THE RELATION OF ANOMALOUS OSMOSE TO THE SWELLING OF COLLOIDAL MATERIAL.

BY F. E. BARTELL AND L. B. SIMS.

Introduction.

During the progress of the work on anomalous osmose in this laboratory, the writers have been greatly impressed by the similarity noted between the phenomena of the swelling of gels, the swelling of organic tissues, the diffusion of liquids through living tissues, and the anomalous osmose observed with different types of membranes when used with solutions of electrolytes. After a rather extensive investigation of these related processes it seems obvious that a satisfactory understanding of the principles underlying them can be obtained only by the study of the principles underlying the phenomena of anomalous osmose.

Much work has been done on the swelling of various materials and many theories have from time to time been presented to account for this phenomenon. Among the more important of these theories are: (a) the capillary theory, (b) the osmotic theory, (c) the lipoid membrane theory, (d) the colloid chemical theory, (e) the repulsion theory, (f) the diffusion theory, and (g) the solid solution theory.

(a) The capillary theory assumes that swelling takes place by passage of liquid through small pores, the impelling force being the difference in surface tension between solvent and solution. This theory does not explain the cases in which the flow of solution is in the direction opposite to the one that would be predicted from difference in surface tensions.

(b) According to the osmotic theory[1,2] liquids pass into the material and cause swelling because of the difference of osmotic pressure between the external and internal solutions. This theory does not *explain* abnormal effects in acid and alkaline solutions, nor cases where the flow is from concentrated to dilute solution.

(c) Overton's[3] lipoid membrane theory is based on the assumption that liquids pass into cells by dissolving in a membrane which surrounds them. Though some substances undoubtedly pass in by dissolving in the membrane, this theory does not explain the passage of a large number of substances which are not soluble in the membrane; nor does it explain how

[1] Pfeffer and de Vries, "Pflanzen Physiol.," Leipzig, 1, 116 (1897).

[2] An article on osmosis and swelling of gelatin by C. P. Smith appeared in THIS JOURNAL, 43, 1350 (1921) just as the present article was about to be sent to the editor. Many of the results given in the article by Smith can be accounted for by applying the principles of anomalous osmose and are in accord with some of the results obtained by the present authors in their work.

[3] Overton, Z. physik. chem., 22, 189 (1897).

the soluble substances are able to pass out again on the other side of the membrane, as they must be considered to do.

(d) In the colloid chemical theory[4] we are to consider that the colloid cell is the unit, and that there is no surrounding membrane. Cells swell in acid and alkali because acid and alkali increase their hydration power. In other words, colloids swell in acid and alkali because acid and alkali cause them to swell, which is offering no explanation of the basic reason nor the mechanics of the process.

(e) The repulsion theory[5] explains swelling on the assumption that all the colloid particles become charged with electricity of the same sign. This causes an electrostatic repulsion and the colloid increases in size. It may be pointed out that gelatin at its iso-electric point has been found to swell more than 600%[6] and while the swelling does increase with increase of concentration of acid or alkali, which would increase the charge, it increases only up to a certain concentration. Above a certain concentration with either acid or alkali a decrease in swelling is observed, even though the charge on the particles may increase. The electrostatic charge undoubtedly has an important effect, but this one factor alone does not seem quite comprehensive enough to cover the whole case.

(f) Proctor and Wilson[7] assume that such substances as gelatin behave amphoterically and, in acid and alkali, form highly ionized salts, the non-colloid ion of which, in diffusing out, exerts a pull that swells the gel. If this is to be accepted as a general explanation of the swelling of animal and vegetable material, it must be considered that there are amphoteric substances in all animal and vegetable material which are capable of forming ionizable salts that cause swelling by diffusion. On this basis such material should swell in any concentration of acid or alkali, yet an actual shrinking has been noted in some cases.

