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.

ANN ARBOR, MICH.

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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]

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

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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

[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).

is a tendency to produce positive osmose, but in some cases the force tending to produce counter or negative osmose becomes the greater. With membranes as nearly semipermeable as copper ferrocyanide the tendency to give positive effects may be very much greater than the tendency to give negative effects. However, the force tending to produce counter osmose may be of considerable magnitude, with the result that the measured maximum pressures resulting from the tendency to produce positive osmose may be less than the theoretical values. This, then, may explain the abnormal osmotic pressure values obtained with the salt solutions investigated by the Earl of Berkeley and Hartley,[1] Morse,[2] Fouard,[3] and others.

The diverse osmotic effects shown by solutions of electrolytes with plant and animal tissues, which have been attributed to an alteration of the permeability of the cell walls, may likewise be explained by making use of the same considerations that are used in the explanation of negative osmose.

The main object of the present investigation has been to study the relation of osmose to membrane potential, and to determine in what manner the osmose varies with the concentration of solutions of electrolyte and with the diffusion of such electrolytes out of the cell. Data are also given which show the effect of the presence of acids and bases on the osmose of some salt solutions.

## Experimental.

**Apparatus.**—The osmotic experiments described in this paper were carried out with simple, single compartment cells such as have been described in a previous article.[4]

The porcelain membranes used in all the experiments were made from a fine-grained, unglazed, porcelain plate obtained from a local dealer. The pore diameters of the largest pores of this porcelain[5] were about 0.2 micron.

**The Osmose of Nitrate Solutions of Different Concentrations.**—The osmotic cells, which were of about 6 cc. capacity, were filled with the solutions to be tested and placed in 800 cc. beakers which contained about 750 cc. of water. At the beginning of each experiment the level of the liquid in the outlet tube of the osmometer was adjusted so that it stood about 50 mm. above the stopper of the cell and at the same time level with the surface of the water in the beaker. The volume of the liquid in the beaker was kept constant throughout the experiments by

[1] *Phil. Trans.*, (*A*) **209**, 177, 391 (1908).

[2] "Osmotic Pressures of Aqueous Solutions" (published by the Carnegie Inst. of Washington), 1914, pp. 211–217.

[3] *Bull. soc. chim.*, [4] 11, 249, 216 (1912).

[4] *Loc. cit.*

[5] Bigelow and Bartell, THIS JOURNAL, 31, 1194 (1909).

TABLE I.

Correlation of Maximum and Minimum Effects.

| Conc. | $KNO_3$. | $NH_4NO_3$. | $NaNO_3$. | $LiNO_3$. | $Ba(NO_3)_2$. | $Zn(NO_3)_2$. | $Mn(NH_3)_2$. | $Mg(NO_3)_2$. | $Al(NO_3)_2$. | $Th(NO_3)_4$. | Sugar. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.0005 *M*..... | 40 | 31 | 34 | 34.5 | 41.5 | 35 | 33 | 37.5 | 35.5 | 26 | 26 |
| 0.001 *M*..... | 40 | 35.5 | 43 | 38 | 46.5 | 38 | 37.5 | 41.5 | 29 | 27 | 36 |
| 0.01 *M*..... | 63 | 49 | 45.5 | 30 | 12.5 | 7 | 10 | 14 | 70 | 20.5 | 35.5 |
| 0.02 *M*..... | 71 | 62 | 32 | 17 | — 1 | —13 | — 7 | — 5 | above 175 | 164 | 40 |
| 0.05 *M*..... | 77.5 | 67.5 | 37 | — 2 | —19 | —37 | —32.5 | —29.5 | 291 | 296 | 40 |
| 0.1 *M*..... | 64.5 | 61 | — 3 | —31 | —38.5 | —45.5 | —42 | —45 | 447 | 479 | .. |
| 0.2 *M*..... | 46 | 35.5 | —19 | below —65 | —49 | —50 | —48 | below —52 | ..... | .. | .. |
| 0.5 *M*..... | 15 | 4.5 | —56 | ..... | .. | .. | —31.5 | ..... | ..... | .. | .. |
| *M*..... | —2.5 | 5.5 | —67 | ..... | .. | .. | — 7 | ..... | ..... | .. | .. |
| (U — V)[1]..... | 2.9 | 2.2 | —18.2 | —28.4 | — 6.3 | —15.1 | —17.7 | —15.1 | —21.8 | —38.3 | .. |

TABLE II.

