the positively charged particles of water will move towards the cathode and if the water particles in contact with the wall are negatively charged they will move towards the anode. On account of the internal friction of the liquid the neighboring layers of liquid will be dragged along with the charged particles. This causes the rise of the liquid on the side of that electrode towards which the particles move.[8]

This electric osmose gives us a chance to test our assumption that the water molecules assume a different charge according to the nature of the electrolyte; namely, (1) that the water molecules assume a positive charge when the collodion bag is filled with solutions of neutral salts with a monovalent or bivalent cation or with solutions of hydroxides with monovalent or bivalent cations, (2) that the water molecules assume a negative charge when the collodion bag is filled with solutions of neutral (or acid) salts with a trivalent or tetravalent cation, or with solutions of acids.

If our assumption is correct, water should move towards the cathode in the case of the electrolytes mentioned in (1) (Group *A*, Table V) and towards the anode in the case of electrolytes mentioned in (2) (Group *B*, Table V). This is actually the case.

The collodion bags, closed by a perforated rubber stopper through the hole of which a glass tube with a bore of 2 mm. was inserted,

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[8] It should be noticed that a collodion membrane belongs in all probability to the type of non-porous diaphragms.

were filled with a dilute solution of the electrolyte the influence of which on the electrification of water was to be tested. The collodion bag was suspended in a beaker containing the same solution of the electrolyte as the bag, the two solutions being identical in every respect, nature of solute, concentration, and pH. By pushing the glass tube (manometer) a little deeper into the bag the liquid was adjusted so that it rose in the glass tube about 25 mm. above the level in the beaker. One electrode (platinum wire) was dipped into the glass tube, another into the beaker, and a constant current was sent through with an intensity of about 4.8 milliampere. This intensity was kept constant whenever possible. The level of the liquid in the glass tube was measured at the beginning of the experiment and it was easy to determine the sign of the electrification of the water molecules by observing whether the current caused the liquid in the glass tube to rise or to fall. When the anode was in the glass tube and the water rose we could be sure that the water was negatively charged, and when the level of the water fell rapidly under such conditions in the tube, we could be sure that the water was positively charged. When it fell very slowly the fall might have been due to the pressure head in the glass tube. A reversal of the direction of the current removed any doubt that might arise. The experiments gave a complete confirmation of the assumption made in the two rules.

It was found that in the presence of solutions of neutral salts belonging to Group *A* (Table V), *i.e.* salts or hydroxides with univalent cations, the water migrated to the cathode and hence was positively charged, as our theory demands. The following salts were tried: M/1000 and M/500 LiCl, M/1000 and M/500 Li_2SO_4, M/256 NaCl, M/1000 Na_2 oxalate, M/128 Na_2SO_4, M/256 Na acetate, M/256 LiOH, M/256 NaOH, M/1000 KCl, M/512 K_2 oxalate, M/1024 K_3 citrate, and M/1000 $K_4Fe(CN)_6$.

In solutions of the neutral salts with bivalent cation, M/512 $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$, water migrated neither to the anode nor to the cathode; these salts did not cause, or only to a very slight degree, an electrification of the water molecules as was to be expected. M/512 $CaSO_4$ on the other hand, induced a slight migration of water to the cathode, as our theory demanded.

In the presence of electrolytes belonging to Group *B* (Table V) water migrated to the anode, as it should on the basis of our rules. The following electrolytes were tried: M/1024 La_2Cl_6, M/1024 lanthanum ammonium nitrate, M/1024 Ce_2Cl_6, M/1024 Al_2Cl_6, M/1024 $Al_2(SO_4)_3$, and M/1024 $ThCl_4$.

In the presence of M/250 HCl and M/250 HNO_3, tartaric and M/512 phosphoric acids water also migrated to the anode, but the rate of migration was very slow; in the case of M/500 or M/1000 H_2SO_4 practically no migration was noticeable.

In the presence of M/512 $BeCl_2$ water migrated also to the anode as was to be expected. Most interesting were the experiments with M/500 H_3PO_4, NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. All, with the exception of H_3PO_4, caused a migration to the cathode, which again is in agreement with our rule. It may also be stated that when M/512 NaCl solution was rendered acid, *e.g.* when the pH was 4.0 or 3.7, the water migrated to the anode.

We may therefore state that our assumption concerning the influence of electrolytes on the sign of the electrical charge of water molecules is supported not only by the facts for the explanation of which it was made but also by the direct experiments with electrical osmose.

