THE
OSMOTIC PRESSURE OF AQUEOUS SOLUTIONS

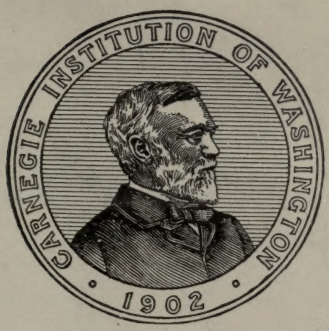
REPORT ON

INVESTIGATIONS MADE IN THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY DURING THE YEARS 1899-1913

By H. N. MORSE

Professor of Inorganic and Analytical Chemistry in the Johns Hopkins University

---



WASHINGTON, D. C.
PUBLISHED BY THE CARNEGIE INSTITUTION OF WASHINGTON
1914

CARNEGIE INSTITUTION OF WASHINGTON
PUBLICATION No. 198

PRESS OF GIBSON BROTHERS, INC.
WASHINGTON, D. C.

CONTENTS.

LIST OF ILLUSTRATIONS.

PLATES.

TEXT FIGURES.

THE OSMOTIC PRESSURE OF AQUEOUS SOLUTIONS

By H. N. MORSE

CHAPTER I.

THE CELLS AND THE MANOMETER ATTACHMENTS.

Having found in the electrolytic method* an excellent means of depositing a considerable number of osmotically active membranes, it was imagined that the principal obstacle in the way of the measurement of osmotic pressure had been removed and that certain obvious mechanical difficulties connected with the preparation of a suitable porous vessel and the assembling of the various essential parts of the cell could be readily overcome. It was soon discovered, however, that the problem of preparing a satisfactory background for the membrane, i. e., the porous wall, was vastly more difficult than had been anticipated.† It was necessary, in fact, to spend a large fraction of the first ten years of the investigation in experimental work in the manufacture of cells. The first four years (1901–1905) were devoted almost exclusively to the solution of that problem. At the close of the latter period (1905), only two porous vessels of faultless wall-structure had been produced. These were the cells which were designated in the published records of the work by the letters "A" and "B."

The first experiments upon the activity of membranes deposited by the electrolytic method were made in such porous vessels as could be found about the laboratory, battery cups, etc. The earliest attempts at quantitative measurement were carried out with a portion of a lot of 100 small porous cups which were manufactured, in accordance with furnished specifications, at a pottery in a neighboring city.‡ In about one-fourth of these, considerable pressures were developed, but in no case the maximum pressure. All of them leaked, and most of them burst under pressures of less than 20 atmospheres. Only one of them survived a pressure of 30 atmospheres, and that for a short time only. It was not then doubted that the defects which had appeared in the first lot of cells from the pottery could be remedied by the potters themselves, provided the exact causes of the failure of their products could be correctly ascertained and explained to them. Accordingly, with that purpose in view, many thin sections were made of the cells with which quantitative measurements had been attempted, and these were examined microscopically and photographed. It soon appeared that most, if not all, of the conditions which determine the

*Amer. Chem. Journal, XXVI, 80 (1901); XXIX, 173 (1903).
†*Ibid.*, XXXII, 93 (1904); XXXIV, 1 (1905).
‡*Ibid.*, XXVIII, 1 (1902).

good and bad behavior of the porous wall of the cell are susceptible of clear definition and of adequate explanation. All the essential facts which had been discovered in the laboratory were given to the potters, and they expressed their confidence in their ability to remedy the defects of the earlier consignment. In this expectation they were greatly mistaken; for, among the nearly 500 cells which were subsequently made for us at various potteries, *not one* was found suitable for the measurement of osmotic pressure. In fact, in attempting to remedy certain defects, they generally aggravated others to such an extent as to render the later cells on the whole distinctly inferior to those of the first lot. Finally we ventured to offer certain suggestions involving methods of manufacture not in use among potters, but these were rejected on the ground that, to those familiar with the conduct of clays, they were obviously futile. As the potters declined to cooperate along lines of manufacture not approved by them, the problem of cell-making was taken out of their hands into the laboratory for solution.

The cells produced at the potteries were defective in various ways, but principally in the particulars enumerated below:

1. All were lacking in the strength necessary to withstand any considerable outward pressure. As mentioned above, only one of the few which proved at all serviceable survived a pressure of 30 atmospheres, while most of them cracked under pressures below 20 atmospheres.

2. All of them contained numerous "*air blisters*," which communicated with each other and with the interior surfaces of the porous wall in such ways as to give rise to the formation of a number of subsidiary interior membranes. Not unfrequently, when a cell was broken for examination, as many as four or five of these minor membranes, often nearly concentric over a considerable area, were found in several localities; and it frequently happened also that the last of them was near, or even at, the exterior surface of the cell.

3. The potters' cells also lacked uniformity in respect to porosity. The same cell would often exhibit the greatest diversity in this particular. In some parts, the structure would be as close as in porcelain, while in others it might be so open that the membrane would form nearly midway between the interior and exterior surfaces of the cell wall.

A microscopic examination of thin sections of the cells in which membranes had been deposited revealed the fact that, excluding the peculiar and often fantastic effects of "*air blisters*," the distance of the membrane from the interior surface of the cell wall is determined solely by the porosity of the latter. The more open the texture is, i. e., the larger the pores are, the more deeply within the wall will the deposition occur; while with a certain degree of closeness in this respect, the deposition is just *within the interior entrances* of the pores, in effect, upon the inner surface of the cell, where it should be. Obviously the copper

ferrocyanide membrane will always be located somewhat nearer the inner than the outer surface of the wall, however large the pores may be.

It was evident that the hope of success in cell-making depended on the following conditions:

1. Great and uniform strength of wall.
2. The elimination of air-blisters.
3. An *excessively* fine and *perfectly uniform* texture of wall, a texture so fine, in fact, as to insure the meeting of the slower anion and the more mobile cation just within the interior mouths of the pores. In other words, the pores must be so small that the cation is able to pass through them, from the exterior to the interior of the wall, during the time consumed by the anion in just entering them from the interior.

The necessity of securing great strength of wall is obvious enough, as is also that of eliminating *"air blisters,"* and the need of depositing the membrane at the *interior surface* of the wall will likewise become apparent if one considers the inequalities in the concentration of the solution which must result from its location elsewhere, i. e., within the wall. In the latter case, owing to the slowness of diffusion within the wall, the liquid in the neighborhood of the membrane will be permanently less concentrated than the main body of the solution. Moreover, since the wall is always necessarily filled with some liquid, it would be impossible to know exactly the final concentration of any solution which is introduced into the cell. On the other hand, if the discharge of the water entering the cell through the membranes is from a free surface, i. e., directly into the unencumbered solution, the conditions will be favorable to its rapid distribution, and, therefore, to the maintenance of uniform concentration.

It was attempted to secure strength of wall by introducing into the clays the maximum allowable portion of cementing material (feldspar)—that proportion, in fact, which is just insufficient to convert the baking cell into porcelain. It was hoped also, by thorough mixing of the constituents, to secure a more uniform texture of cell wall than had been found in the products of the potters.

Washed clays from several sources were mixed with varying quantities of ground feldspar, and the mixtures were burned at different temperatures, either in a Seger experimental kiln with use of Seger cones, or in a calibrated electric furnace which was devised for the purpose. The products were altogether disappointing. They were, in reality, quite as uneven in respect to uniformity of strength and texture as the cells of the potters. The failure was evidently due to imperfect mixing, and it was hoped that better results might be obtained with finer materials. Accordingly, both the clays and the feldspar were elutriated, and the wet mixtures of the finer materials thus obtained were passed repeatedly through silk bolting-cloth having 16,000 holes to the square inch. The bolting process was followed by a long-continued churning

of the mixtures with water, and, finally, by a most thorough kneading of the "putty." The results were still unsatisfactory in that the porosity of the baked samples lacked the high degree of uniformity which is indispensable in the measurement of osmotic pressure. It was evident, moreover, on comparing our products with those of the potters, that we had been trying exactly what they had attempted, except that, in every case but one, they had omitted the elutriation and bolting processes. It was concluded that the necessary binding material *can not* be successfully incorporated with the clays in the form of ground feldspar.

The final solution of the problem was easy and satisfactory. It occurred to us that perhaps sufficiently intimate admixtures could be obtained by bringing together two different clays, one of which is deficient in binding material, while the other is over rich in that constituent. This was the plan which was finally adopted, and with proper selection and manipulation of the materials, it has never failed to give products which are all that could be desired in respect to strength and *uniformity* of texture.

The pores were, however, still much too large, notwithstanding the fineness of the materials, and the *air blisters* were not eradicated by the usual method of forming such vessels. It was attempted to diminish the size of the pores by repeatedly burning the cells at high temperatures, and in this way considerable but not sufficient improvement was effected. Two plans had been proposed to the potters for securing the required density of texture and for the simultaneous elimination of the air blisters. The first of these was to form the cell itself under high pressure, while the second was to form the wet clay into a cylinder under great pressure, and from this to turn out the cell upon the lathe. Both plans were declared to be impracticable by the potters. After many months of futile effort, we were forced to agree with them as to the first project, but the alternative plan—that of cutting the cell from a cylinder which had been formed under high pressure—was finally developed to a successful issue.

TREATMENT OF THE CLAYS.

A considerable number of clays, both American and foreign, were investigated with reference to their suitability for the manufacture of cells, and two were finally selected as being superior to any of the others for the purpose. These were a fire clay from Dorsey,* Maryland, and a so-called ball clay from Edgar, Florida.

The Florida clay had been washed before it came into our hands, while that from Maryland was in its original untreated condition. Two processes have been employed for the separation of the finer portions of the clays. Both give satisfactory products, but the earlier process has been abandoned because the later one is more economical of material.

*Erroneously stated to have been from Mount Savage, Maryland.

FIRST PROCESS.

The dry and pulverized clays are sifted for the purpose of removing the coarsest parts. Three empty alcohol barrels, each with a spigot in the bung hole, are placed one above another, each of the upper two being set a little back of the one below it. The uppermost barrel is nearly filled with water, and into this is stirred about 3 kilograms of the sifted clay. After standing quietly for 3 minutes, the spigot is opened and the contents of the upper half of the barrel are allowed to flow into the barrel below. The residue is removed and the barrel is recharged and again partially emptied, precisely as in the first instance. When the intermediate barrel is nearly full, its contents are likewise stirred and then allowed to settle for 3 minutes, after which the spigot is opened to allow the contents of the upper half to flow into the lowest receptacle. The material which collects in the lowest barrel is bolted (wet) successively through Nos. 10, 14, and 16 silk bolting-cloth, having respectively 11,236, 19,600, and 24,336 holes to the square inch. The proportion of the clay which is thus acquired is not very large. In one instance where the original and final weights were recorded, 500 pounds of the fire clay yielded 180 pounds of the bolted material. In another case, 200 pounds of the Edgar clay gave 75 pounds of the final product.

SECOND PROCESS.

A wooden trough, 6 meters in length, with flat bottom and high sides, is divided into several compartments by means of transverse dams. The trough is given an inclined position, and in the highest compartment the sifted clay is stirred up with water. The water with its suspended matter is pushed from time to time over the dam into the next compartment. By repeating the operation in the successive divisions, the finer constituents of the clay can be quickly and quite completely separated from the coarser. The material which collects in the last compartment, or is allowed to overflow from that into other receptacles, is bolted in the manner described above.

The bolted clay is allowed to subside and the nearly clear water above it is drawn off by means of a siphon, but there still remains a large quantity of water in the clay which must be removed by evaporation, or filtration, or by other means. Its removal by either of the methods mentioned, however, is exceedingly slow and in many ways disagreeable. A much better and more rapid method is that which was suggested to us by our process for removing air from the porous walls of osmotic cells, i. e., the method of "*electrical endosmose.*" A large porous pot (usually a flower pot) is placed in a larger, water-tight vessel of any suitable material. The clay (generally in the form of a thick porridge) is poured into the former. Two electrodes are inserted, the anode into the contents of the porous pot, and the cathode into the water which quickly

collects in the outer vessel. As the level of the contents of the pot recedes, more clay is added until no more can be introduced. In the meantime, the level of the water in the outer receptacle is kept, by means of an automatic siphon, just high enough to permit the complete submersion of the cathode. When the clay becomes so far dried that the mass begins to crack at the top, it is packed down with a heavy pestle. In this way the excess of water can be separated from the clay much more rapidly and even more completely than by filtration under diminished pressure. The method can also be applied with advantage to the separation of water from, and even to the washing of, other solids which, like clay, are filtered with difficulty. The voltage employed is 110 or 120.

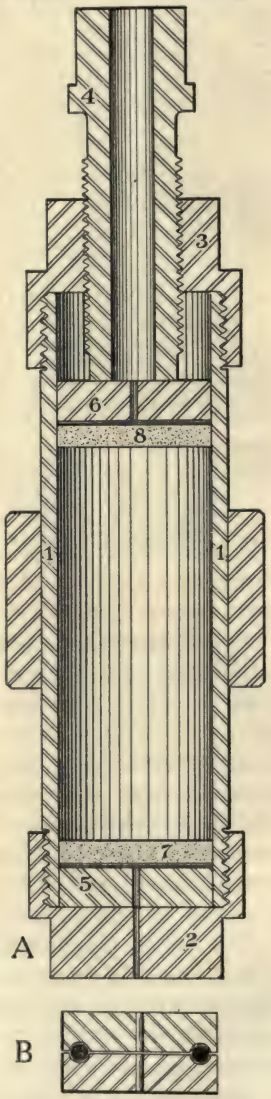


FIG. 1.

A. Steel press for clays. (1) Barrel; (2) lower cap; (3) upper cap; (4) plunger; (5) and (6) steel disk; (7) and (8) porous clay disk.

B. Ball-bearing disk, used in place of (6) to prevent twisting of clay.

THE FORMATION OF THE CYLINDERS.

A section of one of the steel presses in which the clay is formed into cylinders is shown in Figure 1 *A*. The barrel (1) is slightly tapered internally, the diameter at the bottom being 0.005 inch greater than at the top, in order to insure the ready release of the clay cylinder when it is to be pushed out of the lower end of the press. It is threaded at both ends to receive the caps (2 and 3). The cap at the lower end (2) is bored to permit the escape of the water which is squeezed out of the clay. The cap at the upper end (3) is bored and threaded internally to receive the hollow plug (4). The steel disks (5 and 6) are also bored to facilitate the escape of water. The disks (7 and 8) are of porous hard-burned clay or of asbestus.

The upper steel disk (6) is less simple than it appears in the figure. In reality it consists of two grooved disks separated by hardened steel balls (bicycle balls), as shown in Figure 1 *B*. The upper half turns readily with the plug (4), while the lower half remains stationary, thus preventing any twisting of the clay beneath. If a single disk is used, the clay is twisted in a direction the reverse of that of the screw, and

the cell, when burned, exhibits upon its exterior surface a series of spirally arranged elevations or depressions, as if the shrinkage of the clay in baking had not been entirely uniform. Considerable difficulty was experienced at first in securing the correct temper for the grooved disks, which, of course, should be equal to, but not much higher than, that of the steel balls which separate them. If the disks are insufficiently tempered, they are badly lacerated by the balls. On the other hand, if they are made too hard, they frequently crack under the great pressure to which the clay is subjected.

In order that the diameter of the clay cylinders may be varied, the barrel of the press (Figure 1 *A*) is made quite wide (2.5 inches internally) and is provided with a series of steel "sleeves" of various smaller bores—which may be inserted. Each sleeve requires, of course, its own set of disks (Figure 1 *A* 5, 6, 7, and 8, and Figure 1 *B*). The length of the cylinder is regulated by the number and thickness of the disks (5), which are placed in the bottom of the press before introducing the clay.

The two clays, prepared as previously described, mingle readily in all proportions, giving products which, when baked, are uniform in respect to texture and strength. It was found that all the requirements of the situation are best met by mixing them in about equal proportions by weight. The process of mixing is as follows: (1) Equal weights of the air-dried and pulverized clays are mingled and repeatedly sifted; (2) the mixture is churned with water for several hours, after which (3) it is bolted—without unnecessary interruption of the churning process—through Nos. 14 and 16 bolting-cloth; (4) the material is allowed to subside, and the supernatant water is removed by means of a siphon; (5) the major portion of the large excess of water still remaining with the clay is removed by draining upon a filter of bolting-cloth resting upon one of paper, or by the "*endosmose*" method already described; (6) finally the material is extensively kneaded and mixed upon a plate-glass surface until, through evaporation of the water, the "putty" has attained the consistency which experience has shown to be best suited to pressing.

The putty, which must never be touched without first covering the hands with rubber gloves, is "tamped" down in the press with a steel plunger which has been cleansed with ether.