Concentration 0.1 *M*. Solutions of Potassium Salts in Cells.

| Time. (hrs.). | $KNO_3$. | KCl. | KBr. | KI. | KCNS. | $KC_2H_3O_2$. | $K_2SO_4$. | $K_2CrO_4$. | $K_3PO_4$. | $K_4Fe(CN)_6$. | $K_3Fe(CN)_6$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 24 | 24 | 10 | 9 | 5 | 13 | 29 | 37 | 34 | 92 | 41 | 43 |
| 48 | 41 | 28 | 26 | 17 | 36 | 54 | 57 | 55 | 151 | 71 | 78 |
| 72 | 51 | 45 | 41 | 29 | 58 | 72.5 | 78 | 71 | 185.5 | 92 | 104 |
| 96 | 57 | 57.5 | 51 | 37.5 | 74 | 83.5 | 94 | 81.5 | 203 | 104 | 122 |
| 120 | 61 | 66.5 | 60 | 43.5 | 84 | 90 | 104 | 86.5 | 212 | 108 | 134 |
| 168 | 63 | 76 | 68.5 | 53 | 95 | 95 | 113 | 93 | 211 | 113 | 145 |
| 216 | 64.5 | 80 | 71 | 56 | 100.5 | 97 | 115 | 95 | 206 | 113 | 149 |
| (U — V) | 2.9 | —0.7 | —2.9 | —1.7 | —8.0 | 32.6 | —3.7 | .. | .... | .... | .... |

[1] U values as given by A. Heydweiller, *Z. physik. Chem.*, **89**, 281–286 (1915).

careful addition of water from time to time. Maximum or minimum effects were usually obtained within 6 days. The maximum or minimum values, represented in millimeters rise or fall, obtained with nitrate solutions of different concentrations are given in Table I.[1]

The data obtained from the foregoing experiments show the following facts:

Of the nitrate solutions investigated some give positive osmose, attaining a maximum as the experiment proceeds; others give negative osmose, reaching a minimum. At concentrations from 0.0005 *M* to 0.01 *M* all of the solutions tried give positive effects.

The positive effects of potassium and ammonium nitrates increase as the concentration increases from 0.0005 *M* to 0.05 *M*, and then decrease continuously as the concentration increases; sodium nitrate shows a similar maximum at 0.01 *M*, after which the positive effect decreases continuously as the concentration increases; the nitrates of lithium, barium, zinc, manganese, and magnesium give slightly lesser positive effects at 0.0005 *M* than at 0.001 *M*, but attain their maximum at this latter concentration, after which their osmose also decreases.

The positive effects of aluminium and thorium nitrates, and sugar increase as the concentration increases.

At a certain concentration, somewhat different for each salt, all of the nitrates investigated except those of aluminium and thorium, give an effect practically zero. This concentration for potassium and ammonium is about *M;* for sodum, 0.1 *M;* for lithium, 0.05 *M;* for barium, 0.02 *M;* and for zinc, manganese, and magnesium the values of the concentrations lie between 0.02 *M* and 0.01 *M*.

In no case is the decrease in positive effect directly proportional to the increase in concentration. The tendency to give counter effects increases more slowly than the concentration.

The trivalent and quadrivalent cations (aluminium and thorium) give unmistakably greater positive effects than the cations of lower valence after the concentration has been increased to 0.02 *M*, but their effects at lower concentrations are not greater than those of other salts. The salts of all the divalent cations investigated give lesser positive effects than aluminium or thorium above this concentration of 0.02 *M*, but their tendency to give positive effects does not, in turn, exceed those of the univalent cations at this concentration. In the cases of sodium and lithium the counter effects do come to exceed numerically the counter effect of the divalent metals at the concentration of 0.5 *M* or greater, but the osmose of potassium and ammonium nitrates does not become appreciably less than zero at a concentration as great as *M*. It seems,

[1] For purposes of later comparison the values of differences in migration velocities between the cations and anions of these salts (U — V) are appended to the table.

then, that there is no well-defined regularity between the valence of the cations in these salts and the osmotic effects the salts produce.

However, there is some regularity between the difference in migration velocities and osmotic effects. When the value U — V is negative, negative osmose is obtained at some concentration except in the cases of aluminium and thorium nitrates; and, in general, the greater this numerical negative value, the greater the counter osmose. The decreasing positive effect of potassium and ammonium nitrates at concentrations greater than 0.05 *M* is not in accordance with the fact that the U — V value for these nitrates is positive.

**The Osmose of Some Salt Solutions of the Same Cation (Potassium Salts).**—Experiments were carried out to investigate the osmose of salt solutions with a common cation. For these tests potassium salts were employed, and the concentration chosen was 0.1 *M*. These experiments were made with cells submerged in a beaker of water as above described. The results, together with the difference in migration velocities for the ions of some of these salts, are given in Table II.

