3. As a natural consequence of the conclusions noted in (1) and (2), a curious relation was found to exist, *i. e.*, that the density of solutions containing appreciable amounts of each constituent is dependent principally upon the total concentration of the two solutes, and is almost independent of their proportion. (See Table II.) Thus, a solution containing 50 g. per kg. of copper sulfate and 150 of sulfuric acid has practically the same density (1.1355) as has a solution containing 100 g. per kg. of copper sulfate and 100 of sulfuric acid (1.1350). This simple relation, which is apparently only a mathematical coincidence, has been used as the basis for the curve shown in Fig. 2 in which the total concentration, in g. per liter,[1] of copper sulfate plus sulfuric acid is plotted against the density, yielding an almost straight line. The application of such a curve, or of the table derived from it (Table III) in determining the composition of unknown solutions, is obvious, involving only a determination of the density and acidity, the latter then being deduced from the total concentration corresponding to the observed density, to obtain the copper sulfate concentration.

Details of the application of this table in the regulation of electrolytic copper baths will be given in the second edition of Bureau of Standards *Circular* **52**.

In conclusion, the authors desire to acknowledge their indebtedness to Dr. William Blum and Mr. H. W. Bearce under whose direction this investigation was made.

WASHINGTON, November 27, 1915.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN.]

THE RELATION OF OSMOSE OF SOLUTIONS OF ELECTROLYTES TO MEMBRANE POTENTIALS. THEORETICAL.

BY F. E. BARTELL AND C. D. HOCKER.

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The fact that the osmose of solutions of electrolytes shows a close relationship to the differences of potential, which have been found to exist between the two faces of membranes separating such solutions from water, lends support to the theory that the osmose of such solutions is largely dependent upon the electrical condition of the membrane in question. In attempting to explain the osmose of salt solutions by an electrical theory similar to that used to account for electric osmose, two determining factors must be considered: (1) the electric charge of the membrane ma-

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[1] Obviously, the above relation exists whether the concentration is expressed in g. per kg. or g. per liter. The data shown in Fig. 2 and Table III have been calculated to g. per liter since the results of the analysis of solutions are usually expressed in that form.

terial with respect to the liquid layer along the capillary tubes of the membrane (*i. e.*, the value of the electrical double layer existing between the membrane and solution), and (2) the polarization of the membrane (*i. e.*, the difference of potential existing between the two faces of the membrane).

Cohen[1] was led to the conclusion that a substance having a lower dielectric constant than the liquid in which it is placed assumes a negative charge. Porcelain, then, placed in water would bear a negative charge and the outer layer of water the corresponding positive charge. The value of this charge is materially altered by traces of acids or alkalies. Perrin[2] concluded that a concentration of 0.000001 M acid or alkali is great enough to determine the sign of the charge of such a membrane as porous chromium chloride. He suggested that a close analogy exists between the effect of ions on the charge of the membrane and the precipitative power of ions for colloids. Both are generally believed to be due to an alteration of the charge of the solid phase by adsorption of the charged ions.

Undoubtedly, then, the sign of the charge on the membrane is influenced by the relative adsorption of the cation and anion from the solution of the electrolyte with which the membrane comes in contact. Bancroft[3] has been led to the conclusion that adsorption is a specific process, the neutralization of the charge on a given colloid depending on the nature of the colloid, and upon the nature of both cation and anion. These considerations throw some doubt on the generally recognized belief that hydrogen and hydroxide ions are always adsorbed more than other ions, and hardly justifies the view held by Perrin[4] and Girard[5] that the sign of the charge of a body in media of various electrolytes is always attributable to a small preponderance of H or OH ions.

Although the porcelain membranes used in this work probably cannot be termed true colloidal substances, a close analogy is not essential to the conception of their contact electrification in water or solutions. The fundamental ideas used here to explain the unusual osmotic effects observed has as its basis the contact electrification of the porcelain. That the porcelain used in the osmotic experiments actually carries a negative charge has been shown conclusively by the unpublished researches carried out in this laboratory. In neutral solution, under stress of potential, particles of the porcelain finely ground have been found to move toward the anode as though charged negatively. When suspended in very dilute nitric acid they still migrate as though charged negatively, but with a

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

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

[3] *J. Phys. Chem.*, **19**, 394 (1915).

[4] *Compt. rend.*, **136**, 1447 (1903).