The device for compressing the clay is shown in Figure 2, without the framework which holds the various parts in their places. The press (1) containing the clay is secured between two flat bars of steel, a portion (2) of one of which is seen in the figure. The lower end of the vertical shaft (3) is square in form, like the upper end of the plunger of the press (Figure 1 *A*), and the collar (4), which joins the two, has a square hole of the same diameter passing through it. A portion of two of the timbers of the framework is shown in the figure (5 and 6). Through these, the shaft (3) slides freely up and down, except so far as its motion is limited by the set collar (7). The large wooden drum (8)

is firmly attached to the shaft, and around it is wound the steel-wire cable (9). The loose iron pulleys (10, 11, and 12) serve to guide the cable. The large pulley (12) is situated in the attic of the laboratory. The cable, after leaving the horizontal pulley (11), ascends vertically through the ceiling of the room and passes over the attic pulley (12). The descending end of the cable is attached to a heavy iron rod (13), upon which may be loaded any required number of cast-iron weights (14 and 15). At the floor, the weight (consisting of 13, 14, and 15) enters a vertical shaft more than 50 feet in depth. The detachable wrench (16), which is provided with extensions, is employed in raising the weight and coiling the cable about the drum.

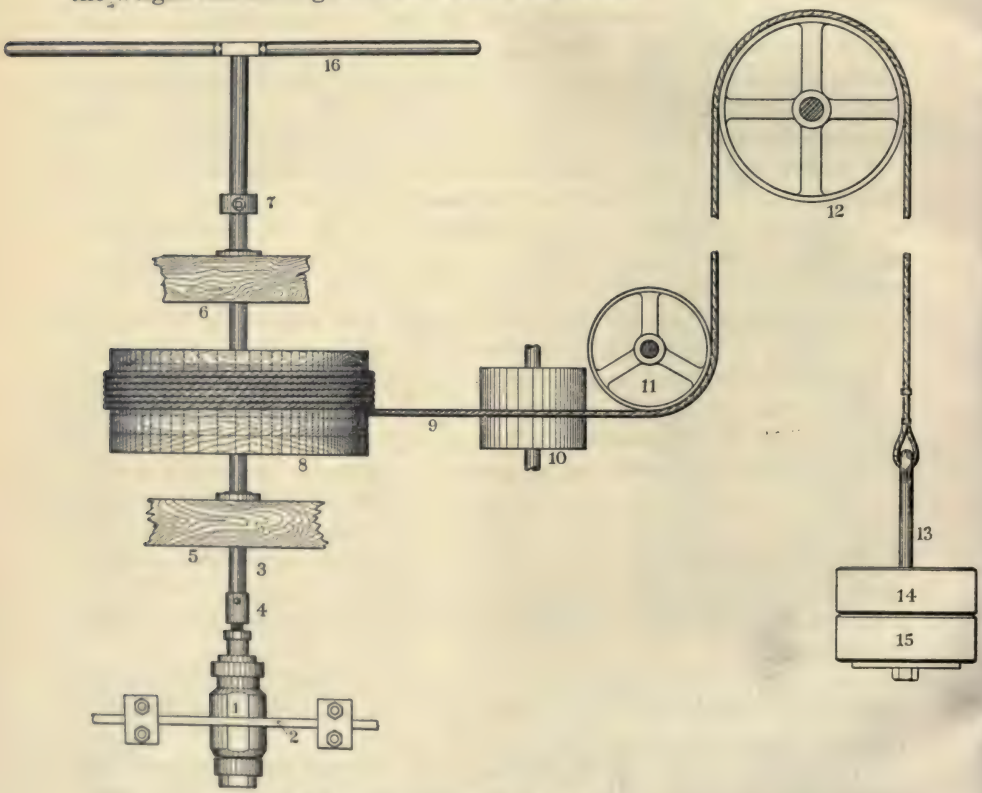


FIG. 2.—Apparatus for pressing clays.

(1) Steel press (see Fig. 1 *A*); (2) steel frame for holding press; (3) movable steel shaft; (4) collar joining (1) and (3); (5) and (6) parts of wooden framework; (7) set collar to limit vertical motion of shaft; (8) drum for coiling cable; (9) steel cable; (10) vertical loose guide pulley for cable; (11) horizontal loose guide pulley for cable; (12) loose cable pulley in attic; (13) saddle for weights; (14) and (15) cast-iron weights.

After filling the press, and before placing it in the position shown in Figure 2, it is put into a vise and considerable of the water is forced out by use of the wrench (16), which is given a turn from time to time as the

escape of water makes further compression of the clay possible. When no more water can be forced out, the press is transferred to its place in Figure 2. The amount of weight to be applied and the duration of the period of pressing are judged entirely by previous observations on the fitness of the products for cutting purposes. In general, the weight employed is that which will give a calculated pressure of 20 tons upon each square inch of the surface of the clay cylinder after an allowance of one-third for loss by friction. The first descent of the weight (53 feet) is usually accomplished in about 2 hours and the second in about 16 hours. Ordinarily the pressing is discontinued at the end of the second excursion of the weight. Equivalent results can be secured by lighter weights and longer pressing or by heavier weights and shorter pressing. The object to be attained is, of course, that condition of the clay which will enable one to cut a perfect cell from the pressed cylinder, and for this purpose the clay must be neither *too wet* nor *too dry*.

When the cylinder is to be removed, the press is again placed in the vise, the upper cap (Figure 1 *A*) is removed and an additional disk is introduced. On replacing the upper cap and removing the lower one, and giving the plunger (Figure 1 *A*, 4) a slight turn, the cylinder is effectively released, and—owing to the tapered form of the barrel (Figure 1 *A*)—uninjured. The form of the cylinder is shown in Figure 3 *A*.

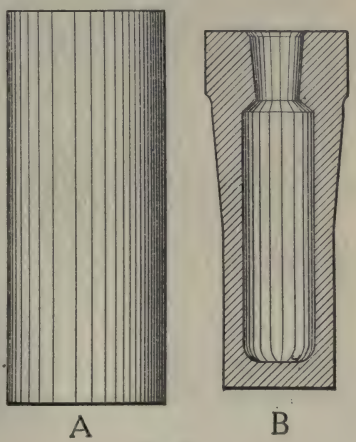


FIG. 3.

A. Clay cylinder after pressing.
B. Clay cell after shaping the cylinder (Fig. 3 *A*) on the lathe.

THE CUTTING OF THE CELLS.

One of the commoner forms of the finished cell as it is turned out of the cylinder (Figure 3 *A*) is shown in Figure 3 *B*. Other forms will be represented when the attachment of the manometer to the cell is discussed.

The cutting of the cells from the cylinders is an exceedingly critical operation, which requires experience and well-developed mechanical instincts. Very few, even of those who have had mechanical training, ever succeed in the undertaking. The explanation of so many failures is very simple: *The cell wall must not be weakened at any point by the pressure of the cutting tools;* because, when the cell is baked, the shrinking material (the shrinkage is between 7 and 8 per cent) necessarily draws away from the regions of relative weakness toward those where the cohesion of the particles is stronger and cracks are developed. It is by no means necessary that the damage done by irregular or excessive pressure from the cutting tools should be apparent in the finished

product. In fact, it is rarely discovered until the cells are taken from the kiln. At first, the failures from the cause alluded to were over 90 per cent. At the present time, about 10 per cent of the cells develop cracks while in the kiln. The improvement has been due in a large measure to improvements in the cutting tools and to the increased attention which has been given to keeping them in good order. It was found impossible to succeed with the usual lathe cutting tools, and others with new forms of cutting edge were designed. One of the more important of these is shown in Figure 4. It is the tool with which all the boring and nearly all the inside work are done. It will be seen that the tool cuts only in the longitudinal direction of the cylinder, bringing no pressure upon the wall of the cell in a transverse direction. The same principle is employed in fashioning the tools with which the outside work is done. But however good the design of the tool may be, failure is bound to attend its use in this work unless it is ground in accordance with correct principles, i. e., with the proper "*clearance*," and is always maintained in a sharp condition.

FIG. 4.—Different views of special tool for cutting cell (Fig. 3 *B*) from cylinder (Fig. 3 *A*).

A multitude of details relating to methods of mounting, speeds of cutting, etc., all of which are of importance to the operator, but of little interest to others, are omitted, and only one instance of the many precautions which it is necessary to observe will be mentioned—the fact, namely, that, when the lathe has once been started, it must not be stopped until the cell is finished, owing to the danger of "*sagging*."

THE BURNING AND GLAZING OF THE CELLS.

The experimental work in the baking of clays was done for several years either in a Seger kiln or in an electric furnace. The electric furnace which was first employed was one in which the platinum wires were woven through holes in the walls and bottom of the furnace, so that the heat generated in the wires must penetrate a considerable thickness of clay before reaching the space to be heated. With such an arrangement a very long time is required to obtain, with a given current, the temperature which

that current will eventually maintain in the furnace. In the case of the instrument here mentioned, from 7 to 9 hours were required for that purpose. A close regulation of the temperature was therefore impossible. Another objection to this furnace was its wastefulness. At 1250° the consumption of electrical energy was equivalent to 1200 watts. The furnace was improved to some extent by certain modifications which were introduced, but not sufficiently to justify its continued use. It was therefore abandoned for one of our own construction,* in which the wires were all exposed in the space to be heated. The saving in electricity thereby effected was over 50 per cent. The new furnace is shown in Figures 5 *A*, 5 *B*, 5 *C*, and 6. It will be seen to consist (Figure 5 *A*) of platinum wires threaded through three clay rings (*a*, *b*, and *c*), which are held apart by three platinum rods. The rods expand in the same degree as the wires, and thus keep the latter taut, whatever may be the temperature of the furnace. Otherwise the wires would "*buckle*" and short circuit at high temperatures. The wires are in two pieces of equal length, so that they may be placed in series or in parallel, according to the amount of current which it is desired to use. Figure 5 *B* shows the furnace in place in the innermost (*d*) of the clay cylinders which surround it when in use. The cover (*e*), the bottom (*f*), and the truncated cones (*g*) on which the furnace rests are also represented in the figure. Figure 5 *C* represents the outer clay cylinder and its various accessories. In Figure 6 all the parts, lettered as in Figures 5 *A*, 5 *B*, and 5 *C*, are assembled as a crucible furnace. The outer covering (*m*) is a sheet-iron cylinder, which is covered, internally and externally, with asbestus paper. The purpose of the remaining parts (*n*, *o*, *p*, *q*, *r*, and *s*) is obvious without explanation.

The electric kilns (of which three were usually in operation) were all calibrated by means of a Le Chatelier pyrometer. They thus became, in themselves, *resistance pyrometers*, the temperature of which could be easily ascertained at all times. The electric kilns answered well the purpose for which they were constructed up to about 1200°, i. e., to a temperature at which platinum begins sensibly to volatilize in an atmosphere containing oxygen. At higher temperatures, the loss of platinum was sufficient to make an occasional recalibration necessary.

The best results were obtained at about 1300°, i. e., between the melting-points of Seger cones Nos. 8 and 9. Having ascertained the most advantageous temperature for burning the cells, there was no longer any good reason for baking them in the laboratory rather than at the pottery. Fortunately, at the opportune time, we were offered the free use of the kilns of the Chesapeake Pottery Company by the late president of that concern, Mr. D. F. Haynes. A similar courtesy was also extended to us by the Bennett Pottery Company. At the

*Amer. Chem. Journal, xxxii, 93.

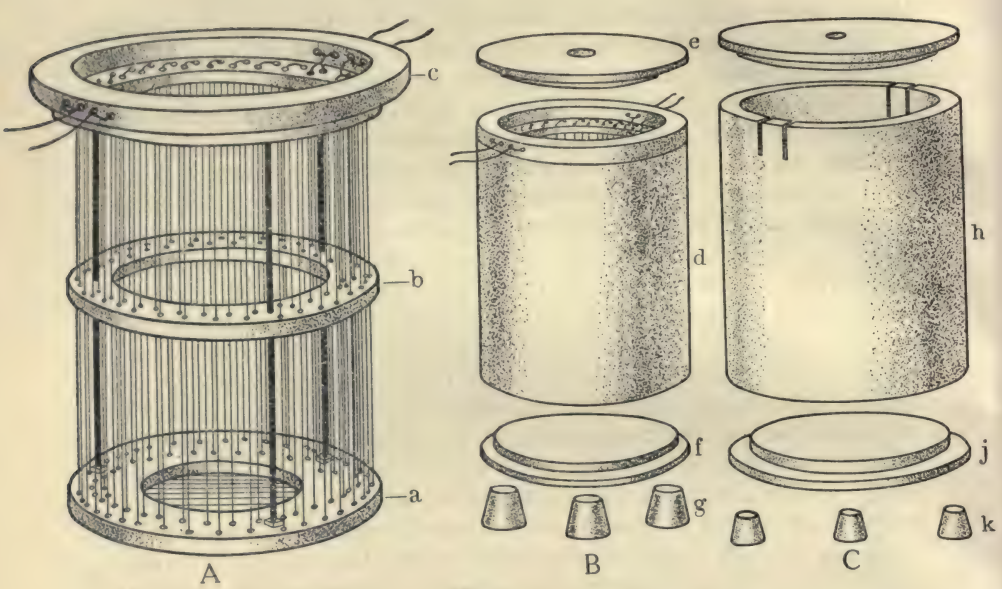


FIG. 5.

A. Electric kiln for baking cells. (*a*), (*b*), and (*c*) perforated clay rings, held in place by three platinum rods which prevent the platinum wires from "buckling" when hot.
B. Inner covering for electric kiln. (*d*) Clay cylinder; (*e*) cover; (*f*) bottom; (*g*) truncated clay cones.
C. Outer covering for electric kiln. (*h*) Clay cylinder; (*j*) bottom; (*k*) truncated clay cones.

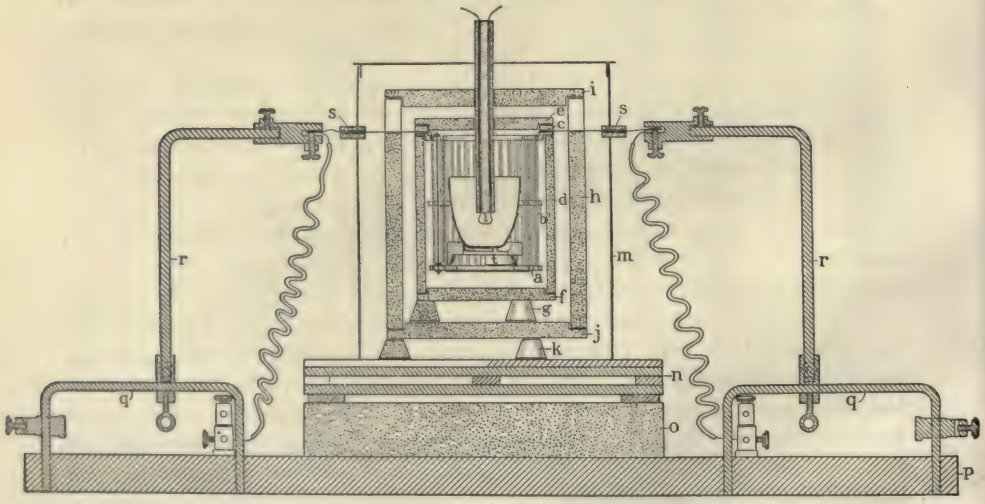


FIG. 6.—Electric kiln arranged as crucible furnace.

(*a*) to (*k*) the same as in Figs. 5 *A*, 5 *B*, 5 *C*; (*l*) Le Chatelier pyrometer; (*m*) sheet-iron cylinder covered with asbestus; (*n*), (*o*), and (*p*) parts of base; (*q*), (*r*), and (*s*) parts of electrical connections; (*t*) rest for crucible.

potteries, we could neither control nor know with certainty the temperature of any part of the kilns, but the places in them where the best results are most frequently obtained were easily found, and since then all of the cells have been burned at the potteries.

It has been stated elsewhere that, in the endeavor to produce the correct texture of cell wall, we made a study of thin sections, both of the potters' cells and of our own. In the course of this work, a considerable number of photographs were accumulated, 6 of which are here reproduced. Three of them (Plate 1, *a*, *c*, and *e*) are from potters' cells, and three (*b*, *d*, and *f*) are from the first cells made by us which proved themselves well suited to the measurement of osmotic pressure. It will be noted that the texture of the cells made in the laboratory is incomparably finer than that of the potters' products. But we were convinced, after nearly five years of laborious investigation, that just this *excessive fineness of texture* is absolutely *indispensable* to the correct measurement of osmotic pressure. It is necessary, in the first place, in order that the membrane may be deposited *exclusively upon* the *inner surface* of the cell wall. It is not meant by this statement that no part of the membrane is to be found *within* the pores. On the contrary, all good membranes are found, on microscopic examination, to be firmly *rooted* in the mouths of the pores which open behind it. It is this feature, in fact, which makes membranes produced by the electrolytic method so much superior to those which were made by the older process. Fineness of texture is also necessary in order to give the membrane a backing which will enable it to withstand pressure. If it is more open than that shown in Plate 1, *b*, *d*, and *f*, the membrane is deposited, at least partially, *within* the cell wall, and it breaks under moderate pressure.

It is desirable to explain the numerous black specks seen in Plate 1, *b*, *d*, and *f*. They are particles of the emery used in grinding the sections, and no part of what the photographs are intended to show.