(g) The solid solution theory was formulated by J. R. Katz[8] who believes that amorphous swelling substances differ from liquids only in viscosity, that swelling may be regarded as the mixing of a highly viscous liquid with some miscible liquid to form a solid solution. This theory offers no explanation of the swelling of a substance in a liquid of one concentration, while an actual shrinking is observed with the substance in this liquid at a slightly different concentration.

It must be admitted that the problem in question is complex. No single, simple theory can account for all the facts. Undoubtedly nearly all the fundamental concepts of the above theories must be used in order

---

[4] Fischer, "Oedema and Nephritis," John Wiley and Sons, 1915, p. 162.

[5] Tolman, THIS JOURNAL, 40, 246 (1918).

[6] Lloyd, Biochem. J., 14, 147 (1920).

[7] Proctor and Wilson, J. Chem. Soc., 109, 307 (1916).

[8] Katz, Z. physiol. Chem., 96, 255 (1916); Verslag Akad. Wetenschappen, Amsterdam, 1911, 958–75; C. A., 5, 3533 (1911).

to make a satisfactory "explanation," or to work out a comprehensive theory which will cover all cases. We must incorporate in addition to the above concepts, others which will take care of those cases in which the above fail to apply. The incorporation of the principles underlying anomalous osmose will go far toward taking care of many of the heretofore unexplained facts.

In much of recent work on anomalous osmose in this laboratory there have been observed so many factors that seem to have an effect on the phenomenon of swelling as well as on the phenomenon of anomalous osmose that the authors have sought to make a comparative study of these processes and to correlate them.

Results of Some Experiments on Osmosis.

The most striking anomalous effects have been obtained when a fairly permeable membrane such as collodion has been used with solutions of electrolytes. When osmotic effects are plotted against concentration of solution, or better, logarithm of concentration, a striking N-shaped curve is obtained;[9] for instance, as the concentration of the solution is increased the osmotic effect first increases, then falls off, then increases again. These effects are readily shown in the following tables and curves.

TABLE I

OSMOSE OF ACIDS OF VARIOUS CONCENTRATIONS WITH CALF'S BLADDER AND GOLD-BEATER'S SKIN[a]

(In mm.)

Conc. of Acid, M	0.000,001	0.00001	0.0001	0.001	0.01	0.1	1	10
HCl								
Calf's bladder..........	0	+2	+2.5	+3	+12	−4	−63	+47
HNO₃								
Gold beater's skin (A)...	...	...	+1	+2.5	+14.5	−2	−28.5[b]	+55
HCl								
Gold beater's skin (B)...	−4	−5	−4	−2	0	−15	−43	+13

[a] The data for gold beater's skin A except the values for 10 M acid and alkali were obtained from work by Bartell and Madison.[10] The values for 10 M acid and alkali were obtained at a later date.

[b] 0.05 M conc. HNO₃.

TABLE II

OSMOSE OF VARIOUS CONCENTRATIONS OF SODIUM HYDROXIDE WITH GOLDBEATER'S SKIN[a]

Conc. of NaOH, M	0.000,001	0.00001	0.0001	0.001	0.01	0.1	0.5	10
Goldbeater's skin (A)...	...	...	+1.5	+3	+5	+1	−5.5	+40
Goldbeater's skin (B)...	...	−3	−5	−18	+5	−0.5	−46	+35

[9] Jacques Loeb has also obtained similar N-shaped curves for collodion membranes, *J. Gen. Physiol.*, **2**, Nos. 4 and 5 (1920).

[10] Bartell and Madison, *J. Phys. Chem.*, **24**, 444, 593 (1920).

Goldbeater's skin A and B were different grades, and Skin A was used with double cells, while the Skin B was used with single cells (*i. e.*, single compartment cells which were placed in a much larger volume of water than was present in the 2-compartment cell), and started under a hydrostatic head of 100 mm.
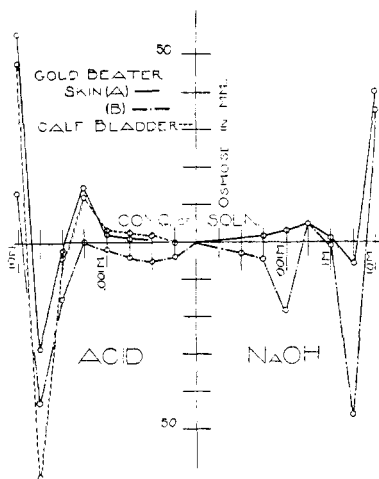
Fig. 1.

