

CATAPHORETIC CHARGES OF COLLODION PARTICLES  
AND ANOMALOUS OSMOSIS THROUGH COLLOD-  
ION MEMBRANES FREE FROM PROTEIN.

By JACQUES LOEB.

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

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I.

When an aqueous salt solution is separated from pure water (both of originally the same hydrogen ion concentration) by a collodion membrane (not treated with a protein) a diffusion of water will occur from the side of the water to the side of the solution; and this diffusion is determined not only by the difference in the osmotic pressure on the opposite sides of the membrane, but in addition also by electrical forces, due to potential differences between membrane and liquid. In these experiments the salt solution is put into a collodion bag of about 50 cc. content, closed by a rubber stopper which is perforated by a glass tube serving as a manometer, as described in previous papers.<sup>1</sup> If the rise of level in the manometer observed after 20 minutes at 24°C. in mm. H<sub>2</sub>O is plotted as ordinates over the salt concentration as abscissæ, we obtain the transport curves, which differ characteristically when the substance in solution is an electrolyte or a non-electrolyte. The transport curves for solutions of non-electrolytes, like cane-sugar, resemble those for electrolytes only in higher concentrations, M/8 or above, while for lower concentrations the transport curves for non-electrolytes and certain electrolytes are typically different, since the curves for these electrolytes show a rise followed by a drop (Figs. 2, 3, and 4) both of which are lacking in non-electrolytes. The drop is followed by a second rise coinciding with the rise observed in the cane-sugar curves, and the second rise may therefore be ascribed in both cases to the purely osmotic forces of the

<sup>1</sup> Loeb, J., *J. Gen. Physiol.*, 1921-22, iv, 463, 621.

solution. The rise and fall of the curves at lower concentrations, however, which are only found in the case of the solutions of certain electrolytes (Figs. 2 and 3) and at definite hydrogen ion concentrations, must be ascribed to electrical forces.

In former papers the writer had arrived at the following formulation of these effects. When salt solutions are separated from pure water by collodion membranes (not treated with protein) the water is attracted by the solutions as if the water (in the pores of the membrane) were positively charged and as if it were attracted by the anion and repelled by the cation of the solution with a force which increases with the valency of the ion.

Girard,<sup>2</sup> and Bartell and Madison<sup>3</sup> had already suggested that two P.D. are active in this case, namely, first, a P.D. across the membrane between the salt solution and the water, and second, a P.D. inside the pore between the wall of the pore and the liquid diffusing through. These two P.D. are at right angles to each other. It seemed necessary to measure both P.D. at the same hydrogen ion concentrations of the solution in order to find out whether or not the transport curves can be explained on the basis of these P.D. If the P.D. across the membrane is designated as  $E$  and the P.D. inside the pore as  $\epsilon$ , then, on the basis of Helmholtz's formula, the values of the electrical share of the transport curves should be parallel to the values of the product  $E \times \epsilon$ . It was shown in two preceding papers<sup>1</sup> that this was approximately true for gelatin membranes—or, more correctly, collodion membranes coated with gelatin on the solution side. These membranes behaved like gelatin membranes, the collodion acting only as a strengthening support of the gelatin film.

We intend to discuss in this paper the electrical part of the transport curves when the membranes are purely collodion membranes free from protein. The difference between the two cases is the following. When the membrane has a protein film, the charge of the water inside the pore (due to the formation of the electrical double layer) varies not only in quantity but in sign with the hydrogen ion

<sup>2</sup> Girard, P., *Compt. rend. Acad.*, 1908, cxlvi, 927; 1909, cxlviii, 1047, 1186; 1910, cl, 1446; 1911, cliii, 401; *La pression osmotique et le mécanisme de l'osmose*, Publications de la Société de Chimie-physique, Paris, 1912.

<sup>3</sup> Bartell, F. E., and Madison, O. E., *J. Physic. Chem.*, 1920, xxiv, 444, 593.

concentration, in a way as if the electrical double layer inside the pore were essentially determined by the Donnan equilibrium between gelatin and liquid. In the case of pure collodion membranes (free from protein), as used in the experiments for the present paper, the sign of charge of the water in the pores remains the same at any hydrogen ion concentration thus far used in the experiments. The water in the pores is practically always positively charged (except in the presence of salts with trivalent and probably tetravalent cations), while the collodion wall of the pores is negatively charged. This was ascertained by experiments on electrical endosmose<sup>4</sup> as well as by experiments on cataphoresis.<sup>5</sup>

When the water in the pores of a membrane assumes a positive charge, an electrical transport of water from the side of pure water into the solution can only take place when, in the P.D. across the membrane, the solution is negatively charged. This had already been suggested by Bartell.<sup>3</sup> We shall see that the results of the P.D. measurements agree with this suggestion and that they furthermore explain why the electrical transport of water into the solution increases with the valency of the anion of the salt used.

The value of  $\epsilon$ , *i.e.* the P.D. between collodion and liquid, was determined by cataphoretic measurements taken from another paper in this number of this Journal.<sup>5</sup> The value of  $E$ , *i.e.* the P.D. across the membrane between solution and water, was measured at the beginning and the end of the diffusion experiments with the aid of a Compton electrometer and saturated KCl-calomel electrodes as described in the preceding papers. The transport curves for the same salt solutions vary with the hydrogen ion concentration. At the beginning of the experiment salt solutions and water were brought to the same pH, the pH being determined colorimetrically. When acid was required HCl was added, and when alkali was required KOH was used.

Fig. 1 gives the transport curves of water from the side of water into salt solutions at an initial pH of 3.0, the acid used being in all cases HCl. The ordinates of the curves are the rise of liquid in the manometers (connected with the solutions) after 20 minutes; the abscissæ

<sup>4</sup> Loeb, J., *J. Gen. Physiol.*, 1919-20, ii, 563.

<sup>5</sup> Loeb, J., *J. Gen. Physiol.*, 1922-23, v, 109.

are the initial concentrations of the solutions. The curves in Fig. 1 are similar to the curves obtained with non-electrolytes like cane-sugar, and hence are entirely or chiefly due to the transport of water by purely osmotic forces. There is no indication of any transport due to electric forces.