From the above results it may be pointed out that:

At the concentration of 0.1 *M* all of the potassium salts investigated give positive osmose.

Among the salts with univalent anions, the order of decreasing positive effects is

$$CNS > C_2H_3O_2 > Cl > Br > NO_3 > I.$$

In general, the salts of the anions of higher valence appear to give greater positive effects than the salts of the anions of lower valence though there are exceptions. Thus it was found that potassium phosphate gives greater effects than either the ferro- or ferricyanide, and potassium chromate gives lesser effects than the thiocyanate or acetate.

There seems to be no relation between the difference in migration velocities and the magnitude of the osmose.

**The Osmose of Acids and Alkalies Alone.**—For these tests hydrochloric acid and sodium hydroxide were employed. Carbon dioxide-free water was used to make the solutions of alkali, and the cells were enclosed in bottles of approximately the same diameter as the 800 cc. beakers in which the other experiments had been run. In each case the cell was suspended by its outlet tube from the stopper closing the bottle so that the bottom of the cell was raised about 2 cm. from the bottom of the bottle, which contained about 750 cc. of carbon dioxide-free water; that is, about the same volume as that employed in the tests made in open beakers. A hole in the stopper permitted the access of air to the bottle, and both this opening and the outlet tube of the cell were closed by soda-lime tubes to prevent the absorption of carbon dioxide from the atmosphere. The

experiments with hydrochloric acid were run in open beakers with the same set up as that above described.

Concentrations of both acid and alkali varying from 0.001 *M* to 0.2 *M* were tried, and the results of these experiments are shown in the following tables:

TABLE III.

Osmose of Hydrochloric Acid Alone.[1]

| Time, (hrs.). | 0.001 *M*. | 0.002 *M*. | 0.005 *M*. | 0.01 *M*. | 0.02 *M*. | 0.05 *M*. | 0.1 *M*. | 0.2 *M*. |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 12 | 5 | 8 | 5 | 3 | 2 | 6 | 2 | 1.5 |
| 24 | 10 | 13 | 8.5 | 5 | 2 | 17.5 | 2 | 30 |
| 48 | 16 | 20 | 14 | 6 | 3 | 38 | 2 | 57 |
| 72 | 16 | 23 | 21 | 7 | 5 | 57 | 31 | 88.5 |
| 96 | 22 | 24.5 | 22 | 10 | 5.5 | 66 | 52 | 110 |
| 120 | 23 | 25.5 | 24 | 12 | 6.5 | 69.5 | 64 | 118 |
| 144 | 24.5 | 27 | 24.5 | 14.5 | 7 | 72 | 81 | ... |
| 168 | 25 | 27 | 25 | 15 | 7 | 73 | 83 | 119 |
| 192 | 25 | 27 | 25 | 15.5 | 7 | 73 | 83 | 119 |

From Table III it is noted that:

The osmose of the acid is positive at all concentrations. The osmose is about the same at 0.001 *M* as at 0.005 *M*, but falls as the concentration increases above these values, reaches a minimum at about 0.02 *M*, after which the maximum values of the osmose grow greater as the concentration of the acid increases.

TABLE IV.

The Osmose of Sodium Hydroxide Alone.[2]

| Time, (hrs.). | 0.001 *M*. | 0.002 *M*. | 0.005 *M*. | 0.01 *M*. | 0.02 *M*. | 0.05 *M*. | 0.1 *M*. | 0.2 *M*. |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 12 | 4 | 3 | 3 | 1 | 2 | 1 | —7 | — 4 |
| 24 | 7 | 7.5 | 8 | 6.5 | 11 | 1 | —19 | —29 |
| 48 | 14 | 15 | 19 | 25 | 22 | — 5 | —23 | .. |
| 72 | 20 | 21 | 25.5 | 51 | 29 | — 9.5 | —34 | .. |
| 96 | 23 | 25.5 | 47.5 | 68 | 34.5 | —14 | —40.5 | .. |
| 120 | 25 | 28.5 | 59 | 75 | 39 | —14.5 | —45 | .. |
| 144 | 26 | 30.5 | 65 | 81 | 41.5 | —15 | —45 | .. |
| 168 | 27 | 32 | 68 | 83 | 44.5 | —10 | .. | .. |
| 192 | 27.5 | 32.5 | 67 | 84 | 48 | .. | .. | .. |

From Table IV it is noted that:

The osmose of sodium hydroxide is positive at concentrations of 0.02 *M* or less, and negative at higher concentrations. The osmose increases from 0.001 *M* to 0.01 *M* as the concentration increases, after which the osmotic effect decreases with increase in concentration, becoming negative at 0.05 *M* and increasingly negative at greater concentrations.

