These results were then plotted as can be seen by the accompanying figure.

Conclusions.

Of all the fractional precipitational methods studied up to the present time, the chromate and phosphate show the greatest efficiency.

Fractional crystallization methods are being carried on in order to investigate the curves obtained by plotting solubilities against atomic weights.

DURHAM, N. H.

NEGATIVE OSMOSE.

By F. E. BARTELL.

Received February 5, 1914.

In the usual osmotic experiments, a solution is separated from the solvent by means of a semipermeable membrane and there is produced, as a result, a flow of liquid through the membrane. The flow of the liquid, as a whole, is toward the more concentrated solution tending, thereby, to increase the volume of the more concentrated solution. This phenomenon is commonly known as osmosis; however, when referred to in this paper, it will be designated as *positive osmose*. In some of the experiments described in this paper the direction of flow of the liquid, as a whole, through the membrane is not in the direction usual in the process of osmosis but is, on the contrary, from the concentrated to the more dilute solution. This latter mentioned phenomenon will be referred to as *negative osmose*.[1]

Numerous experiments have been carried out in this laboratory in an attempt to determine the maximum size of the capillary pores in membranes with which small but definite osmotic effects can be obtained. Plain unglazed porcelain membranes and membranes of porcelain clogged with various insoluble precipitates have been investigated.[2] The main object of these experiments has been to determine the relation of pore diameter to osmotic effects produced when these different membranes are used with one and the same solute (sugar).

An attempt has been made in the present investigation to determine the relation of pore diameter to osmotic effect, when different solutes are used with one and the same grade of unglazed porcelain membranes. The value of the pore diameter of the porcelain selected was near the border line between osmotic effect and no osmotic effect for sugar solutions.

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[1] The terms positive osmose and negative osmose were used by Graham to describe similar phenomena in connection with his work on "Osmotic Force." *Phil. Trans.*, 144, 177 (1854).

[2] Bigelow and Bartell, THIS JOURNAL, 31, 1194 (1909). Bartell, *J. phys. Chem.*, 16, 318 (1912).

Apparatus and Method.

The porcelain was found to be very uniform in structure, the pore diameters being approximately 0.2 micron (*i. e.*, in the area exposed, 1.54 sq. cm., 100 to 125 pores had diameters greater than 0.2 micron).[1] The thickness of the membranes was approximately 5 mm.

The cells used in the osmotic tests were of the simple form shown in Fig. 1. *A*, is a glass cylinder 15 mm. internal diameter with a capacity of about 6.5 cc. The procelain membrane *B* is held in place by a tight fitting rubber band which is in turn held firmly to the cell and to the membrane with copper wire. The outlet tube for measuring the osmotic effect is a capillary of 2 mm. internal diameter. The cell was supported about 15 mm. from the bottom of the beaker (800 cc.) by a tripod of heavy copper wire. A mark, *C*, was made on the capillary tube 50 mm. above the rubber stopper. At the beginning of an experiment the cell was filled to the mark on the capillary tube and the tripod was so adjusted that the surface of the liquid in the beaker was on a level with the liquid in the tube. Rise of liquids in the tubes, due to capillarity, was in no case greater than 8 mm. No corrections were made for capillary ascension in any of the following experiments, consequently, rise of liquids in the tubes to heights of 8 mm. or less cannot be interpreted as indicating osmotic effects: The heights of the liquids in the capillaries were read with a millimeter scale and estimated to 0.5 mm. The temperature, while not constant, was held at approximately 20°. Slight changes in temperature were not taken into consideration, inasmuch as all the experiments in each set were run simultaneously and comparative values only were desired. The volume of the liquid in the beakers in all the experiments was 750 cc. Loss of liquid from the beakers by evaporation was reduced to a minimum by the use of tightly fitting cardboard covers. Before starting the osmotic experiments, distilled water was drawn through the membranes by means of suction for at least 12 hours. No attempt was made to obtain maximum or quantitative effects, qualitative and comparable values only being sought. The results so obtained, however, have brought out some rather unexpected relations which seem sufficiently promising to warrant a further and more exacting research of a truly quantitative nature along similar lines.