(In all figures log. of conc. is plotted on the horizontal.)
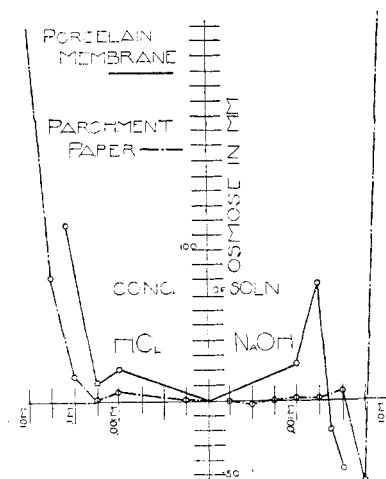
Fig. 2.—Osmose of hydrochloric acid and sodium hydroxide of various concentrations with parchment paper and porcelain membranes.

The experiments with calf's bladder were carried out in single cells but were started under no hydrostatic pressure.

TABLE III

OSMOSE OF HYDROCHLORIC ACID OF VARIOUS CONCENTRATIONS WITH PARCHMENT PAPER AND PORCELAIN MEMBRANES[a]

Conc. of HCl, M	0.000,001	0.00001	0.0001	0.001	0.01	0.05	0.1	0.2	1	10
Porcelain.......	...	...	...	+23	+12	+69.5	+64	+118	...	...
Parchment.....	+0.5	0	+7	0	+2	....	+16	...	+84	+495

TABLE IV

OSMOSE OF SODIUM HYDROXIDE OF VARIOUS CONCENTRATIONS WITH PARCHMENT PAPER AND PORCELAIN MEMBRANES[a]

Conc. of NaOH, M	0.000,001	0.00001	0.0001	0.001	0.01	0.05	0.1	0.2	1	10
Porcelain.........	...	...	...	+25	+75	−14.5	−45	...	..	...
Parchment.......	0	−1	0	+1	+1	....	+6	...	−55	+360

[a] The data for porcelain membrane were obtained from previous work by Bartell and Hocker.[11] The experiments with parchment paper as a membrane were carried out in single cells and were started with no hydrostatic head.

It will be noted that the peculiar N-shaped curves were obtained in every case and that they are very similar even though the nature of the membranes was widely different. From the results obtained, the con-

[11] Bartell and Hocker, THIS JOURNAL, **38**, 1029, 1036 (1916).

clusion was reached that forces other than those responsible for the normal osmotic tendency were operative within the system.

In previous papers[10] from this laboratory the electrical effects due to electrical orientation of the cell membrane system have been discussed; therefore, in this paper only a few general statements relative to the theory will be given.

According to Helmholz, when almost any substance is placed in a solution, a double electrical layer (Helmholz layer) is set up, the substance carrying one sign, and the liquid bathing it the other. If the solution is of an electrolyte, it is generally assumed that the signs of the charges are dependent upon the selective adsorption of the ions by the substance. For example, an acid gives a positive charge due to hydrogen-ion adsorption, and a base gives a negative charge due to hydroxyl-ion adsorption.

We assume, then, that two determining factors must always be considered, namely, the effect due to the electric charge of the capillary pore wall with respect to the charge of the liquid bathing it (which we have called the capillary system), and to the orientation of the electrical potentials existing between the two faces of the membrane (membrane system). The magnitudes of these two electrical factors are dependent upon the extent of diffusion of electrolyte through the membrane, upon the relative migration velocities of the ions, and upon the extent of selective ion adsorption.