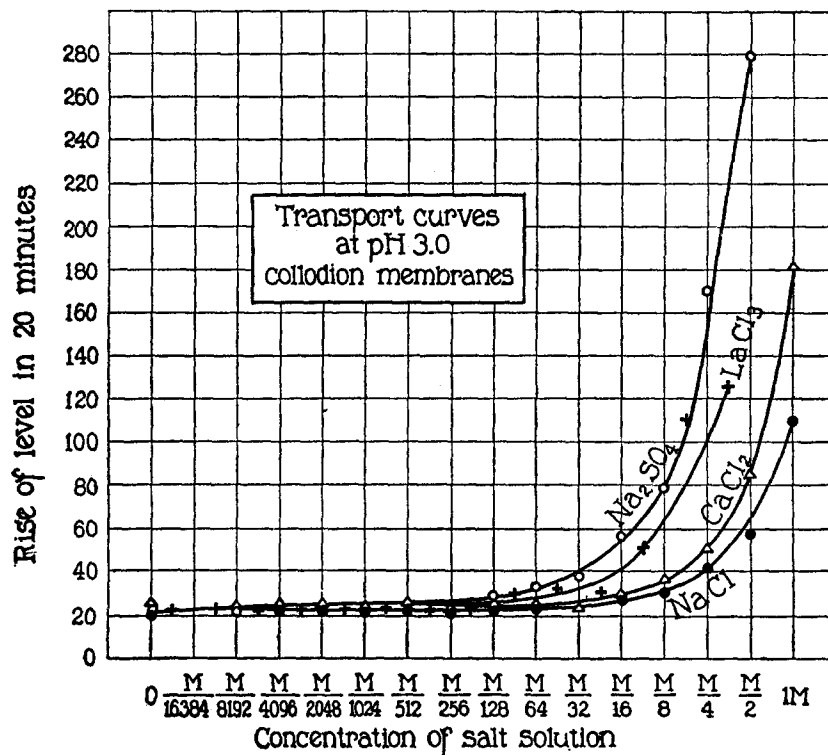


FIG. 1. Transport curves at pH 3.0 through collodion membranes. The ordinates are the rise of level in mm. H<sub>2</sub>O in the manometers connected with the solution; the abscissæ are the concentrations of salt solutions. The curves show that at this pH the diffusion of water is determined purely by osmotic and not by electrical forces.

This result finds its explanation in the values given in Tables I, II, and III. In Tables I and II are given the p.d. across the membrane ( $E$ ) at the beginning of the experiments and at the end (*i.e.*, after 20 minutes). The method of these measurements was described in a previous article. The solution was always positively charged with

TABLE I.  
P.D. in millivolts between salt solutions and H<sub>2</sub>O, of pH 3.0, across colloid membranes, at beginning of experiment. The minus or plus signs designate the sign of charge on the solution side of the membranes.

Concentration.....	0	M/8,192	M/4,096	M/2,048	M/1,024	M/512	M/256	M/128	M/64	M/32	M/16	M/8	M/4	M/2	1 M
Na <sub>2</sub> SO <sub>4</sub> .....	0	-1.0	+1.0	-1.0	-1.0	-1.5	-2.5	-3.5	-5.0	-6.5	-9.0	-12.0	-16.0	-20.0	
KCl.....	+1.5		+0.5	0	+0.5	+0.5	+0.5	+0.5	+1.0	+1.0	+0.5	+1.5	+1.0	+1.5	+1.5
NaCl.....	+1.0		+0.5	+1.5	+2.0	+3.0	+4.5	+7.0	+9.0	+11.0	+13.5	+16.0	+18.0	+21.0	+22.5
LiCl.....	+1.0		+3.0	+3.0	+3.0	+5.0	+7.0	+10.0	+13.0	+17.5	+23.0	+27.0	+31.0	+34.0	+37.0
CaCl <sub>2</sub> .....	+2.0	+2.5	+4.0	+6.0	+7.0	+9.0	+13.0	+17.0	+22.0	+27.0	+31.0	+36.0	+39.0	+41.0	+48.0
Concentration.....	0	M/49,152	M/24,576	M/12,288	M/6,144	M/3,072	M/1,536	M/768	M/384	M/192	M/96	M/48	M/24	M/12	M/6
LaCl <sub>3</sub> .....	+2.0	+1.5	+2.0	+2.5	+3.0	+5.0	+6.0	+9.0	+13.5	+18.0	+23.0	+29.0	+34.0	+41.5	+48.0
															+53.0

TABLE II.  
P.D. in millivolts between salt solutions and H<sub>2</sub>O, of pH 3.0, across colloid membranes, at end of experiment. The minus or plus signs designate the sign of charge on the solution side of the membranes.

Concentration.....	0	M/8,192	M/4,096	M/2,048	M/1,024	M/512	M/256	M/128	M/64	M/32	M/16	M/8	M/4	M/2	1 M
Na <sub>2</sub> SO <sub>4</sub> .....	+1.0	0	0	-1.5	-2.0	-3.5	-5.0	-6.0	-6.0	-6.5	-7.0	-10.5	-11.0	-9.0	
KCl.....	+0.5		+0.5	+0.5	0	0	+0.5	0	-0.5	0	0	0	-0.5	-0.5	0
NaCl.....	+1.0		+1.5	+1.0	+1.5	+2.0	+3.5	+6.5	+7.5	+9.0	+10.0	+11.0	+10.0	+7.0	+7.0
LiCl.....	+0.5		+1.0	+2.5	+3.0	+4.0	+6.5	+8.0	+12.5	+16.0	+19.0	+19.0	+18.0	+17.5	+14.5
CaCl <sub>2</sub> .....	+2.0	+3.0	+4.0	+5.0	+7.5	+9.0	+12.5	+16.5	+19.0	+22.0	+22.5	+22.5	+22.0	+21.0	+18.5
Concentration.....	0	M/49,152	M/24,576	M/12,288	M/6,144	M/3,072	M/1,536	M/768	M/384	M/192	M/96	M/48	M/24	M/12	M/6
LaCl <sub>3</sub> .....	+1.5	+2.0	+2.0	+2.0	+2.5	+3.0	+5.0	+9.0	+13.0	+18.0	+21.0	+23.5	+27.0	+25.0	+24.0
															+25.0

the exception of the  $\text{Na}_2\text{SO}_4$  solution; but at low concentrations of  $\text{Na}_2\text{SO}_4$  the value of  $E$  was too small to have any effect, while at higher concentrations the value of  $\epsilon$  became rather small. In Table III are given the cataphoretic p.d. ( $\epsilon$ ) between collodion particles and water in the same solutions as those mentioned in Tables I and II.