The exact extent to which the sections here represented were magnified can not now be stated, the original records having been mislaid or lost, but it is believed to have been 125 diameters.

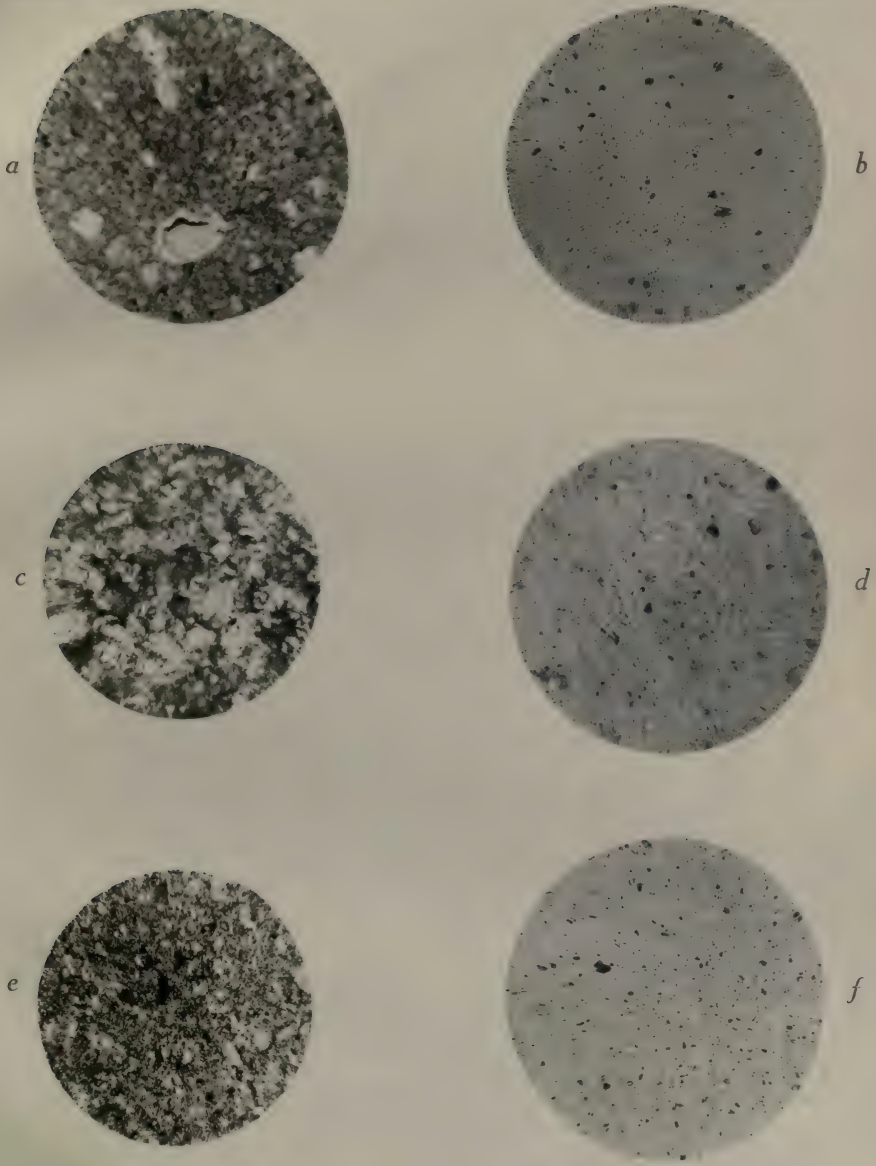
The question naturally arises, whether it is possible to make the texture of a cell wall *too close*, provided, of course, it still remains porous to some extent. The effective area of a membrane is equal to the aggregate area of the pore-openings upon the interior surface of the cell wall, and it has been found quite possible, by *hard burning*, so to diminish this area of membrane as to make the passage of solvent into or out of the cell intolerably slow. Some evidence has also been gathered to show that the reduction in the size of the pores may be carried to such an extent that the membrane no longer *roots* itself firmly into them. This is the explanation given to the formation of the *detachable* membranes which are sometimes deposited in very hard-burned cells. It is imagined that,

in such cases, the ferrocyanogen ions do not get far enough into the pores before meeting those of copper coming from the opposite direction—in other words, that the membrane is formed *at* or *without* rather than *within* the mouths of the pores.

After baking the cells and before glazing them, they are mounted on the lathe and ground under the shoulder with a high-speed carborundum wheel, to fit the brass rings with which the manometers are fastened in their places. The necks are also ground to the exact taper of the cones upon the ends of the manometers.

The finding of a suitable glaze for the upper half of the cells was a matter of considerable difficulty. As might have been expected, the expansion coefficient of products made as these cells are is very different from that of any of the potters' wares. Hence none of the glazes which are used by the potters would meet the requirements of the situation. All such glazes were found to "*craze*" badly upon the biscuit. An attempt was made to glaze with feldspar, but with poor success. A wholly suitable glazing material was finally obtained by adding silica and feldspar to one of the glazes which are used by the potters upon the better grades of their white tableware. The earlier experiments in glazing were carried out in a Seger gas kiln, but at the present time the glazing, as well as the baking of the cells, is done at the potteries.

There is one objection to glazing the cells to which attention should be called. They are glazed, inside and outside, from the middle upward, leaving the lower half of the cells porous. The whole interior of the cell is therefore protected at all times, either by the glaze or the membrane, so that no material in solution can diffuse into the wall from the inside. On the outside, the case is different. There it is quite possible for the dissolved substances to diffuse upward and accumulate between the inner and outer glazed surfaces. If these were allowed to remain and should afterwards diffuse downward and distribute themselves about the membrane, the pressure measured would not be that of the solution within the cell, but rather the difference between the pressures of the solutions on the opposite sides of the membrane. It is not believed that the results to be reported in later chapters have been at all vitiated by this possible source of error; because it has always been necessary, in order to maintain unimpaired the colloidal state of the membrane, to soak the cell for considerable intervals in pure water between any two successive experiments. Nevertheless, it seemed desirable to produce a cell, the upper half of which has the non-permeable character of porcelain, while the lower half remains porous. The difficulty is, of course, to prepare clay mixtures for the two parts of the cell which shall maintain identical expansion coefficients throughout the whole of the baking and cooling periods—at least at all points of union between them. Otherwise cracks or a condition of weakness must develop at the junction of the two clays.



FIGS. *a*, *c*, and *e*, thin sections taken from potter's cells.
FIGS. *b*, *d*, and *f*, thin sections taken from cells made in the laboratory.

Occasional experiments with a view to producing a half-porcelain, half-porous cell have been carried out along two lines: first, by so mixing the two kinds of clays that for a certain distance from the center, upward and downward, each kind would disappear gradually; second, by mixing some of the glazing material with the clay which was to form the upper half of the cell. The results have been encouraging, though up to the present time not wholly satisfactory.

THE MANOMETER ATTACHMENTS OF THE CELLS.

Great difficulty has been experienced in devising suitable arrangements for attaching the manometers to the cells. The problem is less simple than it might appear to be at first sight. Three things must be provided for in any workable device for closing the cell: (1) a junction which will not leak at high pressure; (2) means of adjusting, at will, the pressure in the cell (this is especially necessary when manometers of large capacity are used); and (3) an arrangement so simple in manipulation that the cell can be filled and closed and the proper initial pressure established in a fraction of a minute. Several schemes have been employed for joining the cell to the manometer, all of which, with two exceptions, are still in use. Some of the arrangements which worked satisfactorily at moderate temperatures failed utterly at high temperatures.

The first crude experiments* were made with cells into which rubber stoppers—carrying manometers—were thrust and fastened in place as well as might be with wire. The highest pressure obtained by such means was only 4.5 atmospheres. The manometers were pushed out of the cells and, owing to the tendency of rubber to flow into regions of less pressure, the stoppers were badly distorted. The earlier experiments, however, were only qualitative. They were made in order to test the membrane rather than with a view to measuring osmotic pressure. Other qualitative experiments were carried out later† with somewhat improved apparatus, but the earliest successful attempts‡ to *measure* osmotic pressure were made in the apparatus shown in Figure 7.

The porous cell (*A*), which is unglazed, is ground out internally to a distance from the open end which is a little over one-third its depth, until the shoulder formed at the bottom of the ground part extends entirely around the cell and is of sufficient width to afford an ample support for the soapstone ring (*b*). Afterwards two channels, one of which is designated in the figure by the letter *a*, are cut into the wall to prevent the dislodgment of the cement under pressure. The glass tube (*B*), which connects the cell with the manometer, is enlarged in two places (*c* and *d*) to prevent its displacement, and is contracted at the top to give it a better grip upon the rubber stopper (*e*). The soapstone ring (*b*) is accurately fitted to its place in the cell and also to the glass

*Amer. Chem. Journal, xxvi, 80. †*Ibid.*, xxviii, 1. ‡*Ibid.*, xxxiv, 1.

tube (*B*), the end of the latter having been ground to a perfectly circular form. The lower end of the glass tube is beveled inward to prevent the lodgment of air. The purposes of the brass parts (*g*, *h*, and *o*) are obvious without explanation. The tube (*B*) is set in the brass piece (*o*) and in the cell (*A*) with litharge-glycerine cement. But before proceeding to the latter operation, the glass tube, with the soapstone ring in place, is inverted, and any space which is left between them is filled with molten shellac. The tube and ring are then heated in an air bath until the shellac remains solid at 100°. The cement employed to fix the tube and the ring (*B* and *b*) in their places in the cell (*A*), and also the shellac used to join *b* to *B*, must be effectually protected from any contact with the solution in the cell or the water outside of it. For this purpose, the lower end of the glass tube, the soapstone ring, and the whole of the ground surface within the cell are repeatedly painted with a dilute solution of rubber. When a covering of sufficient thickness has been obtained, the soapstone ring—which is now firmly attached to the glass tube—is crowded into its place on the "shoulder." The operation is liable to lacerate more or less the rubber covering of the cell wall. To repair any damage of this kind, and also to insure a tight joint between the clay wall and the soapstone ring, the whole cavity above the latter is again painted with the rubber solution. The apparatus is then placed in an air-bath and maintained at 100° until the rubber becomes quite hard but not brittle. Finally the space between the glass tube and the cell wall is filled with the usual mixture of litharge and glycerine. The lower end of the manometer is enlarged (*j*) to prevent its being pushed upward through the stopper (*k*). The purposes of the cork (*l*) and of the bottle (*m*) do not require explanation.

A special instrument, which came to be known as the "*fang*," is required both to close and to open the cell. It is shown in Figure 8. It consists of a round, slender, and tapered piece of steel, one end of which has been furrowed out upon one side and bent into the curved form seen in the figure. It was usually made from a small round file from which the temper had been drawn. The "*fang*" is inserted between the rubber and the glass tube at *e*, to permit the escape, through the furrow, of the excess of liquid when the cell is closed, and again to provide for the entrance of air when the cell is opened. It is likewise of great assistance, when manipulated as a lever, in introducing and removing the stopper through the narrow mouth of the tube. The stopper from *e* upward is tightly wound with shoemakers' waxed thread to prevent the

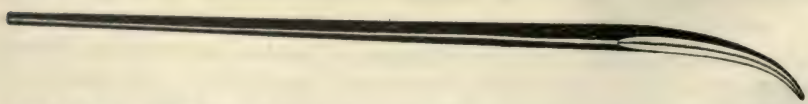


FIG. 8.—The "fang" for the introduction and removal of the rubber stoppers (*k*, Fig. 7).

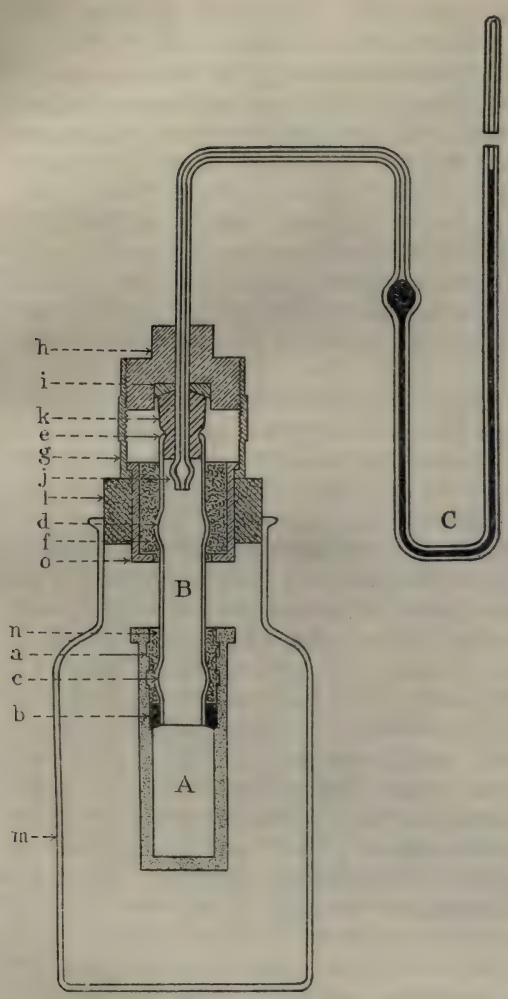


FIG. 7.—First form of complete cell.

(A) Porous cell; (*B*) glass tube; (*C*) manometer; (*a*) groove cut in cell; (*b*) soapstone ring; (*c*) and (*d*) enlargements in glass tube, to prevent slipping; (*e*) contraction at upper end of glass tube; (*f*) and (*n*) litharge-glycerine cement; (*g*) brass collar; (*h*) brass nut; (*i*) concave brass piece; (*j*) enlargement on end of manometer; (*k*) rubber stopper; (*l*) cork; (*m*) glass bottle; (*o*) brass piece.

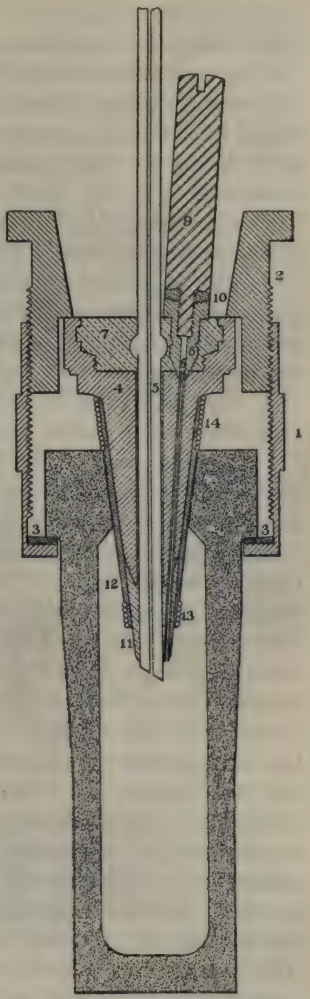


FIG. 9.—Second form of complete cell.

(1) Brass collar; (2) brass nut; (3) lead washer; (4) brass cone; (5) manometer; (6) hollow needle; (7) fusible metal; (8) brass piece to which the needle is brazed; (9) steel screw threaded into (8); (10) packing; (11) fusible metal covering exposed part of needle; (12) rubber tubing; (13) and (14) windings with twisted shoemakers' thread.

rubber from oozing out of the glass tube. The initial pressure in the cell is adjusted by means of the nut (*h*) and the collar (*g*).

The arrangement described above was employed for the measurement of osmotic pressure from 1905, when the first good cells were obtained, until 1908, when, for reasons which will be stated, but not fully discussed until later, it was abandoned for the apparatus which is shown in Figure 9.

The principal objections to the first apparatus employed for quantitative purposes (stated in the order of their importance) were:

1. The length of time required to close and open the cell. During both periods, the contents of the cell, being necessarily under less than maximum pressure, became diluted by the water which entered through the membrane.

2. The difficulty of the manipulation required properly to introduce and remove the rubber stopper without injury to the manometer.

3. The frequent bursting of the glass tube (*B*), which was usually attended by the total loss of the cell (*A*); since, as a rule, the membrane was ruined by the measures taken to replace a broken tube.