[5] *Ibid.*, **146**, 927 (1908).

smaller velocity. The velocity at which they migrate becomes smaller and smaller as the concentration of the acid is increased, until at a concentration of about (0.002 M they reach a turning point, after which they move in the opposite direction. It is interesting to note, however, that the velocity after the reversal does not increase nearly so rapidly with the increase in the concentration of the acid as the velocity in the opposite direction decreases before the reversal. This is probably due to conduction taking place through the medium of the acid rather than by migration of these particles. The velocity of migration of these particles can hardly be considered as a measure of the charge they carry when the concentration of the electrolyte becomes very great, but this velocity is probably a measure of what the electric osmose would be if the porcelain were in a fixed position as a membrane. Neither can it be stated with certainty that the turning point in the charge of the membrane would be at exactly the same concentration of acid as the turning point of these porcelain particles.

To sum up the above considerations: Porcelain immersed in water bears a negative charge, and the layer of water immediately adjacent, the corresponding positive charge. The sign of the charge of the membrane in solutions of electrolytes is influenced by selective adsorption of the ions. There are many cases which indicate that adsorption is specific and not rigorously a function of the valence of the ions; and also that other cations may be as strongly adsorbed as the hydrion. In the light of these facts is does not seem unreasonable to assume that ions other than H and OH may be considered effective in determining the sign of the membrane; and further, that cations for which the porcelain shows a strong preferential adsorption may decrease the magnitude of the negative charge assumed by the membrane when immersed in water, or may even reverse the electrical sign of the membrane.

If adsorption is considered as instrumental in determining the charge that the membrane assumes with respect to the movable water layer, then the possible effect of adsorption on the orientation of the membrane must also be considered. If there is a strong tendency for a selective adsorption of one of the ions, the end of the membrane in contact with the solution of the electrolyte would have more opportunity to become charged with electricity of the kind carried by that ion than the face of the membrane in contact with water or a much more dilute solution. In the case of a salt for which there is a selective adsorption of the cation the membrane potential would be increased above that of the contact potential provided the anion is more rapidly moving, and decreased if the cation is the more rapidly moving. Conversely, for a salt in which the anion is the more strongly adsorbed, the membrane potential would be greater than Nernst's formula demands provided the cation is the more rapidly moving, and less if the anion has the greater velocity. This speculation leaves unsettled the question whether it is possible to think of the migration velocities of the ions as being independent of the amount of adsorption which the ions undergo, or of being independent of the concomitant charge of the water layer along the capillary spaces of the membrane.

The Assumptions Used in this Paper to Explain the Osmotic Effects Observed.—In the light of the above theoretical considerations, experimental evidences seem to point to certain assumptions as the most reasonable to explain the osmotic effects observed. The assumptions used as a working basis in this paper are summed up in the following:

(1) The abnormal osmose is due primarily to an electrical effect and is analogous to electric osmose.

(2) This osmose is brought about by the passage of a charged liquid layer along the capillary tubes of the membrane. The passage of this liquid layer is caused by the driving force of a difference of potential which acts as though it were set up between the two faces of the membrane.

(3) The charge on the membrane—and hence, the charge on the liquid layer—may be modified or the sign may even be reversed by selective adsorption of the ions of electrolytes; and other ions than H and OH may materially affect the charge on the membrane.

(4) The difference of potential, which seems to act between the two faces of the membrane is primarily due to contact electrification, the magnitude of which is dependent upon a difference of migration velocities of the ions in the membrane. However, this difference of potential may be altered by other factors such as adsorption.

(5) The osmose is related to diffusion, for it seems that diffusion of the ions determines to a large extent the polarization of the membrane.

(6) The extent of osmose may be affected by the relative volumes of water and salt solution on the two faces of the membrane, inasmuch as this factor may affect the diffusion of the salt through the membrane.

The membrane when immersed in water or any electrolyte in which there is little tendency for preferential adsorption of ions bears a negative charge and the water layer adjacent bears a corresponding positive charge. Cations are much more adsorbed than anions, the negative ions with the possible exception of OH and a few polyvalent ones having little effect on the charge of the membrane. The alterations of the charge of the walls of the capillary tubes of the membrane by an adsorbed ion will be greater the higher the concentration of the electrolyte. The potential between the two faces of the membrane will be in the direction that Nernst's theory requires, and will be greater the greater the concentration of the electrolyte unless some effect as adsorption interferes.