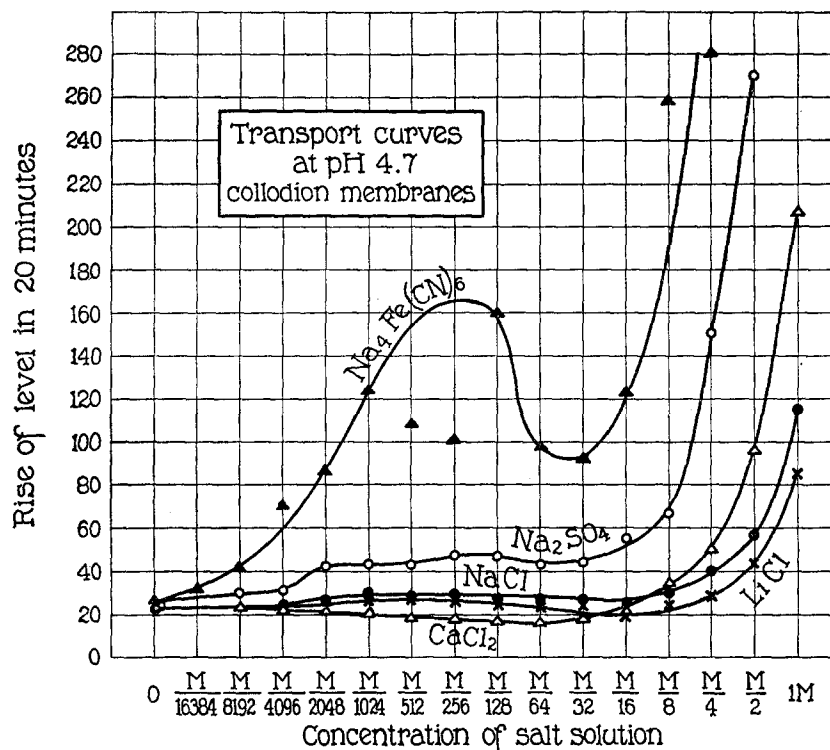


FIG. 2. Transport curves at pH 4.7. The transport curves for  $\text{Na}_4\text{Fe}(\text{CN})_6$  and  $\text{Na}_2\text{SO}_4$  show a slight electrical effect in concentrations below  $\text{m}/32$ . The transport curves for  $\text{NaCl}$ ,  $\text{LiCl}$ , and  $\text{CaCl}_2$  show no electrical effect.

The method of the measurements of the cataphoretic p.d. was that described by Northrop.<sup>6</sup> As Table III shows, the sign of charge of the liquid in the pores of the membrane is also positive. Since the solution and the water inside the pores always have the same sign of charge (except in the case of  $\text{Na}_2\text{SO}_4$  mentioned above), no

<sup>6</sup> Northrop, J. H., *J. Gen. Physiol.*, 1921-22, iv, 629.

TABLE III.

Cataphoretic p.d. in millivolts between colloidion particles and aqueous solutions at pH 3.0. The plus sign designates the charge of water.

Concentration	0	m/32,768	m/16,384	m/8,192	m/4,096	m/2,048	m/1,024	m/512	m/256	m/128	m/64	m/32	m/16	m/8	m/4
Na <sub>2</sub> SO <sub>4</sub>	+63	+72	+63	+73	+68	+65	+51	+46	+35	+28	+12				
NaCl	+60	+62	+57	+59	+59	+46	+39	+38	+29	+20	+14				
CaCl <sub>2</sub>	+62	+40	+37	+34	+31	+27	+24	+19	+16	+14	+7				
LaCl <sub>3</sub>	+68	+32	+18	+14	+8	+7	+5	+3	0	0					

TABLE IV.

p.d. in millivolts between salt solutions and H<sub>2</sub>O, of pH 4.7, across colloidion membranes, at beginning of experiment. The minus or plus signs designate the sign of charge of the solutions.

Concentration	0	m/16,384	m/8,192	m/4,096	m/2,048	m/1,024	m/512	m/256	m/128	m/64	m/32	m/16	m/8	m/4	m/2	1 M
Na <sub>2</sub> Fe(CN) <sub>6</sub>	+1.0	-8.0	-15.0	-21.0	-32.0	-29.0	-28.0	-27.5	-31.5	-32.5	-31.0	-40.0	-46.0	-52.5		
Na <sub>2</sub> SO <sub>4</sub>	+1.5	-10.0	-13.5	-15.0	-14.0	-14.0	-15.0	-17.5	-20.0	-22.0	-24.0	-27.5	-30.0			
KCl	-1.0	-1.5	-3.0	-4.0	-4.0	-4.0	-3.0	-1.5	-2.0	-1.5	-1.5	-1.0	0			
NaCl	+1.5	+4.5	+2.5	+6.5	+10.0	+11.0	+17.5	+21.0	+20.0	+27.0	+28.0	+31.0	+35.0	+35.0		
LiCl	0	+4.0	+6.0	+9.5	+14.0	+19.0	+25.0	+33.0	+38.0	+45.0	+48.0	+54.0	+51.0	+59.0		
CaCl <sub>2</sub>	+2.5	+9.0	+14.5	+21.0	+25.0	+31.5	+37.5	+43.5	+47.0	+52.0	+59.0	+61.5	+67.0			

TABLE V.  
P.D. in millivolts between salt solutions and H<sub>2</sub>O, of pH 4.7, across collodion membranes, at end of experiment. The minus or plus signs designate the sign of charge of the solutions.