The apparatus represented in Figure 9* is a decided improvement on that shown in Figure 7. In it the difficulties enumerated above are obviated, though, as will be seen later, it has certain defects of its own. The function of the brass collar (1) and of the brass nut (2) will be readily understood without explanation. The form of these pieces has varied but little from the beginning. The lead ring (3) separates the shoulder of the cell from the flange of the brass collar and serves to protect the glaze upon the former. A ring of softer material, e. g., leather, can not be used for the purpose, since any upward movement of the collar, due to diminishing thickness of the ring under pressure, leads to an increase in the capacity of the cell and a dilution of the solution. In other words, the ring (3) must be of fairly rigid material. The brass cone (4) has two holes passing entirely through it, one for the manometer tube (5) and the other for the hollow needle (6), both of which (the manometer and the needle) are securely fastened in the cone by some fusible metal (Wood's, Rose's, or Babbit's). The holes through the cone are bored slightly larger than the tubes which are to occupy them, in order that the molten metal may flow down and completely fill the space between the latter and the walls of the former. In this way the tubes are more firmly fixed in their places and all danger of leakage upward through the cone is avoided. The hollow tube (6)—the needle—is nickel-plated and is brazed into the brass piece (8), which is bored out and threaded internally at the upper end to fit the closing plug (9). The upper end of 8 and the lower end of the larger portion of 9 are made concave in form, and between them is placed the packing (10). The concave form of these two surfaces is essential, since it pre-

*Amer. Chem. Journal, XL, 266; XLV, 91.

vents any outward lateral movement of the packing and causes the latter to close up tightly on the thread of the screw. After fixing the needle and the manometer tube (or rather the tube (5) which is to be fused to the manometer) in their places, the cone (4) is extended by means of the fusible metal (11) in order to protect the lower end of the needle. Over the cone, thus extended, is slipped the rubber tube (12) which is tightly wound at the lower and upper ends (13 and 14) with twisted shoemakers' thread. Owing to the ease with which rubber moves in the direction of smaller pressure, the whole space (14) between the shoulder of the brass cone and the top of the cell must be covered and rigidly supported by the thread. In practice, the winding of the upper end of the rubber tube is carried so far down that one or more turns of the thread are forced into the tapered neck of the cell.

A manometer, on whose calibration, capillary depression, and final verification weeks and perhaps months of labor have been bestowed, is too precious an instrument to be unnecessarily exposed to danger. Hence the cones are not attached in the first instance to the manometers, but always to short pieces of tubing of the same kind, which are afterwards fused to the manometers or cut off from them, as the occasion may arise.

At low and moderate temperatures, the arrangement just described renders very satisfactory service, and between 0° and 60° it is still in use. At higher temperatures, it develops certain defects which are so serious as to render its use quite impracticable. Leaks appear, due to increasing difference between the expansion coefficients of brass, glass, and the fusible metal; the alloy attacks the brazing or solder used in attaching the hollow needle to the brass piece (Figure 9); the glass of the manometers becoming brittle after continued use at high temperatures, it is difficult to fuse them on the glass tubes which pass through the cones; finally, at high temperatures, the rubber, used between the brass cone and the neck of the cell, also becomes brittle and liable to crack.

The deterioration of rubber at moderately elevated temperatures—apparently due, in our case, to a resumption and continuation of the vulcanizing process in the baths—has given much trouble, but we have not been able wholly to dispense with its use. We are able to make tight joints without it, but not, as yet, any satisfactory device for adjusting pressure in the cell.

The remainder of the manometer attachments which are here described were devised for use at the higher temperatures or with electrolytes, though they render equally good service at moderate and low temperatures, and, of course, also with non-electrolytes.

In Figure 10, the cone (*a*), which closes the neck of the cell (*A*), is turned on the lower end of the brass tube (*B*). At *b* there is a vent for the escape of air and any excess of solution. The usual collar and nut for fixing the manometer in the cell and for adjusting the pressure are seen at *c* and *d*. The manometer (*C*) is held tightly in its place in the

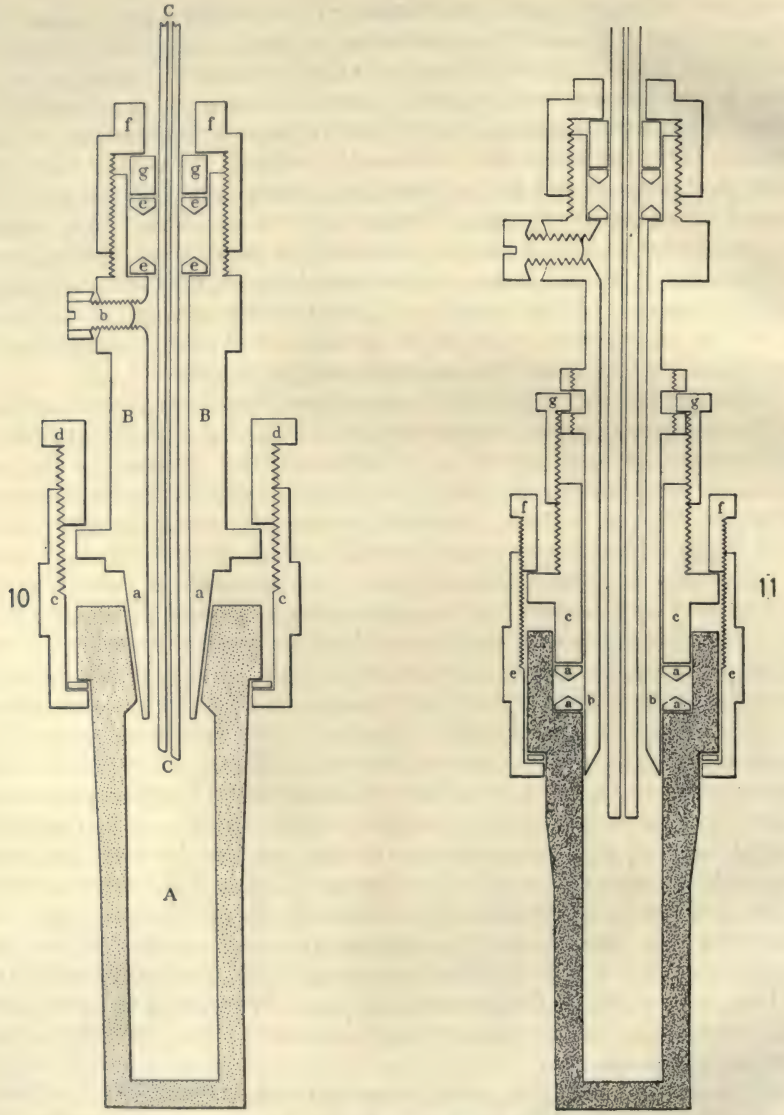


FIG. 10.—Third form of complete cell.

(*A*) Porous cell—upper half glazed; (*B*) brass piece; (*C*) manometer; (*a*) conical end of (*B*); (*b*) vent for solution; (*c*) brass collar; (*d*) brass nut resting on ledge of (*B*); (*e*) and (*e*) brass rings between which packing is placed; (*f*) brass collar screwing down upon (*B*) and compressing the packing between the rings (*e*), (*e*); (*g*) brass ring.

FIG. 11.—Fourth form of complete cell.

(*a*), (*a*) Brass or porcelain rings for compressing the packing and displacing it laterally; (*b*) brass tube around which all metallic parts are assembled, upper end the same as in Fig. 10; (*c*) brass piece employed in compressing packing and in adjusting initial pressure; (*e*) brass collar; (*f*) brass ring; (*g*) brass nut, threaded internally, which is employed in adjusting initial pressure by moving the tube (*b*).

tube (*B*) by packing which is compressed between the rings (*e*, *e*). The form of the rings is such as to force the material of the packing in both of the lateral directions—on the one side toward the manometer, and on the other toward the wall of the brass tube. The compression is effected by means of the hollow nut (*f*). The brass ring (*g*), which serves as a "follower," is made of any required length. A rubber tube is slipped over the cone (*a*) and tied above and below the neck of the cell in exactly the same manner as in the apparatus shown in Figure 9. The reason for the concave form of the surfaces between which the packing of the vent (*b*) is compressed has already been explained. The packing between the rings (*e*, *e*) usually consists of alternate disks of leather and thin rubber, one of the rubber disks being placed below the lower ring, i. e., between it and its "seat." The seat and the under side of the lower ring are grooved to prevent too much lateral movement on the part of the rubber between them in the direction of the manometer; otherwise the greater part of the material of this lowest disk would be crowded into the cavity below the ring. All brass surfaces which are exposed to the liquid contents of the cell are plated with nickel, silver, or gold, according to the character of the solutions whose pressure is to be determined.

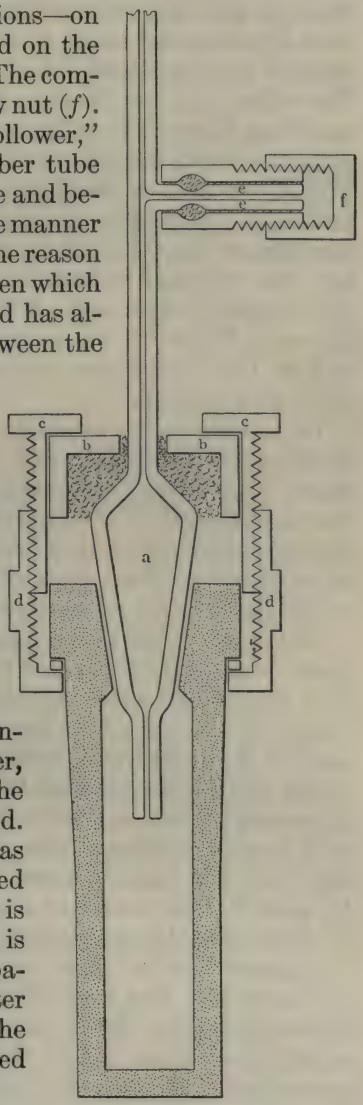


FIG. 12.—Fifth form of complete cell; for use with substances which attack metals.

(*a*) Enlarged end of manometer; (*b*) brass piece fastened to manometer by litharge-glycerine cement; (*c*) hollow brass nut resting upon (*b*); (*d*) brass collar; (*e*) vent for solution; (*f*) brass cap with packing in bottom.

The arrangement shown in Figure 10 has two great advantages over that presented in Figure 9. The use of fusible metal is avoided, and, if the right kind of packing is used, it is not necessary at any time to separate the calibrated end of the manometer from the end entering the cell, since the manometer is always sufficiently released by unscrewing the nut (*f*) to permit of its easy withdrawal from the tube (*B*). It also does away with the plated steel needle (Figure 9, 6), which may be corroded if the solution contains an electrolyte.

In the apparatus seen in Figure 11 the cone (Figure 10, *a*, *a*,) is dispensed

with, and the union between the manometer attachment and the cell is effected by means of the brass rings (*a*, *a*, *a*, *a*) and the packing which is placed between them. The packing is compressed in the vertical direction and made to expand horizontally against the cell on the one side and the brass tube (*b*, *b*) on the other by the sliding piece (*c*, *c*). The collar (*e*, *e*) and the nut (*f*, *f*) do not differ essentially from the corresponding pieces seen in Figures 9 and 10. The vent and the arrangements for fixing the manometer are the same in Figure 11 as in Figure 10. The adjustment of pressure within the cell is effected by means of the nut (*g*, *g*). Turned to the right, it drives the tube (*b*, *b*), and with it the manometer, into the cell, increasing the pressure. If it is turned to the left, the tube and manometer are raised and the pressure diminished. The principal advantages of the arrangement seen in Figure 11 over that shown in Figure 10 are in the better means of adjusting the pressure and in the substitution of packing for rubber tubing in making the joint with the cell.

In measuring the osmotic pressure of electrolytes, it is desirable to avoid, as far as possible, any contact of the solutions with metallic surfaces, even though the same are protected by plating with the more resistant metals. The covering is often imperfect in spots, notwithstanding the care which is taken in the plating. Accordingly, a number of schemes have been devised for joining the manometer and the cell, in which the solution comes in contact only with glass and rubber.

In Figure 12, the hollow glass cone (*a*) serves the same purpose as the brass cones seen in Figures 9 and 10. It is set in the brass piece (*b*) with litharge-glycerine cement. Its use, in connection with the usual collar (*d*) and nut (*c*), is apparent. The cone, like those in Figures 9 and 10, is covered with rubber tubing, which is wound and tied at the upper and lower ends with twisted shoemakers' thread. The side tube (*e*), which serves as a vent for the escape of surplus solution, is embedded with cement in a brass tube, which is threaded externally to receive the cap (*f*). The packing in the bottom of the cap closes the vent. It will be seen that the means of adjusting pressure within the cell is the same in all three of the instruments represented in Figures 9, 10, and 12.

Another form of glass cone which has rendered good service is seen in Figure 13. The cone, which is made of a solid piece of glass, is bored excentrically for the manometer (*a*) and the vent (*b*). The vent is closed at the lower end by the rubber disk (*e*), which is attached to and controlled by a platinum rod running through the hole in the stopper. The upper end of the rod is threaded and provided with a nut, as seen in the figure. To prevent the solution which escapes through the vent from coming into direct contact with the cement, all exposed parts of the latter are painted with a solution of rubber. The solid glass cone has some advantages over the hollow one, as will appear when the manipulation connected with filling and closing the cells is explained.

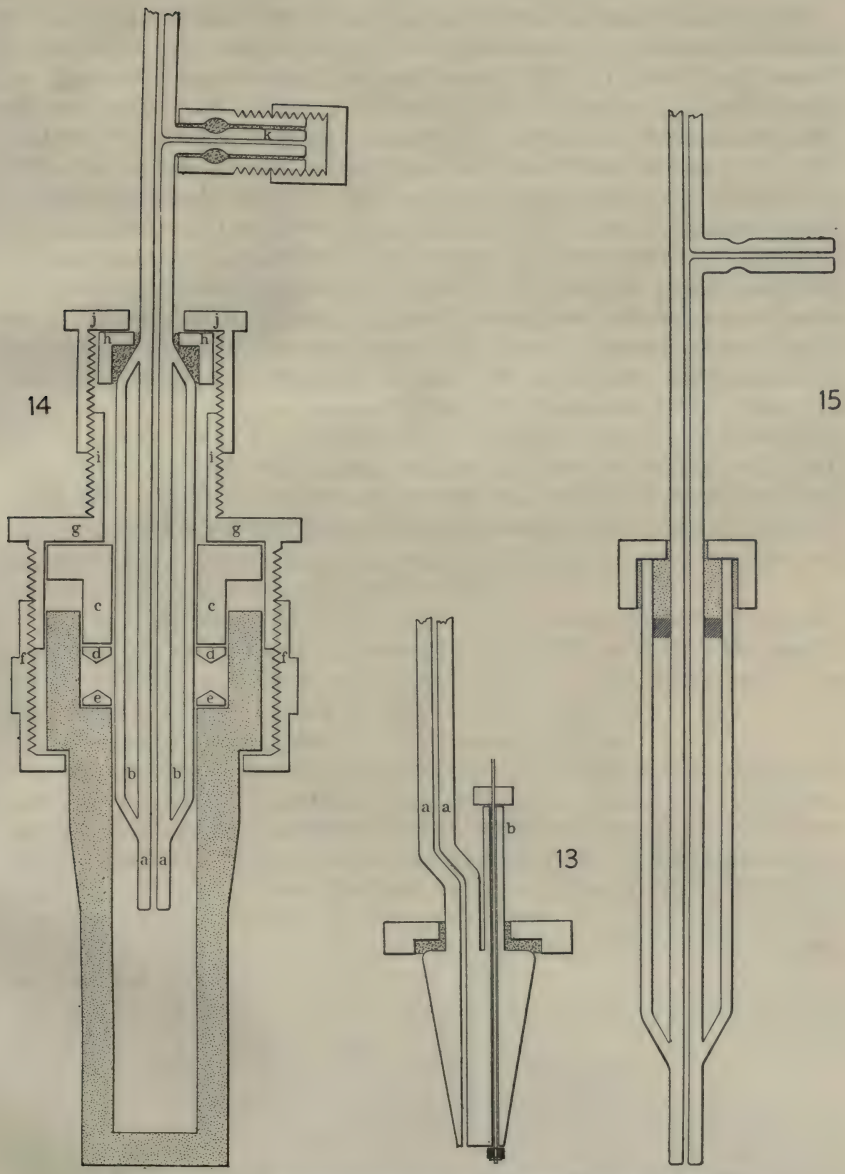


FIG. 13.—Solid glass stopper for use with substances which attack metals.

(*a*) Manometer tube; (*b*) vent for solution, closed by valve at lower end of stopper.

FIG. 14.—Glass manometer attachment for cells with straight necks.

(*a*) Manometer with straight tube fused to lower end; (*b*) space between manometer and glass tube; (*c*) brass ring; (*d*) and (*e*) porcelain rings for compressing packing; (*f*) brass collar; (*g*), (*h*), (*i*), and (*j*), brass pieces with which to close the cell, and also to adjust initial pressure; (*k*) vent for solution.

FIG. 15.—Glass manometer attachment for cells with straight neck.

Like that shown in Fig. 14, except that the glass tube is left open at the top, and then closed with a brass cap and litharge-glycerine cement.

Still another glass device for attaching the manometer to the cell is seen in Figure 14. It was designed for use with the form of cell which is seen in Figure 11. The manometer (*a*) passes entirely through the closed tube (*b*), whose outside diameter is only a little less than the interior diameter of the cell. The means for compressing the packing (*c*, *d*, *e*, *f*, and *g*) and fixing the large tube (*b*) in the cell do not differ essentially from the analogous parts seen in Figure 11, except that the lower ring (*e*) is made of porcelain, in order that the solution in the cell may nowhere come in contact with metal. The adjustment of pressure within the cell is effected by means of the brass pieces (*h*, which is fixed in its place with cement), (*i*), and (*j*). The vent (*k*) is not absolutely necessary, though it is sometimes a convenience. Instead of opening the vent when it is desired to lessen the pressure, the nut (*j*) may be turned slightly to the left.