[1] Difference in migration velocities (U — V) for the ions of HCl = 252.6.

[2] Difference in migration velocities (U — V) for the ions of NaOH = 130.4.

It is a peculiar fact that the turning point for both the acid and the alkali is at about the same order of concentration, namely 0.01 *M* to 0.02 *M*.

The difference in migration velocities of the ions for both the acid and the alkali being a constant factor at all times, Nernst's theory of potentials would require that the potential due to the contact of two concentrations of a solution should be a logarithmic function of the ratio of their concentrations, and that an increase in this ratio (*i. e.*, an increase in the concentration of the electrolyte in the cell) should increase this potential. This factor of difference in migration velocities in the cases of the acid and alkali is not sufficient to account for the fact that the osmose is not a continuously increasing or decreasing function of the concentration.

**The Osmose of Some Salt Solutions with the Membranes Immersed in Acids or Alkalies of Different Concentrations.**—From the data obtained in the foregoing experiments, considerable regularity seemed to exist in many cases between the osmotic effects and the difference in migration velocities of the ions of the electrolyte solutions. This observation lent support to the assumption that the results produced might be due to an electrical effect, the factor of relative differences in migration velocities giving rise to different membrane potentials. If, however, the direction of the flow of the liquid is similar to the direction in electric osmose, both the polarization of the membrane and the sign and magnitude of the charge of the liquid layer adjacent to the walls of the capillary tubes of the membrane should influence the magnitude and perhaps even the sense of the osmose. This latter factor would probably be influenced by the presence of acids and bases which, according to the theories of Perrin[1] and Girard,[2] is the determining factor of the sign of the membrane.

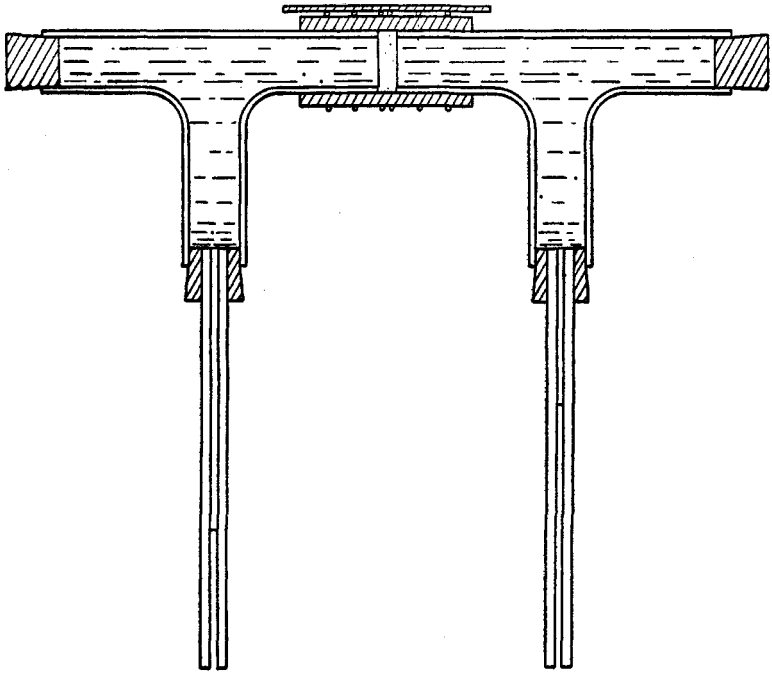
To test this assumption, various attempts were made to determine the osmose of salt solutions with the variation that the membranes of the cells were kept in contact with acids and alkalies. For these tests 0.1 *M* salt solutions were used, and acid and alkali of concentrations varying from 0.0001 *M* to 0.01 *M*. The membranes were first washed by drawing water through them for several hours, after which the acid or alkali of the concentration to be used was drawn through until the membrane in each case was thoroughly saturated. The experiments were then carried out with both faces of the membrane in contact with this acid or alkali while the salt solution to be studied was in contact with one face of the membrane. Attempts were first made to study the effect of the presence of acid and alkalies on the osmose of the salt solutions by employing the same type of cell as had been used in the previous experiments. However, it was found even though great precau-

[1] *Loc. cit.*

[2] *Compt. rend.*, 146, 927 (1908); 150, 1446 (1910); 153, 401 (1911); 159, 99 (1914).

tions were taken to previously saturate the membrane with the acid or alkali solution, that when a cell was filled with this solution and immersed in a bath of the same acid or alkali, there resulted an appreciable osmotic flow.