The osmose due to this superimposed effect is assumed to be caused by the passage of a charged liquid layer along the walls of the capillary pores of the membrane under a driving force of potential which acts as though it were set up between the two faces of the membrane.

Relation of Swelling of Gel to Osmotic Effects.

In relating the process of swelling of gel to the process of osmose we may assume that a gel is built up of a framework of cells, that some unit of this framework may be considered to function as a fairly permeable membrane which would make it possible for this unit of the system to respond to the influences responsible for the process of anomalous osmose; in fact we assume that osmotic flow of solution would actually take place through this portion of the system.

Suppose we consider a cell or group of cells so arranged that within this unit liquid will be enclosed by the membrane thus formed, while at the same time liquid, either of the same or of different concentration, will bathe this membrane on the outside. If we assume the existence of such a membrane we need only to have in mind a picture of an osmotic system and its related electrical factors in order to predict the behavior of the cell system. It seems reasonable to assume that all the factors responsible for anomalous osmose would likewise be in evidence in the process of swelling of cellular gels.

Theory Applied to Swelling of Colloid Material.

In a previous paper we have shown that four distinctly different types of electrification of a membrane system may exist.[10] These four cases may be applied directly to the cell system within gel or other colloid material, as shown in Fig. 3, each diagram of which represents a single osmotic unit of the gel.

An electrical orientation of the cell system as indicated in A would result in operation of the superimposed effect, due to electrical forces,
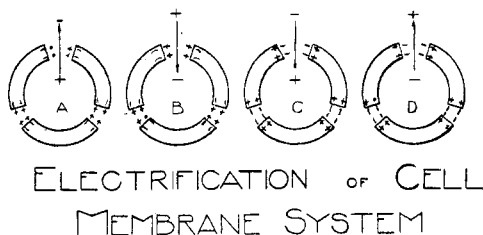

ELECTRIFICATION OF CELL
MEMBRANE SYSTEM

Fig. 3.

tending to cause a flow of solution from the cell; this would produce a shrinking of the cell walls.

Systems represented by Cases B and C would both tend to give swelling effects (comparable to negative osmose) while the system represented by D would tend to give an abnormally positive osmotic effect which would result in a shrinking of the cell.

If it be true that a relationship of this type between osmose and swelling does exist, it should be noted that swelling effects of materials containing pure water, placed in an aqueous solution, should correspond to a negative osmotic tendency, while shrinking effects should correspond to an abnormally positive osmotic tendency.

It must be remembered, however, that this electrical force may be only one of several forces acting. Experiments carried out in this laboratory, but not as yet published, seem to indicate that negative and positive adsorption may have a marked effect on both osmose and swelling.

As a working hypothesis the authors assume that a gel may be considered to be composed essentially of a framework of membranes and that the theory accounting for the flow of liquid through membranes likewise accounts to a certain extent for the flow of solution into a cellular gel. We hold the view that swelling is the result of imbibition (a process which is not well understood and which may be due either to a capillary action or to intermolecular reactions) together with the operation of effects which produce anomalous osmose. From this it would follow, in swelling, that (1) the tendency for normal osmose is always operative; (2) solution in the membrane may take place in some instances; (3) forces of attraction and

repulsion are operative; (4) capillarity plays a part; (5) negative or positive adsorption of solute may have its effect; (6) electrical effects due to electrical orientation of the system may enter in; (7) swelling unaccompanied by electrical effects may occur, as with solutions of non-electrolytes with some gels.

In order to compare as closely as possible anomalous osmotic effects with swelling effects different series of experiments were carried out.

Swelling of Laminaria.

The first series of experiments was made in order to obtain one example of each of the four cases above mentioned. Parchment paper membranes were used for the osmotic experiments while laminaria which had stood for about 24 hours in distilled water was used for the swelling experiments. Laminaria and parchment paper were chosen because both are vegetable materials.