The device shown in Figure 15 is a substitute for that seen in Figure 14. The two differ only in that the large tube (*b*) is closed at both ends in Figure 14, while it is open at the top in Figure 15. The latter is easier to make, and is in no way inferior to the closed form.

CHAPTER II.

THE MANOMETERS.

The possibility of correctly determining osmotic pressure depends upon four fundamental conditions, no one of which can be said to exceed another in importance. They are (1) a suitable cell, i. e., a cell which is able to support the membrane under high pressure and in which the membrane is always deposited upon the interior surface of the porous wall; (2) a truly semi-permeable membrane, i. e., a membrane which does not leak the solute; (3) a perfectly automatic and exact regulation of temperature; and (4) an accurate calibration of the manometers. If any one of these conditions is unfulfilled, all efforts to measure the force must lead to erroneous results, which are not only futile but positively mischievous—mischievous because they furnish the opportunity for an indulgence of the propensity of the over-hasty and unwary to erect elaborate speculative structures upon foundations of what may be justly called *tainted* facts.

The manometers which are used for the measurement of osmotic pressure have an external diameter of about 6 millimeters. The length of the calibrated portion varies from 400 to 500 millimeters. The diameter of the bore ranges from 0.45 to 0.72 millimeter.

The reasons for using tubes of very small bore are:

1. It is necessary to fill the upper ends of the manometers with short columns of mercury, because in closing the instruments, after the introduction of the gas, the caliber of the tubes in that region is affected to an unknown extent. If the internal diameter is large, e. g., 1.0 millimeter or more, the mercury is often dislodged by the severe tapping to which the manometers are subjected at certain times.

2. The compression of the small volume of gas which they contain involves but little dilution of the cell contents.

3. Relatively small volumes of mercury are required by manometers of small bore. The importance of this fact will be better understood when the subject of "*thermometer effects*" is discussed.

The disadvantages of using manometers of small bore are:

1. It is more difficult to deal satisfactorily with the meniscus in a narrow tube.

2. The capillary depression is large in small tubes and it varies greatly with slight irregularities of bore.

3. The movements of the mercury in narrow tubes are strongly influenced by the presence of minute quantities of impurities, whether the same are dissolved in the metal itself or are attached to the surface of the glass.

PURIFICATION OF THE MERCURY.

The material which ordinarily passes for *pure* mercury in the laboratory is by no means suitable for manometric work, and to obtain it in adequately pure condition for this purpose requires unusually thorough treatment. The mercury which is used in our manometers—and also that which is now used in the bath thermostats—is cleansed in the following manner:

1. The commercial material is first filtered through paper filled with pin holes to free it from dirt. It is then heated for four hours to the boiling-point in a glass retort, to the neck of which a long glass tube has been fused for the condensation and return of the vapors; and during this time a current of air is forced through the boiling metal. On cooling, it is again filtered to remove the scum of oxides which usually forms in considerable quantity.

2. It is distilled in a vacuum.

3. The distillate is washed by the method of Lothar Meyer, but with water containing 2 per cent of nitric acid and 2 per cent of mercurous nitrate instead of ferric chloride. The apparatus in which the washing is done consists of a wide tube two meters in length, to the lower end of which has been fused a quite narrow tube of the usual double U form, the proportions of the descending and ascending limbs being so selected that the mercury which supports the cleansing liquid shall lie wholly within the smaller tube. To admit the mercury at the top and to regulate its flow, a separating funnel is employed. The lower end of the funnel, instead of being drawn out to a fine point, as in the apparatus of Meyer, is widened out into the form of an inverted funnel, according to the suggestion of Hillebrand, and over this are tied two or three thicknesses of the finest silk bolting-cloth. The material to be purified is thus made to enter the cleansing liquid in hundreds and perhaps thousands of excessively fine streams. It is passed *1,000 times* through the solution of nitric acid and mercurous nitrate, and is then thoroughly washed with water and dried.

4. After treating the mercury as described under 1, 2, and 3, it is again distilled in a vacuum, but not in the still (2) which is used for the first distillation.

The mercury which has thus been cleansed retains its brilliant luster in the air, and its movements in narrow tubes are highly satisfactory. We have also prepared mercury from the purest oxide which we could make, but have not found it superior in any way to the product obtained by the means desribed above.

CALIBRATION OF THE MANOMETERS.

The tubes which are used in making the manometers are the most nearly perfect for the purpose which it is practicable to obtain. The essential requirements are that any tube shall be of very nearly uni-

form bore throughout, and that the form of the bore in every part shall be circular. Very few, if any, tubes conform perfectly to both requirements. The material from which selections are to be made is imported in lots of several kilograms each, and the purveyors are urged to spare neither pains nor expense in procuring tubes of the highest possible excellence. In each lot of selected material thus obtained, there are usually found—though not always—a few tubes which answer all reasonable requirements.

The first step in making a manometer is to etch upon the tube two fine lines extending completely around the instrument. These are usually referred to as the "upper scratch" and "lower scratch," one being near the upper and the other near the lower limit of the calibrated portion of the manometer. These lines are made no coarser than is absolutely necessary in order that they may be distinctly seen through the telescope, since in small tubes a meniscus behind any line, however fine, is apt to give the observer trouble. No other graduation appears upon the manometers. All readings on the instruments are referred to one or the other of the two "*scratches*." That is, a reading consists always in determining the distance between the meniscus of a mercury column and either one of the lines in question. Since the distance between them is accurately known, readings referred to one line can readily be transferred to the other. The distance between the lines depends upon the length which the manometer is to have—ultimately, of course, upon the height of the available space in the baths. Above the upper and below the lower scratch, a considerable length of tube is left to provide for subsequent operations.

Two methods of calibration have been employed, both of which will be briefly explained, though the earlier one is not now much in use except for preliminary explorations of the tubes.

FIRST METHOD.

Figure 16 represents the instrument which is employed to move and adjust the calibrating thread. A steel screw (*a*), with a long lever, is threaded through a cap of hard rubber (*b*), in which the glass tube (*d*)—enlarged at *c*—is set with litharge-glycerine cement. In order to make a mercury-tight joint, the upper end of the steel screw is slightly lubricated, and around the portion which extends into the glass tube some of the cement is allowed to solidify. The rubber stopper (*f*), carrying the manometer (*g*), is inserted (with the aid of the "fang," Figure 8) in the glass tube (*d*), which is sharply contracted at the upper end (*e*).

The manometer is drawn out at the upper end to a fine tube which is bent into the form of an inverted U. With the apparatus—including the manometer—nearly full of mercury, the screw is turned to the right until the column enters and reaches the highest part of the inverted U.

The outlet is then immersed in a globule of pure mercury and the screw is reversed. This manipulation brings a short calibrating thread (*h*) into the manometer, which is separated from the main body of the mercury by a cushion of air. The thread can now be made to take any desired position in the tube by simply turning the screw and simultaneously tapping the manometer. The electric "hammer" employed for the latter purpose will be described in connection with the process for the determination of capillary depression.

The process of calibration consists in bringing the lower end of the thread to the point at which it is desired to begin, and then setting it exactly end to end up the tube, determining each time the length of the detached column. When the calibration has been carried as far up as is desired, the thread is run out and weighed. Subsequently a long thread of mercury, one filling nearly the whole length of the calibrated portion of the tube, is drawn in and measured, and then run out and weighed. It is evident that the weight of the short thread, multiplied by the number of settings, will be less than that of the long thread filling the same length of tube, by the weight of the mercury required to fill the double meniscus spaces. By means of this relation, the correction for the volume of the double meniscus is readily calculated.

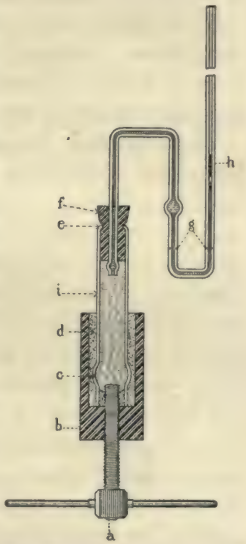


FIG. 16.—First arrangement for calibrating manometers.

(*a*) Screw for setting calibrating thread; (*b*) hard-rubber cup; (*c*) enlargement in glass tube (*i*); (*d*) litharge-glycerine cement; (*e*) contracted end of glass tube; (*f*) rubber stopper; (*g*) manometer; (*h*) calibrating thread separated from main column of mercury by air; (*i*) glass tube filled with mercury.

SECOND METHOD.

The later procedure differs from the earlier one in manner rather than in principle. After etching upon the glass the two lines previously mentioned, a small bulb is blown near each end of the tube outside the portion to be calibrated. These serve to catch and preserve the calibrating thread in case of accident. For calibration, the tube is placed in the horizontal position, over a ruled mirror, on the dividing engine, the screw of which has been carefully compared with the graduated meter scales employed in the measurement of osmotic pressure.

The device employed for shifting the thread from one position to another is shown in Figure 17. *A* is the manometer with its two bulbs (*a*, *a*). The two lines of reference previously referred to as the "*scratches*" are seen at *b*, *b*. The shifting arrangement (*B*) for the calibrating thread (*c*) consists of a steel ball (*d*), a large bicycle ball, which is located in the center of a rubber tube (*e*). *A* and *B* are connected through the glass tubes (*f*, *f*) and the rubber tubes (*g*, *g*).

If it is desired to move the thread to the right, the rubber tube (*e*), to the left of the ball (*d*), is compressed between the thumb and forefinger of the left hand until the meniscus has taken the right position under the miscroscope, when, *without releasing the tube*, the rubber over the ball (*d*) is pinched between the thumb and forefinger of the right hand until a passage for air is opened. The portion of the rubber tube which is held in the left hand may then be released, since any difference in atmospheric pressure at the two ends of the thread is quickly equalized through the passage which has been opened over the ball (*d*), and without disturbing the thread. If the thread is to be moved to the left, the rubber tube to the right of *d* is compressed between the fingers of the right hand, and the passage for air over the ball is made with the left hand. After a little experience, the exact adjustment of the calibrating thread becomes easy and nearly automatic.

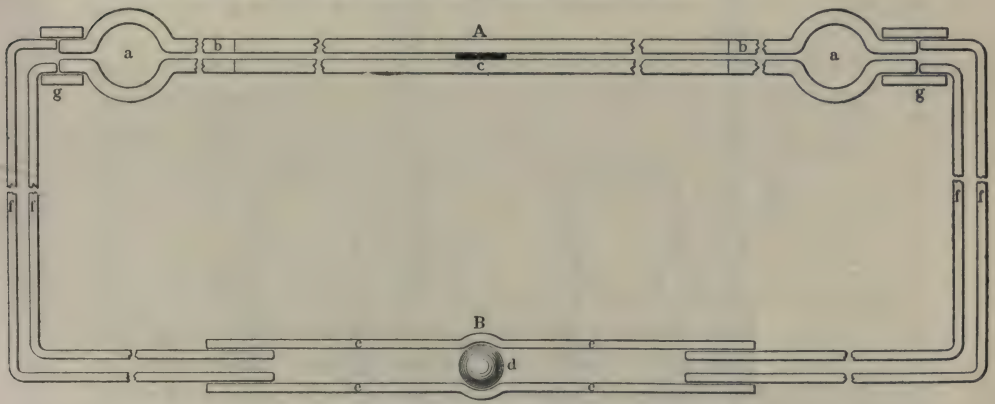


FIG. 17.—Second arrangement for calibrating manometers.

(*A*) Tube to be calibrated (bore from 0.45 to 0.65 millimeter); (*B*) rubber tube; (*a*, *a*) bulbs blown on each end of tube to prevent loss of calibrating thread; (*b*, *b*) lines of reference etched on tube; (*c*) calibrating thread; (*d*) steel ball for setting calibrating thread; (*e*) rubber tubing; (*f*, *f*) glass tubes; (*g*, *g*) rubber tubes.

The calibration is commenced somewhat below the lower scratch—the etched line to the left—and consists, as when the tube is calibrated in the vertical position, in setting the thread exactly end to end and determining its length until the thread has passed the upper scratch. It is then run out of the tube and weighed. Afterwards the whole of the calibrated portion of the tube is filled with mercury, which is also run out and weighed.

From the length and weight of the long thread, the mean diameter of the bore is calculated; and from the observations on the length of the short thread in the different parts of the tube, a mean calibration unit is derived, and a curve of corrections constructed, exactly as in the calibration of a eudiometer. Finally, a mean value for the double meniscus is obtained from the length and weight relations of the long

and short threads. If we multiply the weight of the short thread by the number of times its length is contained in that of the long thread, i. e., by the number of times it was set end to end, and subtract the

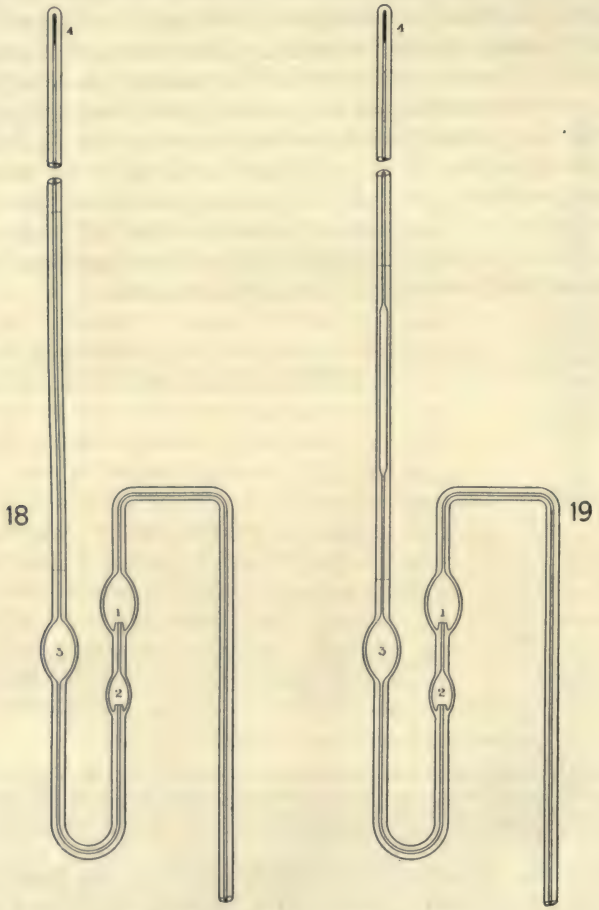


FIG. 18.—Simplest form of manometer.

(1) and (2) bulbs with traps in the bottom to prevent liquids from working their way into the calibrated portion of the instrument; (3) nitrogen reservoir to prevent loss of gas under diminished pressure; (4) mercury filling the portion of tube whose caliber may have been altered in closing the instrument.

FIG. 19.—Manometer for high pressure.

Differs from that in Fig. 18 only in having a nitrogen reservoir within the calibrated portion of the instrument.

product from the weight of the long thread, the difference is the weight of the mercury which would be required to fill all the meniscus spaces which were left vacant in setting the short thread end to end along the tube. Converting this difference in weight into volume, and divid-

ing by the number of settings less one, we obtain a mean correction for a double meniscus, which is the meniscus correction to be applied in all measurements of pressure, since the nitrogen in the manometers is always included between two mercury columns.

The method which is explained above suffices for the simple form of manometer seen in Figure 18, but some modifications are necessary when a manometer of the form seen in Figure 19 is to be calibrated. The peculiarity of the latter instrument is the large reservoir for gas which lies between the two lines of reference and within the calibrated area. The narrower portions—below, from some point under the lower scratch to the bottom of the enlargement, and above, from the top of the wide part to the end of the tube—are calibrated in the manner already described. The meniscus correction also is derived from the weight and length relations of short and long threads. So far the procedure is without change. It remains, however, to ascertain the capacity of the wider part as a whole, and eventually in terms of the calibration unit. To do this, the wider part is slightly more than filled with mercury, so that both the upper and lower meniscus are well within calibrated portions of the narrow ends. From the weight of this mercury—with proper correction for overlapping in the narrower calibrated parts—the total capacity of the wider part of the tube is calculated. Two verifications of the correctness of the previous work are now undertaken. It will be noticed, on referring to Figure 19, that the upper line of reference is not very far above the upper end of the wider portion of the manometer. The first step in the verification is to fill the space between the two scratches with mercury—the upper meniscus may lie somewhat above the upper scratch. The volume of this mercury should, of course, be equal to the sum of the previously found capacities of all of the parts which were filled by it. The final step in the verification is to apply the same test to the whole tube by filling it with mercury from the lower scratch to the upper limit of the calibration.

THE MENISCUS.

In narrow tubes, owing to the small volume of the gas which they contain, the meniscus correction is of considerable importance, since it may amount—especially at high pressures—to an appreciable fraction of the volume of the gas.