It was thought that a trace of dissolved membrane material might cause the solution within the cell to become more concentrated in respect to dissolved material, and that this might be the cause of the failure to give alkali blanks. It was found that this effect shown by the acid and alkali blanks could be obviated by the use of cells in which the volumes of solutions on the two sides of the membrane were the same. The type of cell used for this purpose is shown in Fig. 1.



The two compartments are glass T-tubes, each having a capacity of about 20 cc. The porcelain membrane, as in the other cells, is held in place by tightly wound copper wires, and to support the cell upright legs of heavy copper wire are used. Throughout the experiments the cells were kept in a constant temperature bath maintained at 20°. Considerable difficulty was encountered in making the stoppers water tight. In spite of precautions the fall in one outlet tube would, in some cases, be a few millimeters greater than the rise in the other. Because of this source of error, the data obtained with these cells cannot be regarded as quantitative, but this error is never great enough to change the sense, or

even the magnitude, of the osmose by more than a few millimeters. Some of the advantages of this type of cell are as follows: (1) Any leak in the apparatus is readily detected. (2) A change in temperature causes approximately the same rise in both the capillary outlet tubes (*i. e.*, the hydrostatic pressure on the membrane is practically unaltered by any temperature change). (3) In case any membrane material is dissolved the change in concentration will be the same in the two compartments. (4) The openings of the apparatus to the atmosphere are easily protected from entrance of carbon dioxide, etc.—an important factor when alkaline solutions are used. (5) Evaporation of solutions is practically eliminated.

To determine the effect of the presence of acids and bases on the osmose, experiments were made with 0.1 *M* solutions of three typical salts: potassium, lithium and barium nitrates. Table V shows the effect of these salts with this type of cell in neutral solutions, in hydrochloric acid, and in sodium hydroxide of different concentrations. A positive effect signifies a flow of solution toward the side of the membrane in contact with the salt solution, and a negative effect signifies a passage of solution in the opposite direction. Maximum and minimum values were usually obtained after five or six days. The osmose is expressed in millimeters and the values given are half the difference in height of the water levels in the two outlet tubes. The actual hydrostatic pressure is twice this value.

TABLE V.

Comparison of Maximum and Minimum Values.

| | Concentration of NaOH. | | | | Concentration of HCl. | | |
|---|---|---|---|---|---|---|---|
| Salt. | 0.01 *M*. | 0.001 *M*. | 0.0001 *M*. | Neutral. | 0.0001 *M*. | 0.001 *M*. | 0.01 *M*. |
| $KNO_3$..... | 9 | 30 | 17.5 | 9.5 | 5.5 | —1 | —3 |
| $LiNO_3$..... | —26.5 | —32 | —35 | —26.5 | —33 | —8 | —1 |
| $Ba(NO_3)_2$..... | — 6 | —13 | —18 | —25 | —25 | —9 | —9 |

From these experiments with the membranes immersed in acids and alkalies it may be pointed out that:

The presence of acids or alkalies is not sufficient to definitely determine the direction of the osmose, but their presence may alter the osmose so that the results are different from those obtained in neutral solution. In general, the presence of acid has a more marked effect on osmose than the presence of alkali.

0.1 *M* potassium nitrate shows less positive osmose in the presence of 0.01 *M* sodium hydroxide than when 0.001 *M* sodium hydroxide is used, but as the amount of alkali is decreased below 0.001 *M* the osmose decreases, shows a lesser value at the neutral point, and decreases continuously as greater amounts of acid are added until with the stronger acid solutions the osmose appears to be slightly negative.

The osmose of lithium nitrate becomes less negative as the concentra-

tion of either acid or alkali is increased above 0.0001 *M*. In neutral solution it is, however, less negative than when either acid or alkali of 0.0001 *M* concentration is present.

The minimum effect with barium nitrate seems to be about the neutral point, and the osmose is materially lowered by the presence of amounts of acid or alkali 0.001 *M* or greater.

In all cases, it was noticed that the greatest activity of potassium nitrate came within the first 24 hours, while lithium and barium nitrates showed considerable activity after this period.

Experiments, similar to those just described, were made with solutions of aluminium and thorium nitrates and the following facts noted:

In the presence of acid of concentration as great as 0.01 *M* the osmose is much less than when solutions of these salts alone are used in the cells.

The osmose of thorium nitrate is unmistakably greater than that of aluminium nitrate, whereas when no acid is used in the system there is scarcely enough difference in the effects shown by the two salts to state definitely that thorium nitrate gives the greater effect.