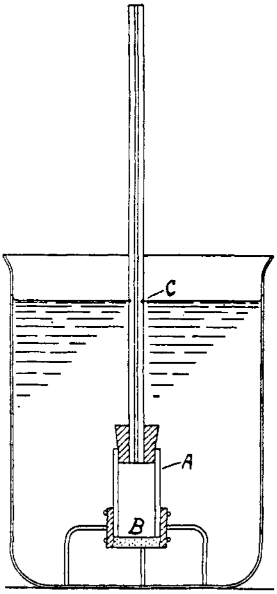

Fig. 1.

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[1] *Loc. cit.*

Experimental.

Cells constructed as above described were filled with sugar solutions of concentrations M,[1] M/5, M/20 and M/50. These cells were then placed in distilled water and tested. Positive osmotic effects were obtained with each of the solutions, the magnitude of the effects varying with the concentration. In the subsequent experiments the same grade of porcelain was used with solutions of sulfates, chlorides and nitrates of K, NH_4, Na, Li, Zn, Mn and Mg; also with acetates of K, NH_4, Na, Zn and Mn.

The salt solutions were put into the osmotic cells which were then placed in the beakers containing distilled water. The results, which are given in Tables I, II, III, IV, V, VI and VII, are expressed in millimeters and represent rise (+) or fall (—) from the zero mark (mark *C*) on the capillary tube:

TABLE I.

Concentration M/10.	Chlorides (solution in cell).						
	KCl.	NH_4Cl.	NaCl.	LiCl.[2]	$ZnCl_2$.	$MnCl_2$.	$MgCl_2$.
Apr. 11, 9 P.M.	0	0	0	0	0	0	0
Apr. 12, 9 P.M.	6	4	—4	— 9	—19	—17	—15
Apr. 13, 9 P.M.	12	6	—8	—18	—29	—29	—29
Apr. 14, 9 P.M.	20	12	—8	—24	—33	—35	—37.5
Apr. 15, 9 P.M.	25	15.5	—8	—27	—36.5	—39.5	—43
Apr. 16, 9 P.M.	27	17	—7.5	—29	—38.5	—43	—48
Apr. 17, 9 P.M.	28.5	19.5	—7	—31	—40.5	—46	—51
Apr. 18, 9 P.M.	28.5	20	—7	—32	—41.5	—47.5	..
Apr. 19, 9 P.M.	28	21	—7	—35	—44.5	—50	..
Apr. 20, 9 P.M.	27.5	21	—7	—34	—45	..	..
Apr. 23, 9 P.M.	26	21	—7	—34	—45	..	..

TABLE II.

Concentration M/10.	Nitrates (solution in cell).						
	KNO_3.	NH_4NO_3.	$NaNO_3$.	$LiNO_3$.	$Zn(NO_3)_2$.	$Mn(NO_3)_2$.	$Mg(NO_3)_2$.
Apr. 11, 9 P.M.	0	0	0	0	0	0	0
Apr. 12, 9 P.M.	11	5	—2	—18	—11	—15	—15.5
Apr. 13, 9 P.M.	21	11.5	—6.5	—33	—19	—26	—23
Apr. 14, 9 P.M.	32.5	19.5	—8	—44	—26	—32	—29
Apr. 15, 9 P.M.	39.5	26	—8	—50	—31	—37	—33
Apr. 16, 9 P.M.	43	29.5	—6	..	—34	—40	—36
Apr. 17, 9 P.M.	45	32	—5	..	—39	—44	—39
Apr. 18, 9 P.M.	47	33.5	—5	..	—42	—45	—41
Apr. 19, 9 P.M.	45	33.5	—5	..	—45	—49	—45
Apr. 20, 9 P.M.	45	33.5	—5	..	—47.5	—50	—46
Apr. 23, 9 P.M.	45	33	—5	..	—50	..	—48

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[1] M, is used to indicate molecular normal.

[2] Other sets of experiments with these chloride solutions have since been carried out in a similar manner. In all the subsequent experiments LiCl was found to give greater negative effects (*i. e.*, greater negative osmose) than $ZnCl_2$, $MnCl_2$ or $MgCl_2$. The exceptional order of LiCl in this set of experiments is due to some cause unknown to the author. The original values are given in the tables in order to preserve the data of the entire series of experiments which were carried out simultaneously.

TABLE III.

Concentration M/10. Sulfates (solution in cell).