The significance of the meniscus correction, *when translated into pressure*, increases with increasing concentration of the solutions with a rapidity which might well astonish one who has not clearly in mind the fact that, though in the first instance it is simply a space of fixed volume, its importance depends, not only on the pressure upon the gas which fills it, but also upon the *volume of all* the gas in the manometer. The effect of this relation in practice is illustrated by means of

the following tabulation of data taken from the record of a single manometer (No. 9). The meniscus correction (double) in this instrument is 0.17 calibration unit, and the volume of the nitrogen under standard conditions of temperature and pressure is 454.14 calibration units. The temperature in all cases is 25°. Column I in Table 1 gives the weight-normal concentration of the solutions; II gives the observed pressure in atmospheres; III shows the volumes of the compressed nitrogen reduced to standard temperature; IV, the corrections in fractions of an atmosphere for the double meniscus; V, the relative osmotic pressures, the pressure of the 0.1 normal solution being taken as unity; and VI, the relative corrections for meniscus, the correction for the 0.1 normal solution serving as the unit.

TABLE 1.

I. Concentration.	II. Osmotic pressure, atmospheres.	III. Vol. N_2 cal. units.	IV. Meniscus correction, atmosphere.	V. Relative osmotic pressure.	VI. Relative meniscus correction.
0.1	2.635	141.15	0.00317	1.0000	1.000
0.2	5.139	80.69	0.01083	1.9503	3.4164
0.3	7.738	55.59	0.02366	2.9366	7.4637
0.4	10.295	42.41	0.04126	3.9070	13.0158
0.5	12.947	34.01	0.06972	4.9135	21.9937
0.6	15.620	28.37	0.09360	5.9275	29.5268
0.7	18.436	24.11	0.12999	6.9928	41.0063
0.8	21.258	20.97	0.17233	8.1055	54.3628
0.9	24.126	18.53	0.22133	9.1558	69.8202
1.0	27.076	16.54	0.27834	10.2755	87.8044

Particular attention is called to columns V and VI, where it will be seen that, while the osmotic pressure increased a little over ten-fold, the value of the meniscus correction increased nearly *88-fold.* Expressed in heights of a mercury column, the correction for meniscus in the case cited in the table increases from a value of 2.4 millimeters to one of 211.5 millimeters.

The method of obtaining the meniscus correction which is given above is believed to be entirely correct in principle. Nevertheless it has been found, in applying it, that the calculated volume of the meniscus is *always less* than it would have been if the form of the meniscus were truly spherical, as it is generally assumed to be. The *experimental* correction is usually just about *three-fourths* that calculated from the supposed spherical form of the meniscus. The difference may be due to unavoidable errors in reading the length of the short calibrating threads. If these are always read "*too short,*" the obvious result would be a too small correction for the meniscus. However, the error, if error it is, is not of a cumulative character. Moreover, if, in calibration, one reads habitually "too short," he will repeat the offense in reading pressures. For these reasons, it is believed to be

safer to employ the *experimental* correction rather than that calculated from the known diameter of the tube and the supposed spherical form of the meniscus.

One great advantage of the practice of deriving the meniscus correction from the calibration data is the excellent means which it affords of detecting faulty calibration. It is known that the best work in calibration leads uniformly to an approximately fixed value for the meniscus, hence it is to be inferred, when another value is obtained, that the calibration which gave it is erroneous.

The inverse relation of the importance of the meniscus correction to the volume of the gas which is measured makes it desirable to increase the quantity of nitrogen in the manometers as far as may be done without creating other difficulties of a serious nature. This has been accomplished by the form of manometer seen in Figures 19, 20, etc., in which the volume of nitrogen is relatively very large. In the manometers of this kind which are in actual use, a length of 1 millimeter in the wider part is about equal in capacity to a length of 16 millimeters in the narrower portion of the tube. The column of mercury which occupies the closed end of the manometer, being in the narrow portion of the manometer, is not easily dislodged by tapping. In this respect, the instrument seen in Figure 19, etc., is not inferior to the earlier form seen in Figure 18. During a measurement of pressure, the whole of the nitrogen is compressed into the upper and narrower portion of the tube, hence the column of the gas is much longer under any given pressure in the latter than in the former instrument, and the errors due to faulty determinations of the value of the meniscus and of the amount of capillary depression are correspondingly less serious in their effects upon the accuracy of the measurement.

Manometers like that shown in Figure 19 are designed more especially for the measurement of the pressure of concentrated solutions where errors of meniscus tell heavily on the results, unless large volumes of gas are used. In the case of dilute solutions, large gas volumes are obviously less necessary as a means of minimizing such errors.

The length of the wider portion of the second form of manometer is varied according to the range of pressure which it is desired to measure with the instrument; e. g., if the pressures in question lie between 4 and 6 atmospheres, the wide and narrow portions are so related that the mercury meniscus will appear in the latter at some pressure slightly below 4 atmospheres. In instruments designed for use with normal solutions, on the other hand, the nitrogen is not all compressed into the narrower portion of the tube until a pressure of more than 20 atmospheres has been reached.

No considerable dilution of the solution results from the larger volume of gas in such manometers, because, at the time of closing the cell, a mechanical pressure—the so-called *initial pressure*—is brought to bear

on the contents, which is nearly equal to the osmotic pressure. Hence the subsequent diminution in the volume of the gas is small. The only disadvantage experienced in the later form of manometer is due to the larger volumes of mercury which must be stored up in them. The "*thermometer effects*," resulting from slight fluctuations in the temperature of the baths, are therefore more pronounced in them than in the other form of instrument.

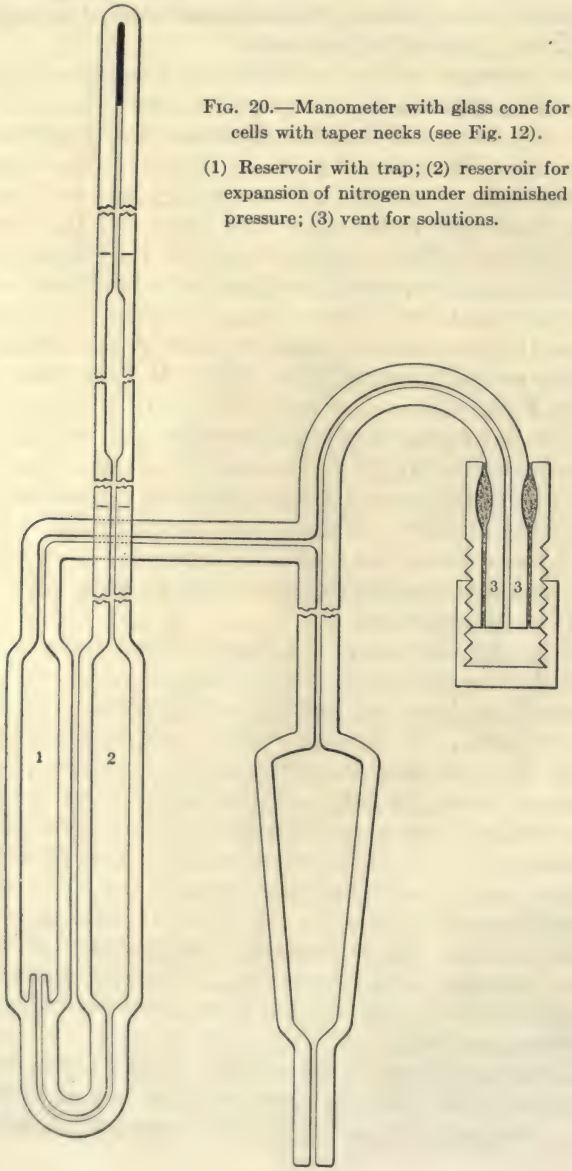


FIG. 20.—Manometer with glass cone for cells with taper necks (see Fig. 12).

(1) Reservoir with trap; (2) reservoir for expansion of nitrogen under diminished pressure; (3) vent for solutions.

THE UNCALIBRATED PORTIONS OF THE MANOMETERS.

It will be noticed (Figures 18, 19, 20, and 21) that the uncalibrated portion of all manometers is provided with two or three bulbs, or their equivalents in the form of inserted short pieces of tubing of larger diameter. The bulb nearest the calibrated end (Figures 18 and 19, 3; 20 and 21, 2) serves as a reservoir in which the nitrogen, when under diminished pressure, may expand without danger of escaping from the instrument. Its capacity is regulated by the volume of the gas to be accommodated, i. e., by its original or usual volume, and the maximum probable amount of diminished pressure to which it will ever be subjected. The bulbs nearest the cell (Figures 18 and 19, 1 and 2; 20 and 21, 1) serve as reservoirs for the mercury which is to be driven forward in compressing the nitrogen, and their total capacity is, therefore, to be regulated by the volume of the gas under ordinary conditions and the maximum pressures to be measured.

For reasons which will appear later, none of the bulbs should be made unnecessarily large. The requirements of the situation may be reduced to the simple rule that some mercury must be left in the bulb nearest the manometer proper under the lowest pressure, and some in the bulb nearest the cell under the highest pressure. It will be noticed that bulbs 1 and 2 in Figures 18 and 19, and their equivalents (1 in Figures 20 and 21) in other manometers, are provided with traps. By means of these, the mercury is made to enter the narrow tubes below at points somewhat above the bottom of the bulbs. The purpose of the arrangement will be understood from the following explanation: When the solution in the cell is under pressure, it drives the mercury before it and enters to some extent the upper end of the nearest bulb. When the pressure is afterwards removed, and the mercury which had been expelled returns, it is apt to entangle minute drops of the solution between itself and the wall of the bulb. Occasionally, during the subsequent movements of the mercury in the tube, one or more of these drops will persistently work its way forward toward the calibrated end of the manometer, making it necessary, sooner or later, to open, cleanse, and refill the instrument. The "traps" are an effectual prevention of such calamities. Before their introduction, it was frequently necessary to inspect the manometers for the presence of these migrating particles of liquid, and it happened at times that, notwithstanding the greatest vigilance, they escaped detection until it was discovered that the manometers were no longer measuring correctly. Straight tubes, because of their greater strength (Figures 20 and 21, 1 and 2), are used for mercury reservoirs instead of bulbs (Figures 18 and 19, 1, 2, and 3) when high pressures are to be measured.

The manometers shown in Figures 18 and 19 have no vents. They are suitable for use in the arrangements seen in Figures 9, 10, and 11,

in which the vents are provided for in the metallic parts of the apparatus. When all contact of the solutions with metals is to be avoided, as in the case of electrolytes, the vent is of glass and is made a part of

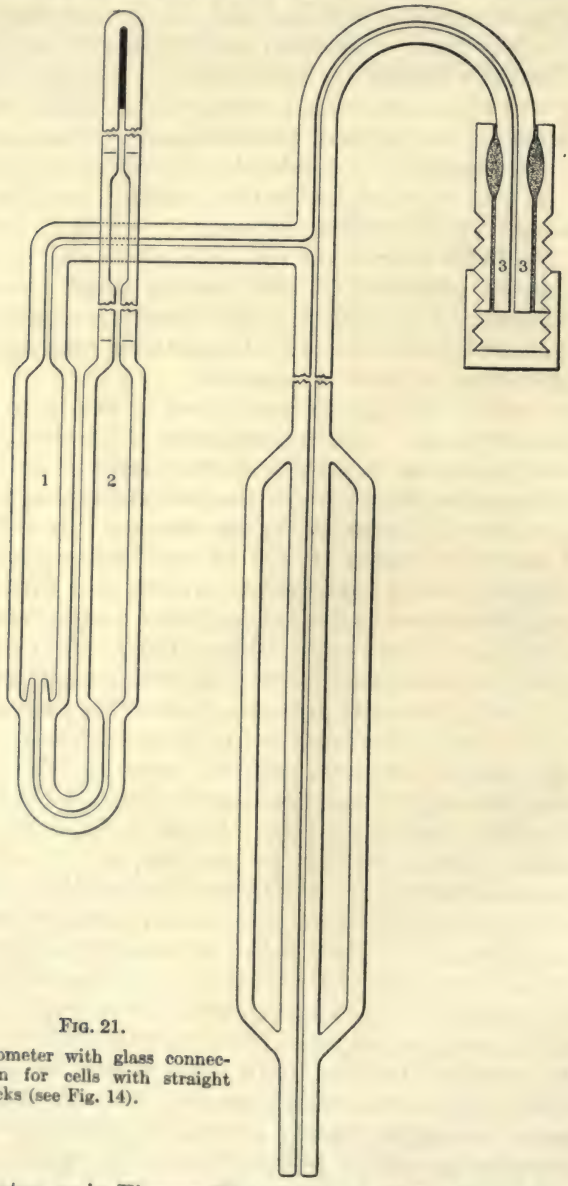


FIG. 21.

Manometer with glass connection for cells with straight necks (see Fig. 14).

the manometer, as in Figures 20 and 21, 3. It has been given a variety of positions on the manometer (see Figures 12, 13, 14, and 15), but on the whole that seen in Figures 20 and 21 is preferred.

CAPILLARY DEPRESSION.

Before joining the calibrated to the uncalibrated portion of the manometer, the former must be subjected to a thoroughgoing investigation of its capillary depression. The mean diameter of the bore of the whole tube is known, that having been calculated from the length and weight of the long thread of mercury which is used in the calibration; also the mean diameters of a considerable number of short spaces, these having been calculated in the same manner from the weight of the short thread and its length in different parts of the tube. But, though such data are useful as a means of judging the excellence of the tube for manometric purposes, they can not be relied upon for the derivation of the capillary depression.

The mean capillary depression of the mercury in the manometer of smallest bore amounts to 18 millimeters, i. e., to more than 0.023 atmosphere. In the remaining instruments, the average depression is about 15 millimeters, or 0.02 atmosphere. The real difficulty with the capillary depression is due to the fact that in most tubes it varies frequently and largely within short distances. In addition to these sharp local fluctuations, there is nearly always a gradual increase or diminution of the depression due to a corresponding general change in the diameter of the bore, the diameter at one end of the tube being usually larger than at the other.

Owing to the large changes which may occur within short distances, it is necessary to determine the amount of the capillary depression at a great many points in a tube. By way of illustrating the importance of doing so, the following partial record of the capillary depressions which were found at different places in one manometer is given. In one column of the table, there are recorded the distances above the lower "scratch" at which observations were made; and in the other, the depressions which were found at these points.

TABLE 2.

Distance above scratch.	Capillary depression.	Distance above scratch.	Capillary depression.
8.65	7.92	117.43	11.42
22.70	10.85	224.12	11.18
47.35	9.87	280.30	11.74
71.38	10.04	361.10	11.80
114.28	10.42	414.10	12.14

A difference of 1 millimeter in the capillary depression is equivalent to about one calibration unit in determining the volume of the nitrogen in the manometer. Suppose now the capillary depression of this tube had been determined only at nine points, beginning with the second one, 22.7 millimeters above the scratch. The mean of the values

is 11.05, which number might have been accepted as the *mean capillary depression* of the manometer. But suppose when the volume of the nitrogen in the manometer is determined, the meniscus stands 8.65 millimeters above the scratch, where the depression is in reality only 7.92 millimeters. The error, if the mean number 11.05 is used in correcting for capillary depression, would be about $11.05-7.92=3.13$ calibration units. The whole of the nitrogen in this manometer amounts to only 400 calibration units. The error made in determining the volume would therefore be 0.78 per cent. This example of what might happen if the condition of the tube at 8.65 millimeters above the scratch had escaped detection will serve to convince one of the necessity of a detailed investigation of the capillary depression in tubes of small bore; also of the advisability of using manometers of large capacity, like those seen in Figures 19–21, in order to minimize errors of capillary depression as well as those of meniscus.

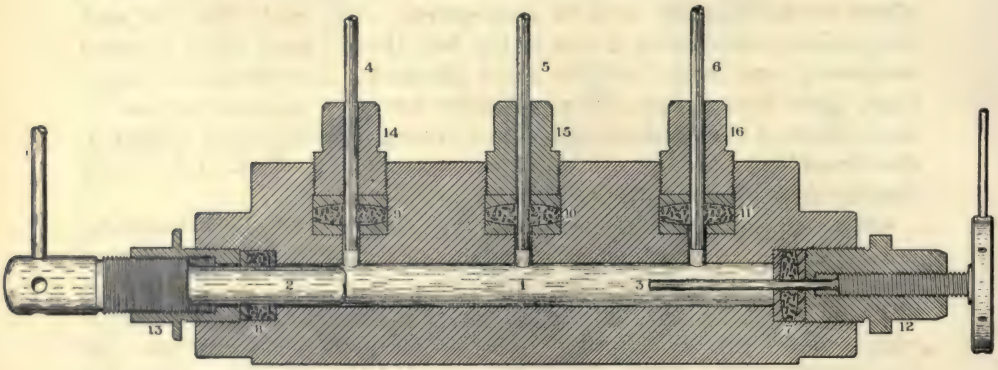


FIG. 22.—"Steel block" for the determination of gas volumes in manometers, for the comparison of instruments, and for the determination of capillary depression.

(1) Mercury reservoir; (2) plunger for coarse adjustment of pressure; (3) plunger for fine adjustments; (4), (5), and (6) manometers; (7), (8), (9), (10), and (11) packing; (12), (13), (14), (15), and (16) nuts for compression of packing.