**Relation of Osmose to Diffusion.**—In order to obtain more information on the mechanism of the osmose of electrolytes with these porcelain membranes, and to learn more about the factors that might influence the electrical orientation of the membranes, a study was made of the rate of diffusion of some electrolytes out of the cells during the process of osmosis. The series of potassium salts whose osmose is recorded in Table II were chosen. As the data in this table were being taken, the course of the osmose was watched, and a time noted (at the end of nine days) when practically all of the cells had just attained their maximum. The cells were then removed from the beakers and analyses made of the solutions left in the beakers. Determinations were made of all of the salts except the nitrate and acetate.

TABLE VI.

Diffusion of 0.1 *M* Potassium Salts Out of Cell.

| Salt. | KCl. | KBr. | KI. | KCNS. | $K_2SO_4$. |
|---|---|---|---|---|---|
| Osmose at end of 9 days..... | 80 | 71 | 56 | 100.5 | 115 |
| Vol. of cell in cc..... | 5.8 | 5.7 | 5.8 | 5.75 | 6.1 |
| No. of mols of salt in cell..... | 0.00058 | 0.00057 | 0.00058 | 0.000575 | 0.00061 |
| No. of mols diffused out..... | 0.000398 | 0.000363 | 0.000297 | 0.000409 | 0.00023 |
| Per cent. diffused out..... | 68.5 | 63.7 | 51.2 | 71.1 | 37.7 |

| | $K_2CrO_4$. | $K_3PO_4$. | $K_3Fe(CN)_6$. | $K_4Fe(CN)_6$. |
|---|---|---|---|---|
| Osmose at end of 9 days..... | 95 | 213 | 113 | 149 |
| Vol. of cell in cc..... | 5.7 | 5.5 | 5.7 | 5.15 |
| No. of mols of salt in cell..... | 0.00057 | 0.00055 | 0.00057 | 0.000515 |
| No. of mols diffused out..... | 0.000164 | 0.000128 | 0.00018 | 0.000219 |
| Per cent. diffused out..... | 28.6 | 23.3 | 31.8 | 42.5 |

To afford a basis for comparison the volume of each cell when it was set up was measured to within 0.05 cc., and from this volume and the strength of the solution, the number of moleculer equivalents originally contained in the cell was calculated. In the following table the number of molecular equivalents contained in the cell in the beginning are compared to the number diffusing out, and the relation between the two expressed as percentages of salt diffused out.

From Table VI it may be noted that:

In the case of the salt with univalent anions, the greater the positive osmose the greater the diffusion of the salt out of the cell.

For salts with bivalent anions, potassium sulfate, which gives the greater osmotic effect, shows greater diffusion than potassium chromate.

For the salts with the anions of higher valence, potassium phosphate offers an exception. It gives the greatest osmotic effect but also shows least diffusion. This case may be an exception either because of the high alkalinity of tertiary potassium phosphate, or because the soluble calcium in the membrane may tend to hold back the phosphate diffusing out.

There seems to be no striking regularity between the amount of diffusion shown by these salts and the valence of the anions.

The amount of diffusion observed here does not seem to be in any way related to the product or difference in the migration velocities of the ions in aqueous solution.

**Relation of Osmose to Membrane Potential.**—In an attempt to determine whether there was any relation between the charge existing on the two faces of the membrane and the osmose produced by that membrane, measurements were made of the actual potential differences existing between the solutions bathing the faces of the membrane. To make the measurements of these potentials, the cells, previously washed with water, were set up exactly as when the osmose was to be determined. They were then allowed to stand various lengths of time and the potentials of the cell systems measured. Calomel electrodes, a potentiometer, and a delicate galvanometer were used for measuring the potentials. One electrode was brought in contact with the solution and the other in contact with the water, giving the chain: Hg—HgCl—*N* KCl—solution—membrane—water—*N* HCl—HgCl—Hg. These measurements are not always reproducible within narrow limits, but the orientation of the cell system with any given concentration of a salt solution was found to be the same in every case when the measurement was repeated. Further, with any series of salts, the order of magnitude of potential differences was found to be reproducible. The data given in the following experiments were obtained by averaging the readings of the potentiometer taken every five or ten minutes successively for thirty

minutes to an hour. In some cases immediately after the difference of potential had been tested in the cell, the solutions were poured into cylinders, connected directly by a siphon without the interposition of a membrane, and measurements made of the potential set up by these systems. In the data subsequently tabulated, such measurements are found under the columns headed: No membrane after standing. In the following data, a + sign signifies that the face of the membrane in contact with the solution is positive, and a — sign means that the solution side is negative:

TABLE VII.