	K_2SO_4.	$(NH_4)_2SO_4$.	Na_2SO_4.	Li_2SO_4.	$ZnSO_4$.	$MnSO_4$.	$MgSO_4$.
Apr. 11, 9 P.M.	0	0	0	0	0	0	0
Apr. 12, 9 P.M.	41	37	27	16.5	0	2	4
Apr. 13, 9 P.M.	67.5	57	42.5	27	—3	—2	2
Apr. 14, 9 P.M.	89	72	55	37.5	—4	—2	1
Apr. 15, 9 P.M.	99.5	80	61	43	—6	—4.5	—1
Apr. 16, 9 P.M.	103	82	62	46	—7	—6	—2
Apr. 17, 9 P.M.	105	84	62	46.5	—8	—9	—4
Apr. 18, 9 P.M.	103	83	60	46	—8	—9	—5
Apr. 19, 9 P.M.	98	80	58	44	—8	—9	—5
Apr. 20, 9 P.M.	96	80	57	43.5	—8	—9	—5

TABLE IV.

Concentration M/5. Sulfates (solution in cell).

	K_2SO_4.	$(NH_4)_2SO_4$.	Na_2SO_4.	Li_2SO_4.	$ZnSO_4$.	$MnSO_4$.	$MgSO_4$.
May 17, 9 P.M.	0	0	0	0	0	0	0
May 18, 9 P.M.	54	43	29	3	—12	— 9	— 7.5
May 19, 9 P.M.	80	62.5	43	3	—16	—13	—11
May 20, 9 P.M.	89	72	49	1	—20	—16	—14
May 21, 9 P.M.	92	75	51	0	—22	—18	—16
May 22, 9 P.M.	91	75	51	0	—24	—19	—17

TABLE V.

Concentration M/2. Sulfates (solution in cell).

	K_2SO_4.	$(NH_4)_2SO_4$.	Na_2SO_4.	Li_2SO_4.	$ZnSO_4$.	$MnSO_4$.	$MgSO_4$.
May 24, 9 P.M.	0	0	0	0	0	0	0
May 25, 9 P.M.	47.5	41	23	4	—12.5	—10.5	— 7
May 26, 9 P.M.	61	51	30	3	—15	—12	—13
May 27, 9 P.M.	81.5	68	40	0	—21	—16	—19
May 28, 9 P.M.	82	69.5	40	0	—23	—18	—21
May 29, 9 P.M.	81	69.5	39	0	—28	—24	—25

TABLE VI.

Concentration M/10. Acetates (solution in cell).

	$KC_2H_3O_2$.	$(NH_4)C_2H_3O_2$.	$NaC_2H_3O_2$.	$Zn(C_2H_3O_2)_2$.	$Mn(C_2H_3O_2)_2$.
May 31, 9 P.M.	0	0	0	0	0
June 1, 9 P.M.	73	48	39	—13	—10
June 2, 9 P.M.	99	53	51	—18	—14
June 3, 9 P.M.	115	55	60	—20	—15
June 4, 9 P.M.	121	55	64	—22	—16
June 5, 9 P.M.	122	55	64.5	—23	—17
June 6, 9 P.M.	123.5	55	65	—24.5	—18
June 7, 9 P.M.	123	54	65	—26	—20
June 8, 9 P.M.	123	53	64.5	—28	—21
June 9, 9 P.M.	121.5	51	64	—28.5	—21

It is noted that all the potassium and ammonium salts investigated gave positive osmose, sodium sulfate and sodium acetate gave positive osmose, lithium sulfate was also positive. All the other salts investigated gave negative osmose. The magnitudes of the negative effects are obviously greater than can be accounted for by differences in density or differences in surface tension of the solutions, in these instances, then the so-called exosmotic current is greater than the endosmotic current. The lowering of the liquid column is of considerable magnitude and must indicate a negative pressure within the cell. In order to obtain better data relative to the direction of flow, pure water was placed within the cells and the salt solutions (750 cc.) outside. The results obtained with this arrangement are as follows:

TABLE VII.

Concentration M/10. Chlorides (solution outside).

	KCl.	NH_4Cl.	$NaCl$.	$LiCl$.	$ZnCl_2$.	$MnCl_2$.
May 17, 9 P.M.	0	0	0	0	0	0
May 18, 9 P.M.	1	0	16	20	20.5	20.5
May 19, 9 P.M.	4	2	21	31.5	23.5	24.5
May 20, 9 P.M.	5	4	24	37.5	23.5	25
May 21, 9 P.M.	5	4	24	40	23	24.5
May 22, 9 P.M.	5	3.5	24	41	22.5	24
May 23, 9 P.M.	5	3.5	24	41	20	22.5

TABLE VIII.