Capillary depression appears twice as an important factor in the measurement of osmotic pressure: (1) in determining the volume of the nitrogen under standard conditions of temperature and pressure; and (2) in correcting its volume under an unknown pressure, which (i. e., the osmotic pressure) is a quotient of the two volumes.

An instrument much used in the determination of capillary depression, and also in the comparison of manometers, is the "steel block" seen in Figure 22. It contains a reservoir for mercury (1) and two plungers, one of which (2) is large, and the other (3) small. The larger one is employed for the coarser, and the smaller one for the finer, adjustments of pressure in tubes 4, 5, and 6. The packing (7, 8, 9, 10, and 11), which may be of leather or rubber, or partly of both, is compressed in each case between the concave surfaces of two steel disks and the required pressure is brought upon these by means of the

threaded plugs 12, 13, 14, 15, and 16. The instrument has been tested and found to be mercury-tight up to 350 atmospheres.

Pure mercury only is put into the block, but it can not be presumed, under the prevailing conditions, to maintain its purity unimpaired; hence some precautions are necessary to prevent contamination of the mercury in the instruments under investigation or a fouling of the glass walls of the tubes. The usual precaution is to fuse the calibrated portion of the manometer to one end of a glass tube of nearly equal bore, which has been bent to a double U form. In the intermediate limb a bulb is blown that serves as a reservoir of pure mercury for use in the manometer proper. Having filled the instrument with pure mercury, it is fastened in place in the steel block. The arrangement for adjusting the height of the mercury in the tube under examination and for determining capillary depression by difference of level consists of a glass tube having an internal diameter of 35 millimeters, which is connected, by means of a rubber tube, with a second glass tube occupying one of the holes in the steel block. In order to render the rubber tube sufficiently rigid, and thereby to avoid unnecessary oscillations of the mercury meniscus, it is tightly wound with several thicknesses of insulating tape. The remaining hole in the block is usually occupied by a tube whose capillary depression has been investigated in great detail.

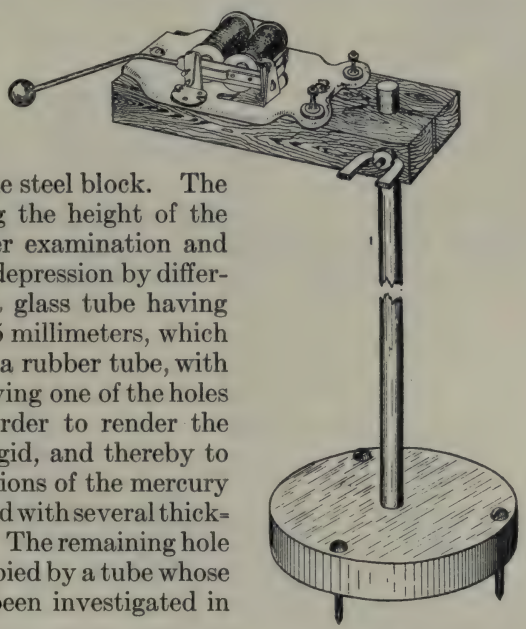


FIG. 23.
Electric hammer for tapping manometers.

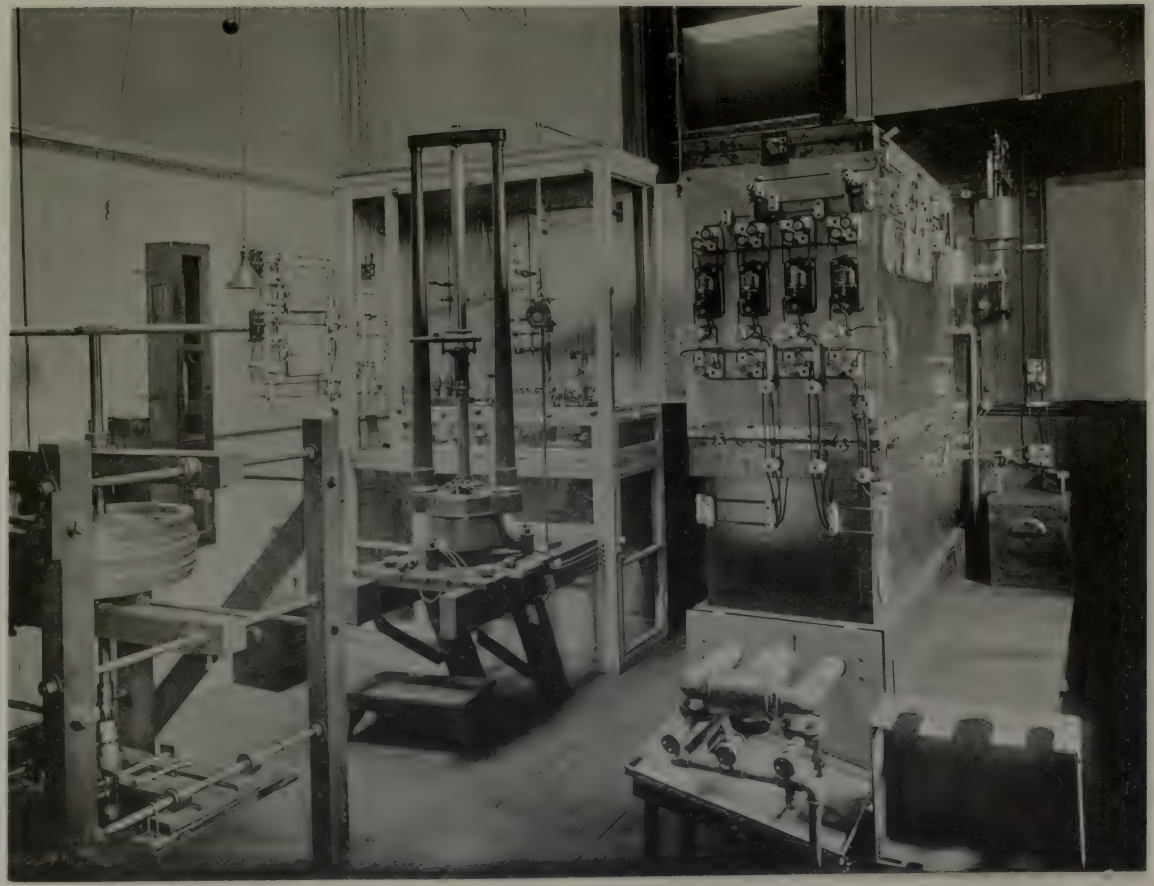
Formerly it was attempted to determine capillary depression by means of comparisons with a *standard*, i. e., by dispensing with the wide tube mentioned above and inserting in one of the holes of the steel block a tube whose capillary depression in every part was known. This is a much more convenient method, but it was abandoned because it was found that the errors of the standard add themselves to those of the other instrument. The same difficulty makes itself felt when it is attempted to compare one manometer with another. In such cases it is impossible to tell to what extent the observed discrepancy is due to the incorrectness of the values assigned to the capillary depression of each instrument. It is as likely to be the sum as the difference of the two. In any event, it is, of course, their algebraic sum.

Another important instrument in connection with the investigation of manometers is the "tapper" seen in Figure 23. In the measurement

of osmotic pressure, the mercury has ample time to adjust itself, or the adjustment is aided by means to be described hereafter; but in operations connected with the determination of capillary depression, and with the comparison and verification of these instruments, the "lag" of the mercury must be overcome by jarring the tubes, and frequently the tapping to which it is necessary to subject tubes of small bore is severe and prolonged. This is notably the case in manometers in which the glass is not perfectly clean or has been slightly roughened by the reagents employed in cleansing it.

The construction of the "tapper" is so obvious that it is only necessary to notice two or three of its features. It is strongly inclined, when in operation, to move away from the tube which the "hammer" is striking. Hence the base is made of lead, for the sake of greater weight, and is mounted upon three very sharp-pointed pegs, which sink somewhat into the wood on which the instrument rests. The hammer is covered with rubber or leather to prevent the possible shattering effect of its blows. The tapper is connected, by means of a flexible wire cord, through the battery, with a portable push-button which is held in the hand of the observer behind the cathetometer, who can therefore at any time hammer the tube without removing his eye from the telescope.

During the determination of capillary depression and other operations which are connected with the preparation of manometers for use, the instruments must be kept at constant temperature. Otherwise the all-important meniscus is continually changing its form, to the great confusion of the observer. The first effective device for the maintenance of temperature was the so-called "*manometer house*," which is seen—stripped of its coverings—in Figure 24 and Plate II. It was in this that, for several years, all experiments on manometers, except calibration in the horizontal position, were carried out. The "house" contains the "steel block," the "brass block"—to be described later—the "tapper," a meter scale, a thermostat for the regulation of temperature, electric heaters (lamps), and a fan motor, all of which will be recognized in the figures. The shelf (Figure 24), on which rest the various instruments, is supported by heavy steel brackets (not shown in the figure), which are bolted to the heavy masonry wall behind, and afford a satisfactory degree of stability. At each end of the shelf, a space 5 centimeters wide is left for the passage of air. Lamps are employed as the source of heat, for the reason that they heat up and cool down more quickly than other electric heating appliances. They are under the control of the thermostat seen in the upper part of the house. The fan is stationed before a hole of equal diameter in the partition 2. By means of it, the air, heated by the lamps, is kept in continuous circulation over all the instruments. The temperature which is maintained in the compartment is always higher by a few degrees than the highest temperature of the room in which it is located.



View of "manometer house," cathetometer, arrangement for pressing clays, and one style of rectangular bath.

The remaining features are better seen in the photograph (Plate 2), where the manometer house is represented with the plate-glass front removed. The end to the right and the top of the house are also of

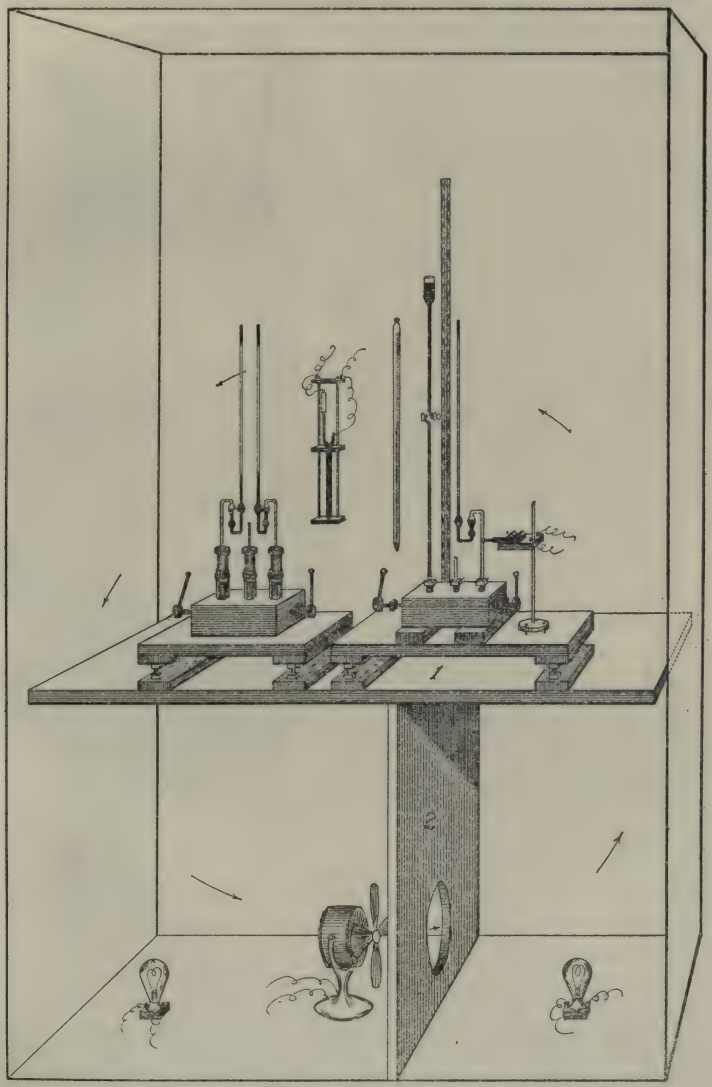


FIG. 24.

"Manometer house" for the calibration and comparison of instruments, etc.

glass, though the latter is usually covered with a thick woolen pad and the former with a flannel curtain. The front is also provided with a flannel curtain (not seen in the figure), which may be parted at con-

venient places for observation. The frame for the glass at the top is removable to provide for the extension of the house upward when very long tubes are to be accommodated. The various windows and doors are made to close tightly against rubber cushions, or the cracks between them and the framework are covered with surgeons' tape. The tubes through which the wires enter the house are, however, left more or less open to provide for equalization of atmospheric pressure.

During the past year or two, the more exacting parts of the investigation of manometers have been carried out in the bath seen in Figure 45. This bath is ample enough to accommodate the steel block, the tapper, and all other accessories required for a determination of capillary depression, or of nitrogen volume, and for the comparison of manometers; and in it temperatures can be maintained for long periods which are constant to 0.01°.

Plate 2 shows the type of cathetometer used, and under it a specimen of the devices by means of which the requisite degree of steadiness for all the instruments is secured, notwithstanding their location in the third story of the laboratory. The foundation for the cathetometer consists of two heavy wooden brackets. One end of the horizontal timbers is buried in the thick brick wall behind the house, while the descending timbers pass through the floor and enter the same wall in the room below. There is nowhere contact with a floor or with a partition wall. Two such brackets are required for a cathetometer and three for a bath.

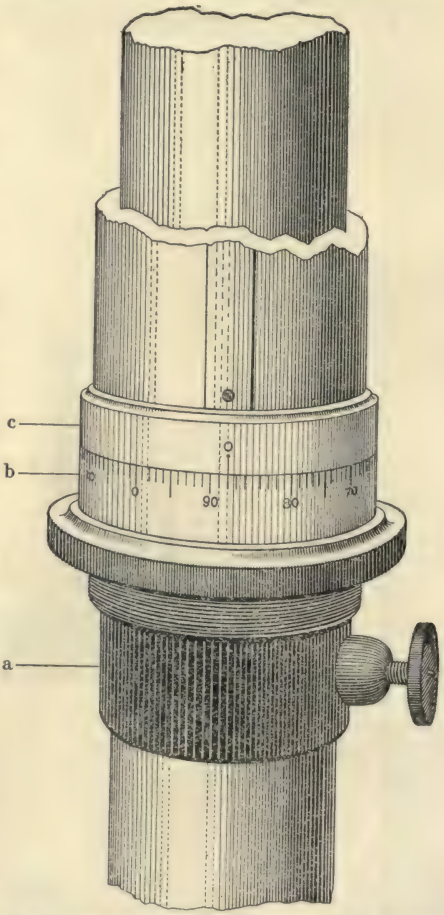


FIG. 25.—Improvement in cathetometers for the fine adjustment of the telescope, which also serves as a substitute for the micrometer eye-piece.

(*a*) Set-collar with upper and thicker end threaded—thread 1 millimeter pitch; (*b*) nut running over (*a*), and graduated in hundredths; (*c*) ring attached to sleeve carrying telescope, and resting on (*b*).

In Figure 25 is shown an improved arrangement for fine adjustment of the height of the telescope, and for reading fractional parts of a milli-

meter on the graduated scale. It consists of a sliding collar (*a*), on the upper and heavier end of which has been cut a thread of 1 millimeter pitch. Over this runs the internally threaded collar (*b*); and upon *b* rests the sleeve (*c*) on which is mounted the telescope. The collar (*b*) is graduated in 100 equal parts, while *c* has engraved upon it a vertical zero line. One entire revolution of *b* corresponds therefore to a rise or descent of 1 millimeter in the telescope, and its movements up and down can be read directly to hundredths, and estimated to thousandths of a millimeter. The device is a substitute for the usual micrometer eye-piece on the telescope, and has the advantage over the latter that it is not necessary to have a precisely fixed distance between the eye-piece and the graduated scale. A second advantage, considered as a means of elevating and lowering the telescope, is that the whole weight of the telescope and its balanced carriage is uniformly distributed upon the top of the collar (*b*) and ultimately upon the upper side of the thread. Hence, when the collar is turned, there is neither any of that "lurching" of the telescope which is so offensive in the older arrangements, nor any "back lash" on the thread.

THE FILLING OF THE MANOMETER.

When the manometer has been calibrated and the value of the meniscus correction ascertained, and the extent of the capillary depression has been determined at a great many points, it is joined to the uncalibrated portion of the instrument and filled with nitrogen.

Originally the manometers were filled with purified and dried air, but it was found that, however pure the mercury in them might be, the volume of the included air slowly diminished. At first it was suspected that this diminution in the volume might be only apparent; in other words, that the capacity of the manometers was increasing under the pressures to which the gas was subjected. To test this suspicion, long columns of mercury were placed in calibrated tubes, like those used for manometers, between columns of air; and these were then subjected to pressures equal to the highest osmotic pressures which were being measured. The purpose was to discover whether the columns of mercury, under such treatment, diminished sensibly in length—either temporarily or permanently. The results were wholly negative. It was therefore concluded that the observed decrease in the volume of the imprisoned air must be due to the action of the oxygen on the mercury, though no fouling of the glass, such as would be expected from the presence of oxides, had been noticed. A third possible explanation, namely, that in the course of the movements of the mercury back and forth some of the gas had been "*rubbed out*" of the tubes, was not seriously considered. If the loss in volume of gas was due to the disappearance of oxygen, the obvious remedy was to fill the manometer with nitrogen. The remedy was so complete that, after years of use, no change in the volume of that gas in the manometers has been observed.