| System. | Differences of potential in the cell after standing | | No membrane after standing | Maximum osmose given in cells. | |
|---|---|---|---|---|---|
| | 24 hrs. | 36 hrs. | 24 hrs. | Single. | Double. |
| 0.1 *M* $KNO_3$ \| $H_2O$.... | —0.0060 | —0.0060 | —0.002 | 64.5 | 9.5 |
| 0.1 *M* $Li(NO_3)$ \| $H_2O$... | 0.0051 | (1) 0.0066 | | | |
| | | (2) 0.0072 | 0.022 | —31 | —26.5 |
| 0.1 *M* $NaNO_3$ \| $H_2O$... | 0.0038 | 0.0039 | 0.006 | — 3 | .. |
| 0.1 *M* $Ba(NO_3)_2$ \| $H_2O$. | 0.0158 | 0.0161 | 0.018 | —38.5 | —25 |
| 0.1 *M* $Al(NO_3)_3$ \| $H_2O$.. | 0.0310 | 0.0303 | slightly above 0.015 | 447 | positive |
| *M* $KNO_3$ \| $H_2O$..... | (1)—0.0070 | | | | |
| | (2)—0.0048 | —0.0070 | —0.0025 | — 3 | slightly positive |
| *M* $NaNO_3$ \| $H_2O$..... | (1) 0.0048 | | | | |
| | (2) 0.0071 | 0.0080 | 0.0070 | —67 | negative |

From Table VI it appears that:

The orientation of the cell system in every case is as Nernst's theory of potentials requires, that is to say, the side of the dilute solution is always charged with the sign of the more rapidly moving ion. However, the potential differs in some cases from that which exists without the interposition of the membrane. Thus with potassium and aluminium nitrates the potential difference is greater than when no membrane is interposed; while with lithium, sodium, and barium nitrates, the potential difference is less than when no membrane is interposed. In the case of the 0.1 *M* solutions, the greatest relative variation in the potential difference with and without the interposition of the membrane is shown in the case of lithium nitrate.

Except in the case of aluminium nitrate, those nitrates which show the solution side negative to the water side, give positive osmose.

The cell potential produced by the 0.1 *M* solutions of some univalent potassium salts were also measured. The results of a determination of the potential differences shown by these potassium salts are given in Table VIII. For purposes of comparison, values showing the osmose obtained are also given as well as the data showing extent of diffusion of these salts out from the cells.

TABLE VIII.

| System. | Cell potential after 24 hrs. | Maximum osmose in single cells. | Diffusion out of cell after 9 da. (p. c.). |
|---|---|---|---|
| 0.1 *M* KCNS \| $H_2O$ | —0.0185 | 100.5 | 71.1 |
| 0.1 *M* KCl \| $H_2O$ | —0.0105 | 80 | 68.5 |
| 0.1 *M* KBr \| $H_2O$ | —0.0094 | 71 | 63.7 |
| 0.1 *M* $KNO_3$ \| $H_2O$ | —0.0060 | 64.5 | .. |
| 0.1 KI \| $H_2O$ | —0.0055 | 55 | 51.2 |

From Table VIII it is noted that:

The order of potential difference is the same as that of the osmose, the greatest numerical cell potential being associated with the salt solution that gave the greatest osmose.

The order of magnitude of the diffusion of the salt outward from the cell is the same as the order of cell potential; again the salt which shows the greatest cell potential showing the greatest diffusion of the salt out of the cell.

TABLE IX.

The Cell Potential of HCl and NaOH Alone.

| System | Difference of potential in cell after standing | | | No membrane after standing | Maximum osmose in single cells. |
|---|---|---|---|---|---|
| | 12 hrs. | 24 hrs. | 36 hrs. | 24 hrs. | |
| 0.01 *M* HCl \| $H_2O$ | —0.0112 | (1)—0.0116 | | —0.0070 | 16 |
| | | (2)—0.0070 | | | |
| 0.2 *M* HCl \| $H_2O$ | 0.0130 | (1) 0.0292 | (1)0.0182 | —0.0350 | 119 |
| | | (2) 0.0220 | (2)0.0125 | | |
| 0.01 *M* NaOH \| $H_2O$ | —0.0225 | —0.0052 | | 0.0075 | 85.5 |
| 0.2 *M* NaOH \| $H_2O$ | 0.0165 | 0.172 | | 0.021 | strongly negative |

Hydrochloric acid at the concentration of 0.01 *M* shows the solution side of the membrane charged negatively as Nernst's theory of potentials requires. However, at a concentration of 0.2 *M* the solution side is charged positively, although, when the solutions after standing 24 hours in the cell, are poured into cylinders and connected by a siphon without the interposition of a membrane, the potential is in the direction that the consideration of difference in migration velocities demands.