Concentration.....	0	M/16,384	M/8,192	M/4,096	M/2,048	M/1,024	M/512	M/256	M/128	M/64	M/32	M/16	M/8	M/4	M/2	1 M
Na <sub>4</sub> Fe(CN) <sub>6</sub> .....	-2.0	-12.5	-17.5	-25.0	-34.0	-34.0	-25.0	-24.0	-26.0	-21.5	-20.0	-18.5	-21.0	-25.0		
Na <sub>2</sub> SO <sub>4</sub> .....	-4.0		-7.5	-14.0	-15.0	-13.5	-17.0	-12.5	-12.5	-11.5	-11.0	-11.5	-11.0	-11.5	-12.5	0
KCl.....	-8.0			-7.0	-8.0	-7.5	-8.0	-4.0	-3.0	-3.0	-1.5	-0.5	0	0	0	0
NaCl.....	-1.0			-1.5	-2.0	+1.5	+5.0	+4.5	+9.0	+10.0	+9.5	+10.0	+9.0	+10.0	+8.5	+7.5
LiCl.....	-4.0			-2.5	-2.5	-1.5	+7.5	+14.0	+18.5	+19.0	+21.0	+20.5	+20.0	+19.0	+17.0	+17.0
CaCl <sub>2</sub> .....	-1.0			+4.0	+10.0	+9.0	+17.5	+22.0	+24.5	+24.0	+23.5	+24.0	+23.5	+20.5	+20.5	+20.5

TABLE VI.  
Cataphoretic P.D. in millivolts between collodion particles and aqueous solutions at pH 4.7. The plus sign designates the charge of water.

Concentration.....	0	M/32,768	M/16,384	M/8,192	M/4,096	M/2,048	M/1,024	M/512	M/256	M/128	M/64	M/32	M/16	M/8	M/4	M/2
Na <sub>4</sub> Fe(CN) <sub>6</sub> .....	+29	+51	+55	+60	+64	+68	+65	+57	+50	+42	+30	+21	+13	+9		
Na <sub>2</sub> SO <sub>4</sub> .....	+28	+47	+47	+56	+59	+65	+70	+69	+63	+56	+43	+36	+26	+19	+13	
KCl.....	+32	+31	+37	+45	+52	+53	+62	+66	+66	+60	+49	+40	+30	+21	+14	+10
NaCl.....	+26			+47	+53	+58	+60	+64	+61	+55	+49	+37	+30	+20	+14	
LiCl.....	+31	+41	+42	+48	+47	+57	+60	+64	+68	+61	+55	+44	+36	+22	+17	
CaCl <sub>2</sub> .....	+36	+17	+30	+31	+32	+35	+32	+28	+26	+22	+17	+14	+10	+8	+6	
LaCl <sub>3</sub> .....	+29		+19	+19	+21	+14	+10	+8	+4	+4	0	0	-3	-6		



electrical transport of water into the solution should be possible, as was found to be the case.

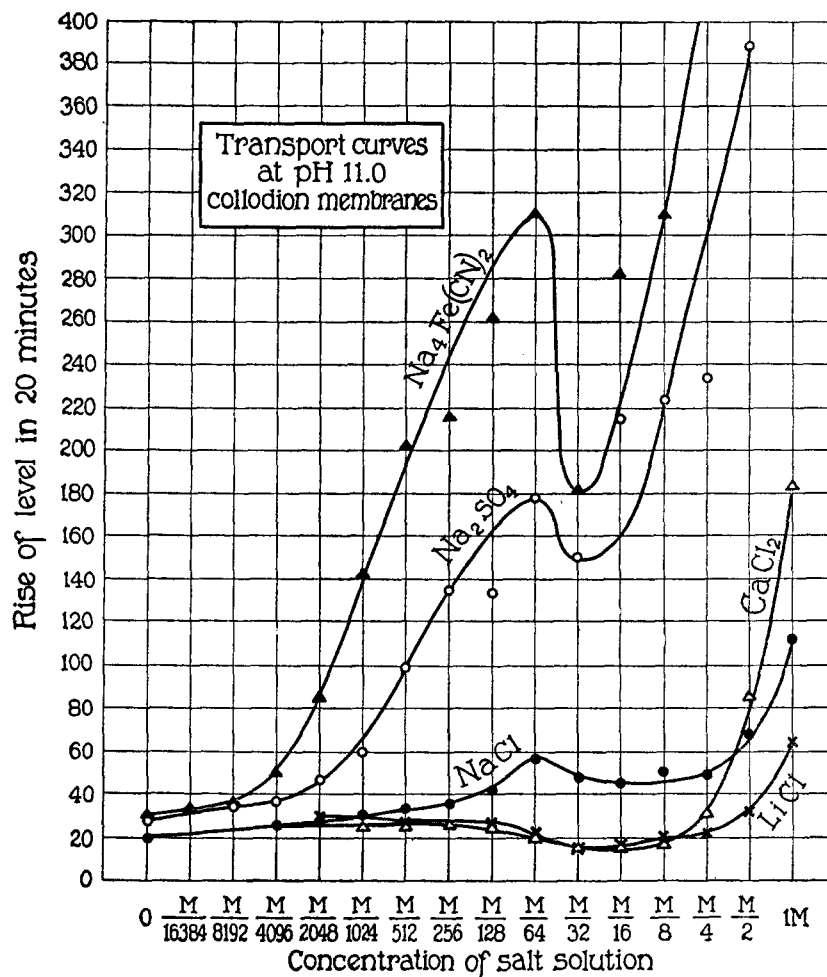


FIG. 3. Transport curves at pH 11.0. The electrical effect is visible only for  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{Na}_4\text{Fe}(\text{CN})_6$  for concentrations below  $M/64$ .