Concentration M/5. Chlorides (solution outside).

	KCl.	NH_4Cl.	$NaCl$.	$LiCl$.	$ZnCl_2$.	$MnCl_2$.
May 24, 9 P.M.	0	0	0	0	0	0
May 25, 9 P.M.	5	1	20	29	15	15.5
May 26, 9 P.M.	9.5	5.5	25.5	43	18.5	19
May 27, 9 P.M.	12	8	28	52	20.5	20.5
May 28, 9 P.M.	12.5	7.5	28	53.5	20	20
May 29, 9 P.M.	12.5	7.5	28	53.5	20	19

TABLE IX.

Concentration M/10. Nitrates (solution outside).

	KNO_3.	NH_4NO_3.	$NaNO_3$.	$LiNO_3$.	$Zn(NO_3)_2$.	$Mn(NO_3)_2$.	$Mg(NO_3)_2$.
May 7, 9 P.M.	0	0	0	0	0	0	0
May 8, 9 P.M.	—3	—3	11	21	9	12	12
May 9, 9 P.M.	0	0	16.5	36	15.5	17	19
May 10, 9 P.M.	1	1	19	44	18	18	21
May 11, 9 P.M.	1	1	19	46	18	18	21
May 12, 9 P.M.	1	1	19	47	18	17	20
May 13, 9 P.M.	1.5	1.5	19	48	18	17	20
May 14, 9 P.M.	1	1	17	46.5	17	15	18
May 15, 9 P.M.	0	1	16	45	16	13	16

TABLE X.

Concentration M/5. Nitrates (solution outside).

	KNO_3.	NH_4NO_3.	$NaNO_3$.	$LiNO_3$.	$Zn(NO_3)_2$.	$Mn(NO_3)_2$.	$Mg(NO_3)_2$.
May 17, 9 P.M.	0	0	0	0	0	0	0
May 18, 9 P.M.	0	1	17	33	9	7.5	10
May 19, 9 P.M.	2	3	23	46	12	8	12
May 20, 9 P.M.	3	4	25	52	13	7	12
May 21, 9 P.M.	4	4	25	55	13	6	12
May 22, 9 P.M.	3	3.5	24.5	55	13	6	11.5
May 24, 9 P.M.	3	3	22.5	53	12	5	9

TABLE XI.

Concentration M/2. Sulfates (solution outside).

	K_2SO_4.	$(NH_4)_2SO_4$.	Na_2SO_4.	Li_2SO_4.	$ZnSO_4$.	$MnSO_4$.	$MgSO_4$.
May 29, 9 P.M.	0	0	0	0	0	0	0
May 30, 9 P.M.	−2	−1	0.5	4.5	5.5	4.5	4.5
May 31, 9 P.M.	−4	−2	0.5	6	8	8	8
June 1, 9 P.M.	−3.5	−2	0.5	5.5	8.5	10	9
June 2, 9 P.M.	−4.5	−3.5	0.5	5.5	9	11	10
June 3, 9 P.M.	−5	−5	0.5	5	10	12	10.5
June 4, 9 P.M.	−5	−5	0.5	5	10	12	10
June 5, 9 P.M.	−5	−5	0.5	5	9.5	13	10

TABLE XII.

Concentration M/10. Acetates (solution outside).

	$KC_2H_3O_2$.	$NH_4C_2H_3O_2$.	$NaC_2H_3O_2$.	$Zn(C_2H_3O_2)_2$.	$Mn(C_2H_3O_2)_2$.
Oct. 20, 9 P.M.	0	0	0	0	0
Oct. 21, 9 P.M.	−13.5	−9	−5	6	6
Oct. 22, 9 P.M.	−19.5	−12	−6	6.5	7
Oct. 23, 9 P.M.	−20	−13	−6	7	8
Oct. 24, 9 P.M.	−21	−14	−6	6.5	9
Oct. 25, 9 P.M.	−21	−15	−6	6	9.5
Oct. 26, 9 P.M.	−21	−15	−6	5.5	9.5
Oct. 27, 9 P.M.	−20	−15	−6	5	9