TABLE V

FOUR CASES OF SWELLING WITH LAMINARIA, TOGETHER WITH OSMOSE VALUES OBTAINED WITH THE SAME SOLUTIONS

Case	Solution	Conc. M	Initial Wt. G.	Final Wt. G.	Swelling %	Osmose Mm.
A	K citrate	0.05	1.243	1.232	− 0.89	+38
B	NaOH	0.0001	0.540	1.081	+100.00	−4
C	HCl	0.0001	0.682	1.103	+ 62.00	−3
D	AlCl₃	0.05	1.750	1.646	− 5.95	+59

The four solutions used were selected because, when tested in osmotic systems, each was found to give a different one of the four possible cases of electrical orientation (Fig. 3). From the results in this table it is noted that the swelling effects fit in nicely with the anomalous osmotic effects. Those solutions which showed negative osmotic tendency with parchment, produced a swelling effect with laminaria, and those which showed a positive osmotic tendency produced a shrinking of the laminaria.

In the second series, osmotic experiments with parchment paper and swelling experiments with laminaria were carried out using solutions of different concentrations. The results are given in the following tables and curves.

TABLE VI

OSMOSE OF HYDROCHLORIC ACID AND SODIUM HYDROXIDE IN DOUBLE CELLS WITH PARCHMENT PAPER MEMBRANE. TIME OF OSMOSE, 8 HOURS. OSMOTIC EFFECTS ARE EXPRESSED IN TERMS OF RISE IN MILLIMETERS

Conc. of Soln., M	0.000,001	0.00001	0.0001	0.001	0.01	0.1	1	10
HCl	0	−5	−3	−1.5	0	+18.5	+33	+675
NaOH		...	−4	0	+2	−8	−25	+354

TABLE VII

SWELLING OF LAMINARIA[a]

A stick of laminaria was allowed to swell for about 24 hours, then was cut into thin sections. Each section was weighed, placed in acid or alkali for 1 hour, and weighed again.

Soln.	Conc.	Initial wt.	Wt. after 1 hr. in Acid or alk.	Swelling
	M	G.	G.	%
HCl	10.0	0.906	0.590	− 34.8
	1.0	0.590	0.518	− 12.2
	0.1	0.864	0.781	− 9.62
	0.01	0.690	0.753	+ 9.13
	0.001	0.790	1.030	+ 30.4
	0.0001	0.682	1.103	+ 61.7
	0.00001	0.611	1.060	+ 73.4
	0.000,001	0.690	1.108	+ 60.6
H₂O		0.765	1.086	+ 41.9
NaOH	0.00001	0.717	1.157	+ 61.4
	0.0001	0.540	1.081	+100.2
	0.001	0.582	1.121	+ 92.7
	0.01	0.704	1.160	+ 64.8
	0.1	0.685	1.090	+ 59.2
	1.	0.571	0.823	+ 44.2
	10.	0.590	0.590	0

[a] A minus sign (−) indicates shrinking of the gel.

TABLE VIII

SWELLING OF LAMINARIA

Swelling in acid and alkali when previously allowed to swell almost to a maximum in water for approximately 48 hours

Soln.	Conc.	Initial wt.	Wt. after 22 hrs. in soln.	Swelling
	M	G.	G.	%
HCl	10	1.136	1.070	− 5.8
	1	1.226	1.111	− 9.4
	0.1	1.531	1.332	−13.0
	0.01	1.213	1.165	− 3.96
	0.001	1.901	1.939	+ 1.99
	0.0001	1.181	1.193	+ 1.02
	0.00001	1.496	1.533	+ 2.47
	0.000001	1.586	1.618	+ 2.20
H₂O		1.463	1.493	+ 2.05
NaOH	0.000001	1.243	1.261	+ 1.45
	0.00001	0.948	0.956	+ 0.84
	0.0001	1.269	1.301	+ 2.52
	0.001	0.933	0.968	+ 3.75
	0.01	1.323	1.403	+ 6.05
	0.1	1.463	1.684	+15.1
	1.	1.481	1.583	+ 6.89
	10.	1.966	1.668	−15.2