Fig. 2 gives the transport curves at a lower hydrogen ion concentration; namely, pH 4.7. We now notice a marked electrical effect in the transport curves for  $\text{Na}_4\text{Fe}(\text{CN})_6$  and a slight one for  $\text{Na}_2\text{SO}_4$ . This is accounted for in Tables IV, V and VI. Tables IV and V show that

TABLE VII.

p.d. in millivolts between salt solutions and H<sub>2</sub>O, of pH 11.0, across collodion membranes, at beginning of experiment. The minus or plus signs designate the sign of charge on the solution side of the membranes.

Concentration.....	0	M/16,384	M/8,192	M/4,096	M/2,048	M/1,024	M/512	M/256	M/128	M/64	M/32	M/16	M/8	M/4	M/2	1 M
Na <sub>4</sub> Fe(CN) <sub>6</sub> .....	-1.5	-2.5	-5.0	-8.5	-13.0	-19.0	-22.5	-30.0	-27.0	-30.5	-29.0	-37.5	-43.0	-47.5		
Na <sub>2</sub> SO <sub>4</sub> .....	-2.0		-4.5	-6.0	-8.0	-14.0	-17.0	-18.0	-17.0	-18.0	-17.0	-19.0	-21.0	-24.0	-29.0	
KCl.....	0			-2.5	-3.0	-3.0	-5.0	-4.0	-4.0	-3.5	-2.5	-2.5	-1.5	-1.5	-1.0	-1.0
NaCl.....	0			-1.5	-2.0	-2.5	-1.5	-1.5	+1.0	+2.0	+6.0	+10.0	+13.0	+16.0	+19.0	+22.0
LiCl.....	-0.5			-1.5	-2.5	-1.5	0	+3.5	+7.5	+13.0	+18.0	+23.0	+27.0	+32.5	+38.0	+41.0
CaCl <sub>2</sub> .....	-2.5			-2.0	-1.0	+1.0	+5.0	+10.0	+15.0	+20.0	+26.0	+31.5	+37.0	+42.0	+46.5	+51.0

TABLE VIII.

p.d. in millivolts between salt solutions and H<sub>2</sub>O, of pH 11.0, across collodion membranes, at end of experiment. The minus or plus signs designate the sign of charge on the solution side of the membranes.

Concentration.....	0	M/16,384	M/8,192	M/4,096	M/2,048	M/1,024	M/512	M/256	M/128	M/64	M/32	M/16	M/8	M/4	M/2	1 M
Na <sub>4</sub> Fe(CN) <sub>6</sub> .....	-3.0	-3.5	-5.0	-7.5	-12.0	-20.0	-25.0	-24.0	-26.0	-25.0	-21.0	-22.5	-23.0	-24.0		
Na <sub>2</sub> SO <sub>4</sub> .....	-2.5		-4.5	-6.5	-6.5	-13.5	-16.0	-18.0	-16.0	-16.0	-14.0	-15.0	-14.0	-13.0	-19.0	
KCl.....	-2.0			-2.0	-2.5	-3.0	-4.0	-4.0	-3.5	-3.0	-2.5	-2.0	-1.0	-0.5	0	0
NaCl.....	-0.5			-2.0	-2.0	-3.0	-2.5	-1.5	-0.5	+1.5	+1.5	+6.0	+7.0	+7.5	+7.5	+8.0
LiCl.....	-2.5			-3.5	-2.5	-2.5	-1.0	+3.0	+7.5	+10.0	+13.0	+17.0	+18.0	+16.5	+13.0	+15.0
CaCl <sub>2</sub> .....	-2.0			-3.0	-1.5	+1.0	+5.0	+8.5	+13.5	+16.5	+19.5	+22.0	+21.0	+23.0	+20.0	+18.0

TABLE IX.

Cataphoretic p.d. in millivolts between colloid particles and aqueous solutions at pH 11.0. The plus sign designates the sign of charge of the water.

Concentration.....	0	m/32,768	m/16,384	m/8,192	m/4,096	m/2,048	m/1,024	m/512	m/256	m/128	m/64	m/32	m/16	m/8	m/4
Na <sub>4</sub> Fe(CN) <sub>6</sub> .....	+59	+64	+66	+74	+71	+71	+70	+69	+52	+41	+32	+24	+16		
Na <sub>2</sub> SO <sub>4</sub> .....	+60	+69	+70	+70	+71	+73	+75	+65	+63	+56	+49	+35	+28	+20	
NaCl.....	+62		+62	+66	+65	+66	+65	+66	+65	+62	+53	+43	+34	+24	+18
CaCl <sub>2</sub> .....	+58	+48	+48	+40	+39	+37	+34	+29	+28	+24	+19	+15	+9	+6	

the solutions of  $\text{Na}_4\text{Fe}(\text{CN})_6$  and  $\text{Na}_2\text{SO}_4$  assume a considerable negative charge in the p.d. across the membrane and that this p.d. is greater in the case of  $\text{Na}_4\text{Fe}(\text{CN})_6$  than in the case of  $\text{Na}_2\text{SO}_4$ . Since, according to Table VI, the water in the pores is positively charged, an electrical transport must occur. In KCl there is a slight negative charge of the solution (Table IV) but too small to have any effect on the transport of water. In the case of NaCl, LiCl,  $\text{CaCl}_2$ , and  $\text{LaCl}_3$  no electrical transport is possible since the solution as well as the water in the pores are positively charged.

Observations taken at pH 5.8 were similar to those at pH 4.7 except that the effects of  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_4\text{Fe}(\text{CN})_6$  were greater than at pH 4.7. The p.d. across the membrane was also greater for these salts. Since otherwise everything was similar to the result at pH 4.7, further discussion of the results at pH 5.8 may be omitted.