The conditions of the above experiments were such that, had perfect semipermeable membranes been used, positive osmose theoretically should have been obtained in every case. The magnitude of the effects, although of the same order, would not have been identical, inasmuch as the solutions were not isotonic (owing to dissociation). The membranes used in these experiments were not semipermeable in the true sense of the word, but permitted the solute to diffuse outward into the pure water. In some cases this *diffusion produced a negative osmotic current which was greater than the positive osmotic current* and resulted in a flow of liquid which increased the volume of the dilute solution. This flow continued even though opposed by hydrostatic pressure which was in some instances as great as 50 millimeters. It seems reasonable to suppose, however, that there is in all cases a tendency to produce positive osmotic effects but that this tendency is, in those instances in which we obtain negative osmose, exceeded by some force which more than counterbalances the positive osmotic tendency.

From the above data it appears that the magnitude of negative osmose is closely related to the migration velocities of the ions. When the cations of the nitrate or chloride solutions are arranged in the order of increasing negative osmose values, this order is found to be the reverse of the order of increasing migration velocity values of these cations. It may be stated then that the greatest negative osmose is obtained with those solutions (of nitrates and chlorides) in which we have the greatest difference between the migration velocities of cation and anion. The sulfate and acetate solutions seem to offer some exceptions to the above rule; consequently, factors other than ionic migration velocities must also be taken into consideration to account for the order of negative osmose of these solutions.

Diffusion of Salt through the Membranes.—Experiments were carried out to determine the extent of salt diffusion during the negative osmotic flow. Pure water was placed within the cells, chloride solutions outside. Equivalent quantities of chloride solutions were used and showed a maximum pressure at the end of six days. The amount of chloride which had diffused into the cells during this period was determined by titrating the contents of the cells with standard $AgNO_3$ solution (M/10). The results are given in Table XIII. Column 2 gives the number of cc. of M/10 $AgNO_3$ solution which was required to precipitate the chloride which had diffused into the cell during the experiment (six days). Column 3 gives the relative equivalent quantities of chlorides which had diffused into the cells (KCl = 1):

TABLE XIII.

	Cc. $AgNO_3$ required.	Equivalents of salt diffused.
M/5 KCl	3.50	1.000
M/5 NH_4Cl	3.00	0.857
M/5 NaCl	2.80	0.799
M/5 LiCl	2.15	0.614
M/10 $ZnCl_2$	2.60	0.743
M/10 $MnCl_2$	2.50	0.714

This experiment brought out the interesting fact that the cells which have the greatest flow of liquid, as a whole, into them (when set up in this reverse order) have, on the other hand, the smallest quantities of the salts diffusing into them.

Nernst[1] pointed out that the diffusion velocity of salts is proportional to the product of the velocities of the cation and anion. J. C. Graham[2] has shown experimentally that this generalization holds for a large number of salts investigated by him and also that, when the cations and anions are arranged according to diffusion velocities, the order is very similar to that when they are arranged according to their mobilities under influence of electric potential. That this order is also similar to the order of diffusion quantities of the corresponidng salts through porcelain membranes is shown by the following table. Column 1 gives values representating relative diffusion velocities of the salts (Graham). Column 2 gives the relative ionic migration velocities of the cations (Arrhenius). Column 3 gives the ratio of equivalent quantities of salts which diffused through the porcelain membranes:

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[1] *Z. physik. Chem.*, **2**, 613 (1888).

[2] *Ibid.*, **59**, 691 (1907).

TABLE XIV.

Salt.	1.	2.	3.
KCl	1.000	1.000	1.000
NH_4Cl	0.984	0.983	0.857
NaCl	0.744	0.673	0.799
LiCl	0.718	0.517	0.641
$ZnCl_2$	0.558	0.722	0.743
$MnCl_2$	0.584	...	0.714

Dutrochet[1] was the first to give an account of negative osmose with inorganic membranes (1827).