If the movable water layer and the solution end of the membrane are charged with electricity of opposite sign then the osmose will be positive; if they are charged with the same sign the osmose will tend to be negative.

Applications of the Assumptions to the Experimental Facts.—By application of the assumptions outlined above, it is possible to ascribe an explanation to most of the osmotic effects observed and described in the preceding paper.

Consider first the osmose of nitrates of different concentrations. Potassium nitrate shows positive osmose increasing continuously as the concentration increases up to 0.05 *M*, after which the osmose decreases. The electrical orientation of the cell is the same at all concentrations, and the difference of potential of the two ends of the membrane is appreciable despite the fact that there is little difference of migration velocities of the ions when the membrane is not considered. Above the concentration of 0.05 *M* the negative charge of the membrane will become materially lessened owing to the selective adsorption of the potassium ion. The positive osmose then decreases as the concentration increases, becoming practically zero or slightly negative at the concentration of *M*. In double cells, in which the volume of water is small on the water side of the membrane, the rate of diffusion of potassium nitrate soon decreases owing to an equalizing of the concentrations of the salt on the two sides of the membrane. Because of this effect on the rate of diffusion, the membrane potential in the double cells is neither as great, nor able to be maintained as long as in single cells. Hence the positive osmose is less and reaches its maximum much more quickly.

Ammonium nitrate acts in all ways analogous to potassium nitrate. It has been shown that sodium and lithium possess little tendency for adsorption with this porcelain,[1] and the osmotic effect of the nitrate decreases as the concentration increases. Negative osmose of greater numerical value is shown by lithium which has the greater difference in migration velocities, and hence the greater cell potential.

The bivalent cations, Zn, Mn, Mg, and Ba, show decreasingly positive effects as the concentration increases; however, the negative effects do not increase nearly so rapidly as the concentration increases. With manganese, for which tests were made at concentrations as high as *M*, the negative effects began to decrease numerically at these higher concentrations. This may be explained by assuming either that the natural tendency to give positive effects, such as sugar displays at these concentrations, causes the numerical decrease in negative osmose; or that at these higher concentrations the manganese ion is adsorbed enough to materially lessen the negative charge of the membrane. The latter explana-

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[1] From unpublished data obtained in this laboratory.

tion can hardly be disregarded when attention is called to the fact that the higher concentrations of sodium and lithium, isotonic with those of manganese, do not tend to give decreasingly numerical negative effects as the concentration increases.

Aluminium and thorium nitrates give positive effects at all concentrations, a fact which indicates that with these solutions the face of the membrane in contact with the solution bears at all times the sign opposite to that of the movable water layer. The measurements of the cell potential for aluminium show that the orientation is the same as that required by the migration velocities, but somewhat larger than migration velocities would require. Hence, the movable water layer must be negative, a condition which is brought about by the adsorption of the polyvalent cation by the membrane, or by the presence of acid in these salt solutions which cannot be prepared neutral.

The osmose of salt solutions which were made to contain small amounts of acids or alkalies in addition to the salt show that the sense of the osmose is not easily determined by the presence of small amounts of acids or alkalies.[1] It has been pointed out that the effect of small amounts of acid or alkali are not additive in producing the resultant osmose. In one case the addition of a certain amount of acid or alkali to a salt may make its osmose more positive, whereas the addition of the same amount of acid or alkali to another salt may make the osmose of that salt less positive. Thus 0.001 *M* nitric acid decreases the positive osmose of 0.1 *M* potassium nitrate and at the same time numerically decrease the negative osmose of 0.1 *M* lithium nitrate. It seems more logical, then, to assume that the alteration of the osmose by the addition of acids or alkalies depends on the alteration of the electric charge on the walls of the capillary tubes of the membrane, rather than upon any additive polarizing effect that would be produced by diffusion of the acid or alkali through the membrane. With potassium nitrate, the presence of OH ions when alkali is added does not decrease the negative charge on the membrane and experiment shows that the positive osmose is not lessened. When acid is added the presence of H ions does decrease the magnitude of the negative charge of the membrane and the osmose is materially decreased. Similarly, for lithium nitrate the presence of acid decreases the negative charge of the membrane, thereby lessening the passage of liquid through the capillary tubes of the membrane, while the presence of alkali does not materially affect this charge. Similar reasoning may be applied to other salts where the effects produced by the addition of small amounts of acid or alkali are conclusive enough to admit of a definite interpretation. With aluminium nitrate the presence of a small amount of acid increases the osmose. This substantiates the supposition that

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[1] The results mentioned in this paragraph are taken from unpublished data.

the membrane is charged positively with this salt and the presence of a small additional amount of acid increases the magnitude of this positive charge.