TABLE IX

OSMOSE OF CHLORIDES

In double cells with parchment paper membrane, acid and alkali throughout the cell

Time of osmose, 6 hours

Molar conc. of acid or alkali throughout	Osmose Set A 0.05 M KCl Mm.	Osmose Set B 0.05 M MgCl$_2$ Mm.	Osmose Set C 0.05 M AlCl$_3$ Mm.
0.001 HCl	3	6.5	18
0.0001 HCl	6	9.5	24
Dist. H$_2$O	6	7	25
0.0001 NaOH	4.5	6	21
0.001 NaOH	3	5	20.5

TABLE X

SWELLING OF LAMINARIA

First soaked in acid or alkali, then allowed to swell in a solution of chloride in acid or alkali of the same concentration as the acid or alkali in which it was soaked.   Time of swelling, 5 hours

Molar conc. of acid or alkali used	Set A 0.05 M KCl %	Set B 0.05 M MgCl$_2$ %	Set C 0.05 M AlCl$_3$ %
0.001 HCl	−1.69	−1.49	−2.33
0.0001 HCl	−3.2	−6.96	−7.87
Dist. H$_2$O	−2.23	−7.07	−9.08
0.0001 NaOH	−2.64	−5.68	−7.46
0.001 NaOH	−0.735	−5.12	−6.90

Figure 4 gives the curves obtained from Tables VI and VII.   The osmose of hydrochloric acid and sodium hydroxide in double cells with parchment
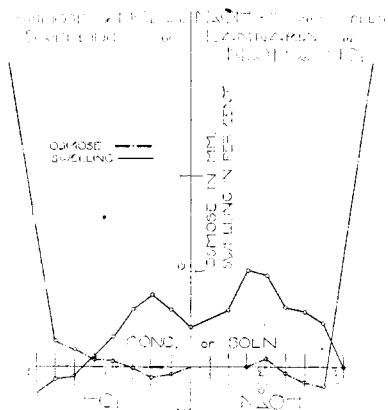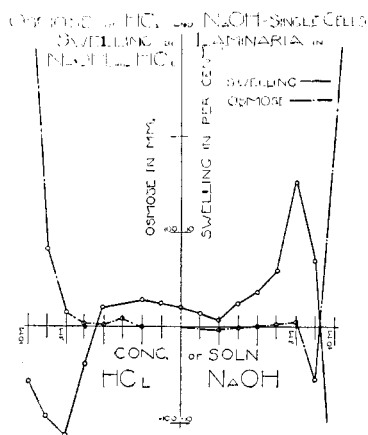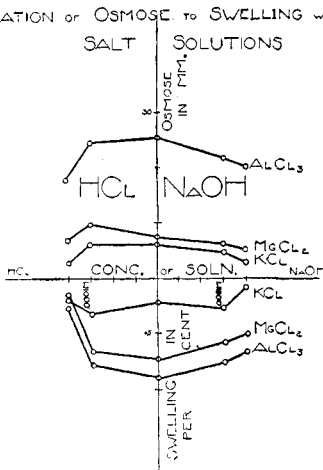

Fig. 4.

Fig. 5.

paper membrane is plotted on the same coördinates as the swelling of laminaria in hydrochloric acid and sodium hydroxide. The laminaria was softened in distilled water until it could be cut, was then cut into thin slices, each slice weighed, and placed in a solution of acid or alkali for one hour, and weighed again.

Figure 5 gives the curves obtained from Table VIII and from the values of osmose with parchment from Tables III and IV. The osmose of hydrochloric acid and sodium hydroxide in single cells with parchment paper membrane is plotted on the same coördinates as the swelling of laminaria in hydrochloric acid and sodium hydroxide. In this case the laminaria was cut in thin sections and then placed in distilled water until it had swollen nearly to a maximum in the water, when it was placed in solutions of acid and alkali and allowed to swell further. This gave a curve similar to that for laminaria in Fig. 4 but the swelling was, for the most part, not so great and the maximum points came at higher concentrations.