Fig. 3 gives the transport curves at pH 11.0, the solutions being brought to this pH by the addition of KOH.  $\text{Na}_4\text{Fe}(\text{CN})_6$ ,  $\text{Na}_2\text{SO}_4$ , NaCl, and KCl (not shown in the figure) gave electrical transport curves. In this case the salt solutions mentioned were negatively charged (Tables VII and VIII), while the water in the pores was as usual positively charged (Table IX); the negative charge in the solution (Tables VII and VIII) increased in the order of KCl and NaCl  $<$   $\text{Na}_2\text{SO}_4 <$   $\text{Na}_4\text{Fe}(\text{CN})_6$ , as did the electrical part of the transport curves in Fig. 3. In the case of LiCl and  $\text{CaCl}_2$  the solutions were positively charged and hence the transport curves are the effect of the osmotic forces alone.

The p.d. measurements therefore explain the transport curves in a semiquantitative way in all these experiments.

## II.

While all these results show that the electrical transport of water in these experiments varies semiquantitatively with the value of the product  $E \times \epsilon$ , some difficulties are encountered when we compare the effect of  $\text{Na}_2\text{SO}_4$  or  $\text{Na}_4\text{Fe}(\text{CN})_6$  on the electrical transport at pH 11.0 with that at pH 5.8. In Fig. 4 are presented the transport curves for  $\text{Na}_2\text{SO}_4$  at different pH, varying from 2.0 to pH 12.0.

At pH 2.0 and pH 3.0 the p.d. across the membrane (Table X) is small, and this accounts for the fact that at both pH the transport

curves are purely osmotic in character (Fig. 4). At pH 4.7 the electrical transport of liquid from water into the  $\text{Na}_2\text{SO}_4$  solution

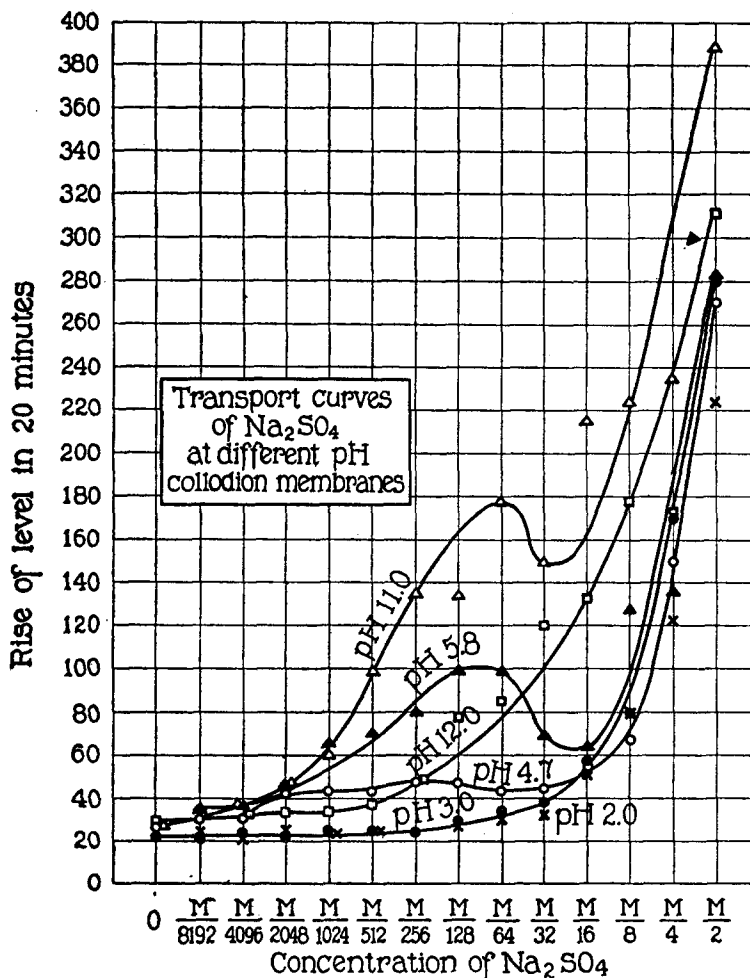


FIG. 4. Transport curves for  $\text{Na}_2\text{SO}_4$  at different pH showing that the electrical effect for the same salt varies considerably with the hydrogen ion concentration of the solution.

becomes noticeable, as already mentioned. At pH. 5.8 (Fig. 4) the electrical transport of water from the side of pure water into the  $\text{Na}_2\text{SO}_4$  solution is greater than at pH 4.7, and at pH 11.0

TABLE X.  
p.d. in millivolts between solutions of Na<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O of same pH across a collodion membrane, at beginning of experiment. The plus or minus sign designates the sign of charge of the solutions.

Concentration of Na <sub>2</sub> SO <sub>4</sub> .....	0	m/8,192	m/4,096	m/2,048	m/1,024	m/512	m/256	m/128	m/64	m/32	m/16	m/8	m/4	m/2
pH 2.0.....	+0.5	+0.5	+0.5	+0.5	+1.0	+1.0	+1.0	+1.0	+1.0	0	-1.0	-4.0	-7.0	-12.0
pH 3.0.....	0	-1.0	+1.0	1.0	-1.0	-1.5	-2.5	-3.5	-5.0	-6.5	-9.0	-12.0	-16.0	-20.0
pH 4.7.....	+1.5	-5.5	-10.0	-13.5	-15.0	-14.0	-14.0	-15.0	-17.5	-20.0	-22.0	-24.0	-27.5	-30.0
pH 5.8.....	-2.0	-20.0	-21.0	-30.0	-29.0	-23.0	-22.0	-24.0	-21.0	-15.0	-24.0	-30.0	-26.0	-34.0
pH 11.0.....	-2.0	-4.5	-6.0	-8.0	-14.0	-17.0	-18.0	-17.0	-18.0	-17.0	-19.0	-21.0	-24.0	-29.0
pH 12.0.....	0	-0.5	-1.0	-1.0	-1.0	-1.5	-3.0	-4.0	-5.5	-8.0	-10.5	-13.5	-16.5	-21.0

TABLE XI.  
Cataphoretic p.d. in millivolts between collodion particles and Na<sub>2</sub>SO<sub>4</sub> solutions at different pH. The plus sign designates the sign of charge of the water.