Thomas Graham[2] observed a negative osmotic flow in connection with his work with solutions of electrolytes and porcelain membranes. He did not, however, measure either positive or negative pressures; in fact, he prevented inequality of pressure on the membrane by keeping the level of the water adjusted to the height of the liquid in the "osmometer" tube and measured only the change in volume of the solution. The apparent irregularities obtained with porcelain membranes and solutions of electrolytes were believed by him to be due mainly to chemical interaction between electrolyte and membrane. Solutions of alkalies gave negative effects and it was believed that "The caustic alkalies have probably too strong a disorganizing action upon the septum to allow osmose to proceed undisturbed." Owing to the unsatisfactory behavior of the porous membranes he did not give results of his "numerous experiments which had been made with the earthen osmometer" but confined his data to work with other membranes which had proved less troublesome. In general, the results obtained by Graham with porcelain membranes are very similar to the results given in this paper. The irregularities encountered by him can be explained by use of the theory which is outlined in the theoretical part of this paper and which is offered to account for the behavior of solutions of electrolytes in the osmotic cells of porcelain above described.

Relation of Pore Diameter to Negative Osmose.—A number of experiments have been carried out to determine to what extent pore diameter effects negative osmose. With M/10 $MgCl_2$ solutions, and with porcelain membranes having pore diameters greater than 0.4 micron, no apparent osmotic effects were obtained. With pore diameters between 0.4 and 0.1 micron negative osmose was noted. By using a denser grade of porcelain, one with pore diameters somewhat less than 0.1 micron, positive osmose was obtained, *i. e.*, the flow was in the direction that is usual with osmotic experiments when "semipermeable" membranes are used. It seems probable, therefore, that negative osmose with $MgCl_2$ solution predominates only when pore diameters of the membrane lie between the 0.1 and 0.4 micron

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[1] *Ann. Chim.*, **35**, 393 (1827).

[2] *Phil. Trans.*, 144, 177 (1854).

value. With pore diameters greater than 0.4 micron there is no measurable flow through the membrane. With pore diameters somewhat less than 0.1 micron positive osmose predominates.

Theoretical.

A consideration of the above described experiments makes it seem probable that the phenomenon of negative osmose is closely related to the process of electric endosmose and that the flow of liquid through the membrane is brought about by a difference in electric potential, the two ends of the capillaries of the membrane becoming, in some way, oppositely charged.

Potential differences have been shown to exist in such membranes as animal cells,[1] frog muscle,[2] vegetable skins,[3] and other living tissue;[4] also membranes of copper ferrocyanide,[5] clay[6] and other insoluble substances. Nernst's theory of potentials in which use is made of the well known formula, $E = \frac{RT}{nF} \frac{U - V}{U + V} \ln \frac{C_1}{C_2}$,[7] together with the theory of selective permeability of the ions, has been employed in practically all such cases to account for this phenomenon.

While Nernst's theory may account for the difference in potential existing between two solutions of different concentrations it does not, alone, account for the polarization of the capillaries and flow of solution through the membrane. The polarization of such membranes has been ascribed by Perrin[8] to be due to contact electrification, the potential of the wall being largely dependent upon the preponderance of H ion or OH ion. Girard[9] found that this theory satisfactorily accounted for the direction of flow of various solutions in osmotic experiments with membranes of pig bladder. Unquestionably the relative absorption of the cations and anions by the membrane must also be taken into consideration in order to account for the polarization; however, it appears that this adsorption is closely related to ionic migration velocities.

Cohen[10] was led to the conclusion that a substance having a lower dielectric constant than the liquid in which it is placed assumes a nega-

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[1] Oker-Blom, *Pflüger's Archiv.*, **84**, 191 (1901). Ostwald, *Z. physik. Chem.*, **6**, 71 (1890).

[2] Brünings, *Pflüger's Archiv.*, **48**, 241 (1903).

[3] Loeb and Beutner, *Science*, **34**, 866.

[4] Lillie, *Am. J. Physiol.*, **28**, 194 (1911). Girard, *Revue générale des Science*, **20**, 694 (1909).

[5] Beutner, *J. Phys. Chem.*, **17**, 344 (1913).

[6] Brünings, *Pflüger's Archiv.*, **117**, 409 (1907).

[7] Nernst, *Z. physik. Chem.*, **9**, 137 (1892).

[8] *J. chim. phys.*, **2**, 601 (1904).

[9] *Loc. cit.*

[10] *Wied. Ann.*, **64**, 217 (1898).

tive charge. Porcelain placed in water would give the Helmholtz double layer,[1] the porcelain bearing the negative charge, the outer layer of water the positive charge. It has been shown by Perrin[2] that a porous membrane in sufficiently strong acid solution becomes charged positively, while in sufficiently strong alkaline solution the membrane becomes charged negatively. Electric endosmose with a porcelain membrane and a sufficiently strong acid solution produces, then, a flow of solution through the membrane from cathode to anode; with an alkaline solution the direction of flow is from anode to cathode.