Figure 6 gives the curves obtained from Tables IX and X. The osmose of chlorides in double cells using parchment paper membrane with the same concentration of acid or alkali in both compartments of the cell is plotted on the same coördinates as the swelling of laminaria in solutions of chlorides in acid and alkali. The laminaria had previously been soaked in acid and alkali of the same concentration as that in the chloride solution in which it was subsequently allowed to swell.

Fig. 6.

The curves for osmose and swelling are not quantitatively comparable, as the substances used are not identical. Also, the liquid on the inside of the laminaria was not pure water, but contained dissolved material. Besides this there was a difference in the volume ratios of dilute and concentrated solution used in the swelling and osmose experiments which would tend to make a difference in the final results. It would seem, however, that conditions were nearly enough alike to warrant a qualitative comparison.

In general the osmose curves, when plotted as above, are the opposite of the swelling curves. That is, a negative osmotic tendency corresponds to a swelling effect, while a positive osmotic tendency corresponds to a shrinking effect.

Data and curves for the swelling of such substances as gelatin,[6] barley,[12] fibrin,[13] glutin,[14] sunflower seeds,[15] and protoplasm[16] are to be found in the literature. The similarity of the swelling curves for these widely different

[12] Hoagland, *Soil Science*, **3,** 547 (1917).

[13] Fischer, *Pfluger's Arch.*, **125,** 99 (1908).

[14] Upson and Calvin, THIS JOURNAL, **37,** 1295 (1915).

[15] Borowikow, *Biochem. Z.*, **48,** 236 (1913).

[16] Lloyd, *Trans. Roy. Soc. Canada*, [3] **11,** 133 (1917).

substances would lead us to believe that the manner of swelling was similar in all cases. Different conditions and materials give the same general type of curve, but with maximum and minimum values coming at somewhat different concentrations. In all cases the swelling seems to increase with addition of acid or alkali up to a certain point, when it decreases again. The authors believe that a further study of anomalous osmose and its relation to the swelling of colloid materials should find important applications in various problems of biology; also in such every day problems as tanning, the preservation of fruits, meats, etc.; in fact in all problems in which the direction of flow of solutions through membranes cannot be predicted from a knowledge of the isotonic values of the solutions concerned.

ANN ARBOR, MICHIGAN.

GERMANIUM. III. GERMANIUM TETRABROMIDE AND GERMANIUM TETRACHLORIDE.[1]

BY L. M. DENNIS AND F. E. HANCE.

Germanium Tetrabromide.

Winkler[2] prepared what he assumed to be germanium tetrabromide by heating germanium in vapor of bromine, and also by heating a mixture of pulverized germanium and mercuric bromide. He stated the product to be a mobile, fuming liquid which solidified at $0°$ or slightly below that temperature to a white crystalline mass. He did not analyze or make a detailed study of the compound because of lack of material.

The present investigation describes the preparation and further study of this substance.

Material.—Germanium was prepared in finely divided form by reducing[3] germanium dioxide in a current of hydrogen at temperatures between $550°$ and $600°$. Toward the end of the reduction the temperature was raised to $900°$.

Bromine was purified by first digesting it with calcium bromide and zinc oxide,[4] then distilling the bromine, converting the middle fraction to hydrobromic acid by treating it with sulfur dioxide in the presence of water, distilling the hydrobromic acid, and liberating the bromine from this by means of pure manganese dioxide. This bromine was redistilled, was next dried over phosphorus pentoxide, and was then again distilled. The middle fraction was used.

Preparation of Germanium Tetrabromide.—Powdered germanium was placed in alundum boats which were inserted in a tube of Jena glass lying in an electric combustion furnace. A thermometer was laid in the combustion tube beside the boats.

---

[2] Winkler, *J. prakt. Chem.*, 144 (N. S. 36), 193(1887).

[3] Further details concerning this reaction will be given in a later article.

[4] Richards and Merigold, *Proc. Am. Acad. Arts Sci.*, 37, 387 (1901-2).