Concentration of Na <sub>2</sub> SO <sub>4</sub> .....	0	m/32,768	m/16,384	m/8,192	m/4,096	m/2,048	m/1,024	m/512	m/256	m/128	m/64	m/32	m/16	m/8	m/4
pH 2.0.....	+37	+43	+43	+54	+41	+40	+42	+41	+42	+38	+32	+25	+19	+10	+12
pH 3.0.....	+63	+47	+47	+72	+72	+63	+73	+68	+65	+51	+46	+35	+28	(+6)	+13
pH 4.7.....	+28	+50	+58	+56	+59	+65	+70	+69	+63	+56	+43	+36	+26	+19	+21
pH 5.8.....	+21	+69	+70	+70	+60	+64	(+90)	+67	+62	+55	+46	+36	+27	+21	+20
pH 11.0.....	+60	+47	+50	+50	+49	+52	+50	+49	+63	+56	+49	+35	+28	+20	+19
pH 12.0.....	+45	+47	+50	+50	+49	+52	+50	+49	+47	+42	+37	+31	+25	+19	+19

(Fig. 4) the electrical transport of water is still greater than at pH 5.8. At pH 12.0 (Fig. 4) the electrical transport diminishes again. The fact that the electrical transport is less at pH 12.0 than at pH 11.0 finds its explanation in Table X showing that the p.d. across the membrane is considerably smaller at pH 12.0 than at pH 11.0.

A difficulty arises, however, if we wish to account for the fact that the electrical transport curve for  $\text{Na}_2\text{SO}_4$  is higher at pH 11.0 than that at pH 5.8, since the p.d. across the membrane is greater at pH 5.8 than at pH 11.0 (Table X), while Table XI shows that the value of  $\epsilon$  is practically identical at both pH.

The same difficulty occurs in the case of the transport curves for  $\text{Na}_4\text{Fe}(\text{CN})_6$  at pH 5.8 and 11.0, these transport curves being higher at pH 11.0 than at pH 5.8, although the values  $E \times \epsilon$  do not warrant the difference in the transport curves. It seems to follow that some other variable in the equation for the diffusion of water (besides  $E$  and  $\epsilon$ ) is affected by the pH. The low value of the electrical transport in  $\text{Na}_2\text{SO}_4$  solutions at pH 2.0 is accounted for by the low value of the p.d. across the membrane (Table X).

The electrical part of the transport curves lies in a concentration of the salts between zero and about  $m/8$  or  $m/4$ . The transport curves for  $\text{Na}_4\text{Fe}(\text{CN})_6$  or  $\text{Na}_2\text{SO}_4$  rise at first with increasing concentration until a maximum is reached at a molecular concentration of between  $m/32$  or  $m/16$ , then drop slightly, and then rise again sharply (Figs. 2, 3, and 4). This latter rise is probably due exclusively to the osmotic effect of the salt in solution and need not be considered for our present purpose. The initial rise in the curves with increasing concentration of  $\text{Na}_2\text{SO}_4$  or  $\text{Na}_4\text{Fe}(\text{CN})_6$  is, however, electrical in character and is accounted for by a corresponding rise in the value of  $E$  with increasing concentration, as is shown in Tables IV, VII, and X.

The drop of the electrical transport curves at a concentration of between  $m/32$  and  $m/16$  at pH 5.8 and pH 11.0 is explained by a corresponding drop in values of  $\epsilon$  as is shown in Tables VI and IX. We can therefore say that from the influence of electrolytes on the p.d. across the membrane ( $E$ ) and on the cataphoretic p.d. ( $\epsilon$ ) it is possible to explain semiquantitatively the phenomena of anomalous osmosis through a collodion membrane with the exception of some minor discrepancies.

## III.

We may finally inquire into the nature of the P.D. across the membrane. It was pointed out that it was essentially, but perhaps not exclusively, a diffusion potential due to the difference in the rate of migration of the oppositely charged ions of a salt through the membrane.

The liquid in the pores of a collodion membrane is generally positively charged; only solutions of salts with trivalent (and probably tetravalent) cations can, in sufficiently high concentrations, cause the liquid to be negatively charged. If we omit these exceptions, it follows that an electrical transport of liquid through the membrane from the side of the water into the solution can only occur when in the P.D. across the membrane a sufficiently large negative charge is found on the solution side. The experiments show that this occurs in a pronounced way only when the anion of the salt is plurivalent, *i.e.*  $\text{SO}_4$ , oxalate,  $\text{PO}_4$ ,  $\text{Fe}(\text{CN})_6$ , etc., while the cation is univalent, and the question arises, why this should be so. The answer is given by the measurements of diffusion potentials of solutions of salts against pure water of the same pH without the interposition of a membrane, which show that in the diffusion potentials of solutions of salts with plurivalent anions and univalent cations against water, the solutions assume a negative charge which increases with the valency of the anions and the concentration of the salts. This is obvious from the results in Table XII giving the diffusion potentials for a series of salt solutions against water without the interposition of a membrane at pH 4.7. When the anion is plurivalent and the cation univalent, the solution assumes a negative charge in the P.D. across the membrane and the negative charge increases with the valency of the anion and the concentration of the salt. The same is true for the charge of the solution when the diffusion occurs through a collodion membrane. Since the salts can diffuse through the collodion membrane, diffusion potentials are bound to occur and we cannot doubt that these diffusion potentials explain the peculiar effect which the sign of charge and valency of ion have on the electrical part of the transport curves; *i.e.*, on anomalous osmosis. The P.D. across the membrane is essentially due to the diffusion potential of the solution.



TABLE XII.  
Diffusion potentials in millivolts between salt solutions and H<sub>2</sub>O of pH 4.7.