The effects given by the nitrates of potassium, lithium and barium when the osmose is tested by completely immersing the membranes in acids and alkalies are amenable to similar interpretations. Potassium nitrate gives greater positive effects when the membrane is immersed in alkali than when immersed in acid. The osmose in acid becomes very small or even slightly negative when enough acid is added to reverse the sign of the membrane. Lithium and barium nitrates also show relatively little osmose when the membranes are immersed in larger amounts of acid. When the membranes are immersed in alkalies, lithium nitrate shows greater negative osmose and potassium nitrate shows greater positive osmose than in neutral solution. Barium nitrate offers an exception. With this salt the osmose is lessened numerically, and to about the same extent, by immersing the membrane in either acid or alkali. In the presence of large amounts of either acid or alkali, as 0.01 *M*, the osmose of all of these salts is numerically less than that shown by the salt in neutral solution.

In the osmose of hydrochloric acid alone, the membrane must be assumed to have a positive charge at all concentrations of acid great enough to reverse the sign of the membrane. At concentrations below which the osmose displays a minimum, measurements show that the polarization is in the direction required by Nernst's theory. The movable water layer must then be charged positively and the fact that increase in concentration of acid decreases the osmose may be taken as indication that the greater amounts of acid are decreasing the magnitude of the negative charge of the membrane. At higher concentrations the membrane polarization is found to be the reverse of that required by the migration velocities of the ions, but at these higher concentrations the movable liquid layer must be negative. At these higher concentrations, the solution end of the membrane is charged positively and the movable liquid layer bears the opposite sign, so the positive osmose is accounted for. The reverse orientation of the membrane is probably due to the adsorption of H ions charging the solution face of the membrane positively, this factor becoming greater as the concentration increases, and overcoming the tendency for polarization in the usual direction. This assumption is borne out by the knowledge that H ions are readily adsorbed by the porcelain, and by the observation that when the volume of water on the water side of the membrane is increased, that is, when a condition is brought about that facilitates diffusion of the acid, the positive osmose does materially decrease.

In the osmose of sodium hydroxide alone, it must be assumed that the membrane is negative at all concentrations while the movable liquid layer carries a corresponding positive charge. As the concentrations of this electrolyte are successively increased, the osmose passes through a maximum. Measurements have shown that opposite electrical orientations of the cell exist on the two sides of this maximum. For some reason the cell shows the reverse orientation from that required by difference in migration velocities when low concentrations of the alkali are tested, while at higher concentrations as 0.2 M the orientation is in the usual direction. At concentrations of the alkali lower than 0.01 M, at which the osmose reaches its maximum, the solution side of the membrane is negative, which accounts for the movement of the positively charged liquid layer into the cell. As the concentration of the alkali is increased above 0.01 M, the solution side of the cell becomes less negative until at the higher concentrations, the orientation of the cell becomes reversed. When this condition is reached the positively charged movable liquid layer passes toward the water side of the cell, giving rise to negative osmose.

A series of experiments similar to those above described for porcelain have recently been carried out with animal and vegetable membranes such as gold beaters skin, and parchment paper. The data obtained are, in many respects, similar to those obtained with porcelain. The results may, for most part at least, be explained by making use of the theoretical considerations outlined above. This data will be published in the near future.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN.]

THE OSMOSE OF SOME SOLUTIONS OF ELECTROLYTES WITH PORCELAIN MEMBRANES, AND THE RELATION OF OSMOSE TO MEMBRANE POTENTIAL.[1]

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It has been shown in a previous paper in THIS JOURNAL[2] that some salt solutions with certain grades of porcelain membranes give negative osmose, *i. e.*, 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.

It seems reasonable to suppose that in all osmotic experiments there

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[1] The work described in this article constitutes part of a dissertation submitted by Carl D. Hocker in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] THIS JOURNAL, 35, 646 (1914).