Sodium hydroxide at the concentration of 0.01 *M* in the cell shows the water side of the membrane to be charged positively, and not with the sign of the more rapidly moving ion as is shown by the measurements of the contact potential of the solutions contained in the two compartments, when after standing 24 hours, they are transferred to cylinders and measured. When the greater concentration of the alkali is used, however, the system shows the orientation that would be expected of a concentration cell.

The two concentrations of acid measured here are chosen on opposite sides of the minimum osmose point given by the acid in successive changes of concentration; similarly the two concentrations of the alkali are on op-

posite sides of the maximum given by the base. It is significant that both the turning point in the osmose and the turning point in the orientation of the membrane lie between these concentrations in both the case of the acid and of the alkali.

Some potential measurements were also made with cells containing salt solutions in which the membranes were immersed in acids and alkalies. The results obtained did not show definitely that there is any difference in the cell potential after standing 24 hours whether the membrane is immersed in acid, in alkali, or in neutral solution. Inasmuch as the data thus far obtained do not seem to be conclusive, they are not given in this paper.

## Summary.

1. Cells were constructed using porcelain membranes of different degrees of porosity, and measurements were made of the relative pore diameters of these membranes. The grade of porcelain chosen as suitable for the osmotic experiments was such that the diameters of the largest pores were about 0.2 micron.

2. The osmose of solutions of various electrolytes was tested in these cells. The range of substances investigated included: (*a*) nitrates of several univalent, bivalent and polyvalent cations of concentrations from 0.0005 *M* to *M;* (*b*) 0.1 *M* solutions of a number of potassium salts; (*c*) hydrochloric acid and sodium hydroxide at several concentrations from 0.001 *M* to 0.2 *M;* 0.1 *M* solutions of some typical nitrates when the membranes were immersed in different concentrations of acid and alkali.

3. It was found that the osmose of these electrolytes varies in divers ways with the concentration. Some electrolytes give positive effects which increase continuously as the concentration of the electrolyte increases; others give positive effects at low concentrations and negative effects at higher concentrations, the positive osmose decreasing continuously as the concentration of the electrolyte is increased. For some electrolytes there is a concentration which gives the maximum positive osmose, while concentrations either higher or lower give smaller positive effects; and finally for other electrolytes there is a concentration that gives the greatest negative osmose (or least positive) while all concentrations either higher or lower give effects that tend to be more positive

4. At a certain concentration, somewhat different for each salt, all of the nitrates investigated, except those of aluminium and thorium, give an effect practically zero. This concentration for potassium and ammonium is about *M;* for sodium, 0.1 *M;* for lithium, 0.05 *M;* for barium, 0.02 *M;* and for zinc, manganese, and magnesium the values of the concentration lie between 0.02 *M* and 0.01 *M*.

5. Osmose seems to be closely related to the electrical orientation of

the membrane, and to the magnitude of the difference of potential which exists between the solutions bathing the two faces of the membrane. In most cases the orientation of the membrane is that which would be expected from the difference in migration velocities of the ions without considering the membrane, but in a few cases the orientation is the reverse.

6. In all cases of the monobasic salts studied, the greater the rate of diffusion of salt through the membrane of the cells the greater the positive osmose. This rate of diffusion is always closely related to the magnitude of cell potential.

7. The facts brought out seem to indicate that the osmose of these solutions of electrolytes is primarily due to an electrical effect, and is analogous to electric osmose. The explanation which seems most reasonable is that the osmose is due to the passage of a charged liquid layer along the capillary tubes of the membrane under the driving force of a difference of potential which acts as though it were set up between the two faces of the membrane. The charge of the movable liquid layer is determined by the charge which the porcelain assumes when immersed in water, but this charge may be altered by selective adsorption of ions when the membrane is brought in contact with solutions of electrolytes; and other ions than H and OH may effect the charge on the membrane. The polarization of the membrane is probably determined by the relative rates of diffusion of the ions through the membrane, but may be altered by such factors as ionic adsorption.

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

# THE QUANTITATIVE DETERMINATION OF SILICA.

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The conventional method of attack of silicates in general consists in the sodium carbonate fusion, the treatment of this fusion with hydrochloric acid for the purpose of separating out the silicic acid, and the subsequent evaporation for the purpose of dehydrating this silicic acid and rendering the silica insoluble in water and in dilute hydrochloric acid. This method of separating silica from the bases has received a great deal of study, yet the results obtained are not all that might be desired. There is considerable uncertainty regarding the necessary length of time and temperature of dehydration, the need of repeated evaporation, the solubility of silica in acids and in the wash solutions used, and the presence of ferric oxide, alumina, lime, magnesia, potash and soda in the nonvolatile residue which remains when the weight of the silica