The sign of the charge on a membrane depends, undoubtedly, on the relative adsorption of cation and anion. The membrane becomes positive if the cation, and negative if the anion, is adsorbed to the greater extent.[3] By taking into consideration the relative adsorption of all ions present the polarization of the membrane and the direction of flow of the solution can thus be accounted for. If we assume, for instance, that adsorption of relatively more cation than anion were to take place at one end of a capillary, that end would become charged positively and would, therefore, function as does the anode in the process of electric osmose. The direction of flow through a tube so polarized would be toward the end charged negatively. In the various salt solutions the differences in potential would, to a large extent, depend on the relative adsorption of the ions by the walls of the tube and on the concentration of the solutions. To account for the relative osmose of the sulfates, chlorides and nitrates in the above experiments we must assume that relatively more sulfate ion is adsorbed than chloride or nitrate ion.[4] In a porcelain membrane we are undoubtedly dealing with a somewhat complex system of short capillaries;[5] however, the same reasoning can be applied.

The well known fact that the amount of a dissolved substance adsorbed by a solid mass increases much more slowly than the concentration of the solution would account for the comparatively slight differences of osmose with the different concentrations.

Summary.

1. Salt solutions of sulfates, chlorides, nitrates and acetates were placed in osmotic cells which were constructed of porcelain membranes of the same degree of porosity. Some of the solutions gave positive osmose, *i. e.*, the direction of flow of liquid was from the dilute to the more concen-

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[1] *Wied. Ann.*, 7, 351 (1879).

[2] *Loc. cit.*

[3] Bancroft, *J. Phys. Chem.*, 16, 312 (1912).

[4] These results are in accord with assumptions made by Bancroft in order to explain some apparent exceptions to the general rule in experiments of electric osmose. *Loc. cit.*

[5] Bigelow, THIS JOURNAL, 29, 1675 (1907).

trated solution; others gave negative osmose; the direction of flow in these unusual cases was from the concentrated to the more dilute solution.

2. Cells were set up with pure water inside and salt solutions outside. When set up in this reversed manner, the solutions which had previously given decreased pressure within the cells now gave increased pressure, that is, the direction of flow was from concentrated to dilute solution even though opposed by hydrostatic pressure.

3. The quantities of the salts which diffused through the membranes were determined. It was found that the order of diffusion quantities of the salts through the porcelain membranes is practically the same as the order of diffusion velocities when no membrane is present. Also it was found that the membranes which have the greatest negative osmose through them have, on the other hand, the smallest quantities of salts diffusing through them.

4. The flow of the solution as a whole through the membrane, in all the experiments with the nitrates and chlorides, was toward the more dilute solution, provided the anion had a somewhat greater migration velocity than the cation; also the greater the difference between the migration velocities of anion and cation the greater the rate of flow.

5. It has been shown that the appearance of negative osmose is dependent on the pore diameter of the membrane. Negative osmose of $MgCl_2$ in neutral solution, and with porcelain membranes, predominates only when the pore diameters are somewhat less than 0.4 micron.

6. The facts brought out in this investigation seem to indicate that negative osmose is dependent on the electrical polarization of the capillaries of the membrane, also it seems probable that this polarization is largely brought about through ionic adsorption by the membrane.

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NOTE.

Convenient Standard End Point in the Titration of Alkali Carbonates with Hydrochloric Acid.—As long ago as 1897, Küster[1] pointed out that, in the titration of sodium carbonate against hydrochloric acid, when equivalent amount of acids and base have been used, the solution contains free carbonic acid, and that this acid exerts an appreciable effect on the color of an aqueous solution of methyl orange. A tenth normal solution of carbonic acid, which results from titration with fifth normal solutions, is a little more than saturated with carbon dioxide at 20°.

Küster recommends adjusting the color of the solution obtained in titration to that of a saturated aqueous solution of carbon dioxide containing methyl orange. Unfortunately, this standard end point is not permanent, even in corked vessels, owing probably both to the escape of carbon dioxide

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[1] *Z. anorg. Chem.*, 13, 141 (1897).