Concentration.....	m/1,6,384	m/8,192	m/4,096	m/2,048	m/1,024	m/512	m/256	m/128	m/64	m/32	m/16	m/8	m/4	m/2	1 M
Na <sub>4</sub> Fe(CN) <sub>6</sub> .....	-2.5	-4.0	-7.0	-10.0	-14.0	-18.0	-24.0	-27.0	-32.0	-36.5	-43.0	-49.0	-55.0		
Na <sub>2</sub> SO <sub>4</sub> .....		-2.5	-4.0	-5.5	-7.0	-9.0	-11.5	-13.5	-15.5	-18.0	-23.0	-26.0	-29.0	-34.0	0
KCl.....		0	+1.0	+0.5	+0.5	+0.5	+0.5	0	0	0	0	0	0	0	0
NaCl.....		+7.0	+9.0	+11.5	+14.0	+18.0	+20.5	+22.5	+25.0	+27.0	+29.5	+33.5	+36.0	+39.0	+42.0
LiCl.....		+6.0	+9.5	+16.5	+20.5	+23.5	+30.0	+37.5	+42.5	+46.5	+50.0	+55.0	+60.0	+63.5	+68.5
CaCl <sub>2</sub> .....		+16.0	+21.0	+26.5	+31.0	+35.0	+41.0	+47.0	+53.0	+59.0	+64.5	+70.0	+76.0	+78.0	+84.0
BaCl <sub>2</sub> .....		+6.5	+10.0	+15.0	+20.0	+26.0	+31.5	+36.5	+43.0	+47.5	+52.5	+57.0	+61.5	+67.5	+75.0
MgCl <sub>2</sub> .....		+7.0	+11.0	+17.5	+24.0	+30.0	+36.0	+41.0	+46.5	+53.5	+62.0	+68.0	+72.5	+78.5	+86.5
MgSO <sub>4</sub> .....		+5.0	+6.0	+6.0	+7.5	+8.5	+9.0	+10.0	+11.0	+11.0	+11.0	+11.5	+11.0	+10.0	
LaCl <sub>3</sub> .....		+10.0	+14.0	+19.0	+24.0	+29.0	+36.0	+43.0	+49.0	+55.0	+61.0	+67.0	+74.0	+80.0	+88.0

TABLE XIII.

P.D. in millivolts across the membrane minus diffusion potential without membrane, at pH 4.7.

Concentration.....	m/8,192	m/4,096	m/2,048	m/1,024	m/512	m/256	m/128	m/64	m/32	m/16	m/8	m/4
Na <sub>4</sub> Fe(CN) <sub>6</sub> .....	-11.0	-14.0	-22.0	-15.0	-10.0	-3.5	-4.5	-0.5	+5.5	+3.0	+3.0	+2.5
Na <sub>2</sub> SO <sub>4</sub> .....	-3.0	-6.0	-8.0	-8.0	-5.0	-2.5	-1.5	-2.0	-2.0	+1.0	+2.0	+1.5
NaCl.....	-4.5	-9.0	-9.0	-7.5	-8.0	-9.5	-5.0	-4.0	-7.0	-2.5	-5.5	-5.0
CaCl <sub>2</sub> .....	-9.5	-12.0	-12.0	-10.0	-10.0	-9.5	-9.5	-9.5	-12.0	-12.5	-11.0	-14.5

While the diffusion potentials of salt solutions against water without a membrane agree to a large extent with the P.D. across the collodion membrane, the two P.D. are by no means identical. If the diffusion potentials without interposition of a membrane in Table XII are compared with the P.D. across the collodion membrane at pH 4.7 given in Table IV, it is noticeable that the values for diffusion potentials differ in a definite sense from the values for the P.D. across the membrane, especially for the concentrations below  $M/128$  or  $M/256$ . This difference between P.D. across the membrane minus diffusion potential without a membrane has in this case always a negative value, as is shown in Table XIII. It looks as if the rate of diffusion of the anions was comparatively more retarded by the membrane than the rate of diffusion of the cations. Since the collodion membrane is negatively charged, it might be argued that the retardation is due to a repulsion of the anions by the negatively charged membrane and an attraction of the positive ion of the salt. While this is possible, it is also possible that another P.D. is superposed upon the diffusion potential. It will be necessary to return to this subject in a subsequent paper.

#### SUMMARY AND CONCLUSIONS.

1. It had been shown in previous papers that when a salt solution is separated from pure water by a collodion membrane, water diffuses through the membrane as if it were positively charged and as if it were attracted by the anion of the salt in solution and repelled by the cation with a force increasing with the valency. In this paper, measurements of the P.D. across the membrane ( $E$ ) are given, showing that when an electrical effect is added to the purely osmotic effect of the salt solution in the transport of water from the side of pure water to the solution, the latter possesses a considerable negative charge which increases with increasing valency of the anion of the salt and diminishes with increasing valency of the cation. It is also shown that a similar valency effect exists in the diffusion potentials between salt solutions and pure water without the interposition of a membrane.

2. This makes it probable that the driving force for the electrical transport of water from the side of pure water into solution is primarily a diffusion potential.

3. It is shown that the hydrogen ion concentration of the solution affects the transport curves and the diffusion potentials in a similar way.

4. It is shown, however, that the diffusion potential without interposition of the membrane differs in a definite sense from the P.D. across the membrane and that therefore the P.D. across the membrane ( $E$ ) is a modified diffusion potential.

5. Measurements of the P.D. between collodion particles and aqueous solutions ( $\epsilon$ ) were made by the method of cataphoresis, which prove that water in contact with collodion particles free from protein practically always assumes a positive charge (except in the presence of salts with trivalent and probably tetravalent cations of a sufficiently high concentration).

6. It is shown that an electrical transport of water from the side of water into the solution is always superposed upon the osmotic transport when the sign of charge of the solution in the potential across the membrane ( $E$ ) is opposite to that of the water in the P.D. between collodion particle and water ( $\epsilon$ ); supporting the theoretical deductions made by Bartell.

7. It is shown that the product of the P.D. across the membrane ( $E$ ) into the cataphoretic P.D. between collodion particles and aqueous solution ( $\epsilon$ ) accounts in general semiquantitatively for that part of the transport of water into the solution which is due to the electrical forces responsible for anomalous osmosis.