VIII. Influence of the Concentration of the Electrolyte in Solution on the Electric Effect.

When water diffuses from pure solvent to a solution, the initial rate of diffusion seems to vary approximately with the concentration of the solute, as long as the latter is a non-electrolyte. When it is an electrolyte the laws of gas pressure are not suspended but may be masked by the electrical forces which act simultaneously with the laws of gas pressure. It seemed of interest to determine the influence of the concentration of the electrolyte upon the rate of diffusion of water through the collodion membrane. To accomplish this the balancing solution of cane sugar was determined for various concentrations of the electrolyte. Table VIII gives the results of such measurements for various concentrations of KCl, of Na_2SO_4, and of $MgCl_2$.

The effects observed in the solutions of $MgCl_2$ may be only osmotic pressure effects with little or no influence of an electrical character.

In the case of KCl and of Na_2SO_4 it seems that the maximal effect of *e* is reached at a very low concentration of the electrolyte, near M/320 in the case of KCl and near M/960 in the case of Na_2SO_4. A further increase of the concentration to 100 times or more caused no further increase in the value of the balancing concentration. This would be intelligible on the assumption that the electrical effect is of the order of a saturation phenomenon; *e.g.*, the saturation of the membrane with electrolyte. Following ideas suggested in Langmuir's papers,[9] we may assume that electrolyte, collodion, and water arrange themselves in the collodion membrane in a definite pattern or space-lattice held together by chemical forces very much as the particles in a crystal, with this difference only that the molecules of water and the ions of the salts in the pattern have the degree o mobility characteristic of liquids. The electric fields created at the two surfaces of the membrane determine the charge of the particles of water impinging upon or lying adjacent to the surface of the membrane. On the solution side the membrane is bounded by the ions of the solute while on the side of pure solvent it is bounded by water alone and this difference determines the direction of the

TABLE VIII.

Molecular concentration of KCl.	Concentration of balancing cane sugar solution.	Molecular concentration of Na_2SO_4.	Concentration of balancing cane sugar solution.	Molecular concentration of $MgCl_2$.	Concentration of balancing cane sugar solution.
M/2560	M/64	M/15,360	M/64	M/192	0
M/1280	M/64	M/7680	M/16	10M/192	0
M/960	M/32	M/3840	3M/32	25M/192	0
M/640	M/16	M/1920	M/8	50M/192	Slightly above 3M/32
M/320	M/8	M/960	M/4	100M/192	3M/16
M/128	M/8	10M/192	M/4	150M/192	3M/8
10M/128	M/8	50M/192	3M/16	200M/192	About M/2
100M/128	M/8				

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[9] Langmuir, I., *J. Am. Chem. Soc.*, 1916, xxxviii, 2221.

diffusion under the influence of these forces, which may be electrostatic in character.

It follows from the data of Table VIII that the balancing concentrations given in Table V are the maximal values for e for each of the electrolytes mentioned and that it is not necessary to deduct $\frac{1}{64}$ from this value. The real deduction to be made is so small that it falls within the limits of error of the determination of the balancing concentration and the latter may therefore be taken as the rough expression for the value of the electrical forces.

SUMMARY.

1. When pure water is separated by a collodion membrane from a watery solution of an electrolyte the rate of diffusion of water is influenced not only by the forces of gas pressure but also by electrical forces.

2. Water is in this case attracted by the solute as if the molecules of water were charged electrically, the sign of the charge of the water particles as well as the strength of the attractive force finding expression in the following two rules. (*a*) 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. (*b*) 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, the high electrostatic effect of the hydrogen ion being probably due to its small "ionic radius."

3. The correctness of the assumption made in these rules concerning the sign of the charge of the water particles is proved by experiments on electrical osmose.

4. A method is given by which the strength of the attractive electric force of electrolytes on the molecules of water can be roughly estimated and the results of these measurements are in agreement with the two rules.

5. The electric attraction of water caused by the electrolyte increases with an increase in the concentration of the electrolyte, but at low concentrations more rapidly than at high concentrations. A tentative explanation for this phenomenon is offered.

6. The rate of diffusion of an electrolyte from a solution to pure solvent through a collodion membrane seems to obey largely the kinetic theory inasmuch as the number of molecules of solute diffusing through the unit of area of the membrane in unit time is (as long as the concentration is not too low) approximately proportional to the concentration of the electrolyte and is the same for the same concentrations of LiCl, NaCl, $MgCl_2$, and $CaCl_2$.