The nitrogen used in the manometers is obtained by passing air first through an alkaline solution of pyrogallol, and then, in the order named, over heated copper oxide, heated copper, heated copper oxide, calcium chloride, fused potassium hydroxide, and resublimed phosphorus pentoxide. The glass tubes containing the dry reagents are all connected with each other and with the receptacle for the nitrogen by fusing the ends together.

The arrangement of apparatus for filling the manometers is shown in Figure 26. The method of filling, because of its complexity and the difficulty of some of its parts, will be described in considerable detail.

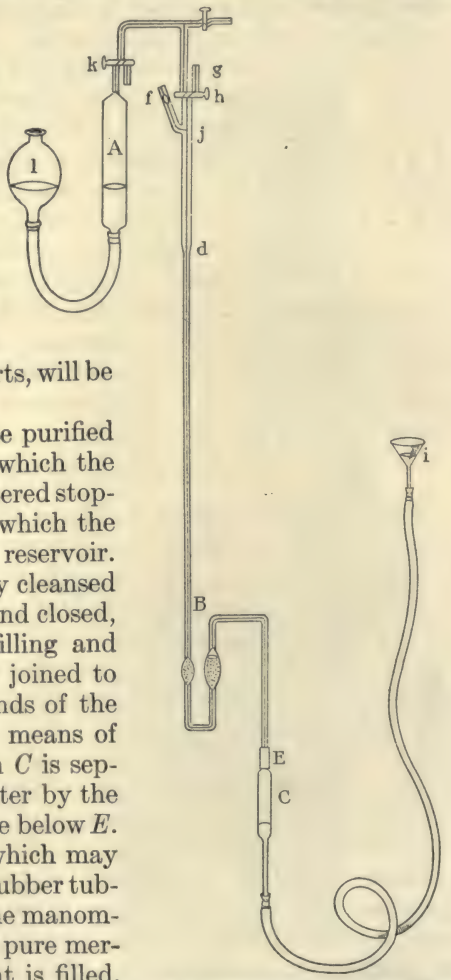


FIG. 26.—Arrangement for filling manometers with nitrogen.

(*A*) Nitrogen reservoir; (*B*) calibrated manometer; (*C*) air chamber to separate mercury in (*i*) from pure mercury in manometer; (*E*) connector between (*B*) and (*C*); (*l*) and (*i*) mercury reservoirs; (*k*) and (*h*) two-way stopcocks; (*f*) and (*g*) vents.

A is the reservoir in which the purified nitrogen is stored up, and from which the manometers are filled. The unlettered stopcock at the top is that through which the gas, after purification, enters the reservoir. *B* is the calibrated and thoroughly cleansed manometer which is to be filled and closed, and *C* is an arrangement for filling and emptying the manometer. *B* is joined to *A*, at *d*, by fusing together the ends of the glass tubes; and to *C*, at *E*, by means of rubber tubing. The mercury in *C* is separated from that in the manometer by the air which nearly fills the wide tube below *E*. In this way, the mercury in *C*, which may be impure from its contact with rubber tubing, is prevented from entering the manometer and contaminating the very pure mercury with which that instrument is filled. This air also plays an important role when the manometer is closed.

Before joining the manometer *B* to *A* and *C*, its lower end is immersed in pure mercury and, with the instrument in an inclined position, gentle suction is applied until the two bulbs are filled as nearly as may be with mercury. Owing to the presence of one or more traps, some air will be left in the bulbs, and this must be expelled by bringing the instrument into the vertical position and forcing the

mercury in the other direction. When the bulbs and more or less of the tube *B* have been filled, and the junctions at *d* and *E* have been made, the manometer is repeatedly washed out with air which has been dried by resublimed phosphorus pentoxide. For this purpose, by lowering the reservoir (*i*), the dried air is admitted through the stopcock at the top, and likewise through *f*, which is also provided with a drying tube. By raising *i*, it is again expelled, mostly through *g*, but partly through *f*.

The next step, after drying the manometer, is to fill it with nitrogen from the reservoir (*A*). The reservoir (*i*) is raised and the air in the manometer is expelled through *g* until the mercury column reaches *j*, when the stopcock (*h*) is closed, and a small quantity of mercury is driven into the side tube (*f*). This is the mercury which is afterwards to occupy the upper end of the closed manometer. The rubber tube connecting *f* with its drying tube is tightly closed and the air remaining between *j* and the stopcock (*h*) is expelled through *h*, care being taken not to allow the mercury quite to reach the stopcock, lest it should be contaminated by some of the lubricant on the latter. Some of the nitrogen in *A* is repeatedly wasted through the stopcock at the top and through *g* in order to remove any air still remaining in the upper part of the apparatus. Then by lowering *i* or raising *l*, with stopcock *k* open, the manometer is filled with nitrogen. This is wasted through *g*, and the manometer is again filled from *A*, and the operation of filling and emptying it is repeated as many times as may be thought necessary.

When the manometer has been filled with nitrogen for the last time, the reservoir (*i*) is adjusted to the right level, and the gas is placed under a slight over pressure by raising *l*. The stopcock (*h*) is opened and then quickly closed. This leaves the nitrogen in the manometer under a pressure equal to that of the atmosphere.

By gently pinching the rubber tube which closes *f*, a little mercury is forced out of the side tube into the vertical one between *j* and *d*. If it breaks into globules at *j*, they are reunited at *d* by tapping the tube. The mercury thus transferred does not enter the manometer, because of its small bore.

The reservoir (*i*) is now lowered until all the mercury collected at *d* has been drawn into the manometer to some convenient distance below that point, when the glass at *d* is softened in the blowpipe flame and the manometer is detached, but so as to leave both tubes sealed.

The glass at the detached end of the manometer is again softened in the flame and then drawn out to an exceedingly fine capillary tube, which is afterwards filled with mercury by raising *i*. Finally the capillary is closed in the flame, and the walls are thickened under slightly diminished pressure. Care must be taken, in closing the manometer, not to convert any considerable amount of the mercury into vapor, and to heat the glass so uniformly that the vapor which is necessarily

formed can not recondense until the operation of closing is finished. Otherwise the violent agitation of the mercury, due to rapid vaporization and condensation, is apt to shatter the tube. When closed, no bubble of air should be discernible at the top of the short mercury column. First attempts at closing usually fail in this respect, but after a little practice, one is able to perform the operation with perfect success.

The short column of mercury in the upper end of the manometer has a twofold purpose. It prevents, during the closing of the instrument, any contamination of the nitrogen with air or with the combustion products of the flame; and it fills up all that portion of the instrument whose caliber may have been altered to an unknown extent by heating.

DETERMINATION OF THE VOLUME OF THE NITROGEN.

For this purpose, the manometer is placed in the steel block within the bath (Figure 45), and the pressure upon the gas is regulated by the device used in the determination of capillary depression, i. e., a glass tube having an internal diameter of 35 millimeters, which is connected with the steel block by means of a flexible tube. Formerly it was attempted to use a stationary "side" tube. This consisted of a short piece cut from the same tube as the manometer itself and, like the manometer, it was fixed rigidly in the block, the pressure being regulated by the plungers. The practice was, however, based on the mistaken assumption that in any given, fairly good tube the capillary depression is nearly uniform throughout. It was discontinued when it was discovered that the best tubes we could obtain were very uneven in this respect.

The volume of the nitrogen is determined under a number of different pressures, all of them, of course, quite near that of the atmosphere. To determine it under high pressures, it is necessary to employ another closed manometer—a so-called "*standard manometer*." There is, however, the same objection to the employment of standard manometers as to the use of narrow side tubes in the determination of capillary depression and of gas volumes, the objection, namely, that all the errors of both tubes—principally of capillary depression—are charged to the tube under investigation.

Sometimes, in order to increase the quantity of the gas in the manometer, more than the calibrated portion of the tube has been filled with nitrogen. This was frequently done before the introduction of manometers with large reservoirs of known capacity (Figure 19, etc.). In such cases the use of a *standard manometer* could not be avoided.

For the comparison of one manometer with another, the steel block and also the "brass block" seen in Figure 27 are used. The latter does not differ in construction from the former, except in the means for fixing the tubes in their places. The arrangements employed for that purpose are identical with those used in joining the cells and the manometers. Some other liquid than mercury—either water or a solution—is used in the brass block.

When any operation is to be performed with a manometer which might endanger the calibrated portion, or contaminate the mercury in it, or foul the walls, the instrument is cut into two parts, the point of severance being usually between the bulbs, when that is practicable. If necessary, another piece of suitable form is then attached to the manometer, e. g., as when the instrument is to be placed in the steel block. Afterwards the detached portion is restored to its place.

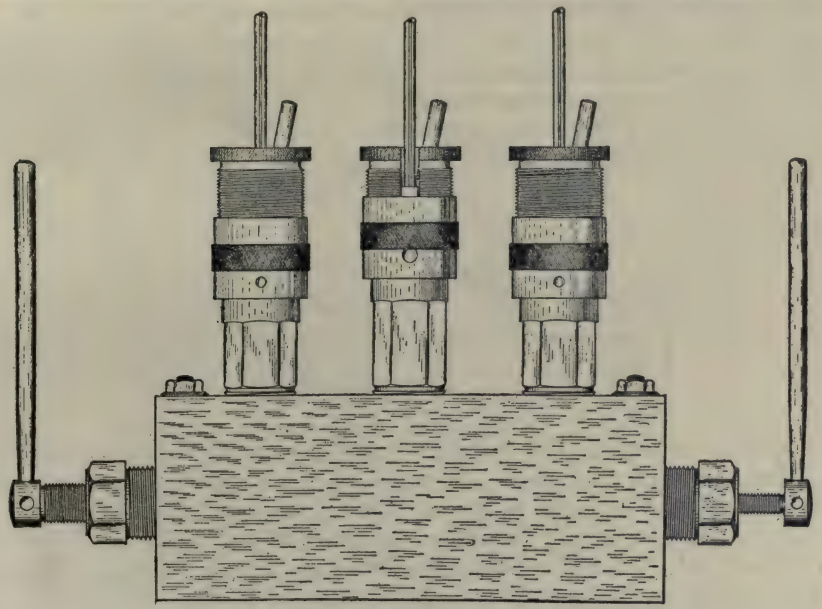


FIG. 27.—"Brass block."
Construction like that of "steel block" (see Figure 22), except the manometer attachments, which are like those used with the cells.

In Figure 28 is seen an instrument much used in the manipulation of the manometers. The manner of its use will be best illustrated by describing a few of the operations in which it is most frequently employed.

1. Suppose the whole instrument (Figure 18 or 19), except the space occupied by the nitrogen, is filled with mercury, and it is necessary to cut the tube between the bulbs 1 and 2, either for the purpose of replacing the detached piece by another of similar form, or by a simpler piece of glass tubing. The rubber-covered cone which is usually upon the open end of the manometer, or a sharply sloping stopper through which the end has been passed, is placed in the cup 1. The air is then exhausted through a rubber tube attached to the stem at 2. When a sufficient quantity of mercury has been drawn into the cup, the whole arrangement is tipped backwards until the end of the manometer is exposed. Air is then cautiously readmitted to fill the space in the instrument which was previously occupied by the mercury removed.

2. Suppose the open end of the manometer, e. g., to the middle of bulb No. 1, is filled with air and it is desired to replace it with mercury. A quantity of mercury is poured into the cup, the manometer is inserted and, with the instrument tipped so as to expose the open end, the air is exhausted until the mercury begins to run out. On bringing the manometer again to the upright position, so as to immerse the open end, and readmitting air, the mercury flows into the tube to replace the air which has been withdrawn.

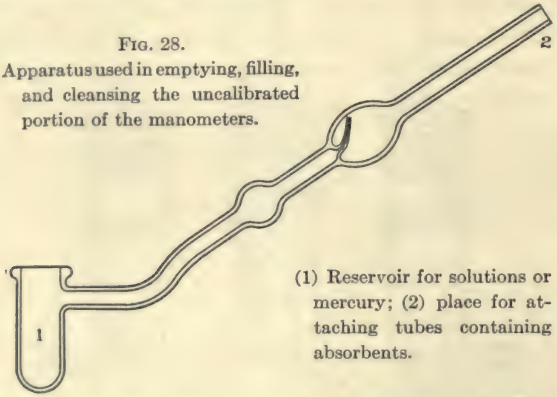


FIG. 28.
Apparatus used in emptying, filling, and cleansing the uncalibrated portion of the manometers.

(1) Reservoir for solutions or mercury; (2) place for attaching tubes containing absorbents.

3. Suppose, again, the manometer has been used in a measurement of pressure, and the open end—perhaps also a small portion of bulb No. 1—is filled with the solution. Before the instrument can be used for another experiment, this must be removed and replaced, either by mercury or by some of the solution whose pressure is to be determined. The necessary manipulation is as follows: (1) the old solution is removed and replaced by air; (2) the air is replaced by the new solution, and this, in turn, is replaced in succession by other portions of the same solution, until there is no danger that the concentration of the new solution will be affected by the older one. If mercury is to be substituted for a solution, the tube must be washed and dried before introducing it. In this case, portions of the wash liquids—water, alcohol, and redistilled ether—are introduced and removed in exactly the same manner as when one solution is to be substituted by another. The final drying of the manometer is accomplished by attaching a tube containing drying agents or absorbents to the stem (2) and alternately exhausting and readmitting air. When manometers of the forms seen in Figures 20 and 21 are to be dealt with, the instrument (Figure 28) is attached to the vent. The manipulation is then more complex but not less effective.

The time consumed in preparing a manometer for the measurement of osmotic pressure is usually about one month.

CHAPTER III.

THE REGULATION OF TEMPERATURE.

THERMOMETER EFFECTS.

Because of certain obvious analogies between a closed osmotic cell and a sensitive thermometer, the name "*thermometer effects*" has been given to a large group of exceedingly troublesome manifestations which follow even slight fluctuations in bath temperature. The name is appropriate only in a very restricted sense. The phenomena thus classified are complex and often they are difficult to analyze satisfactorily. To understand them, one needs to keep constantly in mind three fundamental facts: (1) That the capacity of the closed osmotic cell is a nearly fixed quantity; (2) that every change in the volume of its contents—due to rise or fall of temperature—is followed by a discharge or intake of solvent through the membrane, both of which acts also modify the volume and the osmotic pressure of the solutions; and (3) that the passage of the solvent through the membrane, in either direction, is usually a much *slower* process than the changes in the volume of the cell contents which result from fluctuations of temperature. The first and second of the enumerated facts are obviously true, but the third, which is responsible in largest measure for the complex and often perplexing results, can be learned only by experience.

The four elementary fluctuations of temperature and their consequences will be considered:

(1) The temperature of the bath (previously constant) rises and becomes again constant at the higher level.
(2) After rising, it falls again to the original level.
(3) The temperature of the bath (previously constant) falls and remains constant at the lower level.
(4) After falling, it rises again to the original level.

The question to be answered is, what changes in cell pressure will the observer at the telescope see in consequence of the temperature fluctuations enumerated above? For convenience, all positive pressure in the cell which is not *osmotic* will be called *mechanical*, and the sum of the two will be spoken of as the *total* pressure.

1. The conditions which are supposed to prevail are as follows: The cell contains a solution of known concentration, the temperature is constant, and the solution is exhibiting its true osmotic pressure only. Subsequently the temperature rises and becomes constant again at the higher level. This is the simplest of the four cases previously mentioned. The volume of the liquids in the cell—the mercury in the manometer and the solution—and the tension of the gas in the manom-

eter increase. The total pressure is now the sum of the osmotic pressure of the solution and a considerable mechanical pressure due to the expansion of the liquid contents of the cell. In consequence of this *over*-pressure—the difference between the total and the osmotic pressures—the gas in the manometer is compressed to a smaller volume, and the mercury meniscus is seen to rise and finally to attain to a maximum height. Simultaneously with the expansion of the liquids in the cell, there is, in consequence of the over-pressure, a very slow outward discharge of the solvent through the membrane, the effect of which is twofold. First, there is a reduction in the volume of the solution which reduces the mechanical pressure; and, second, an increase in osmotic pressure due to the increasing concentration of the solution. The two effects are of a mutually compensatory character, but they are not equal in their opposite influences upon the magnitude of the pressure in the cell. Hence the meniscus does not remain at the highest point reached by it, but sinks again and becomes stationary at a lower level only when the mechanical pressure has wholly disappeared and the only pressure in the cell is the osmotic pressure of a solution more concentrated than the original one. To recapitulate, the meniscus, in the case under consideration, takes three positions in the manometer, which may be called, in the order of their relative heights, the lowest, the intermediate, and the highest. The first and the second of these correspond to the true osmotic pressures of two solutions of different concentration, while the third is temporary and corresponds to the sum of an unknown mechanical pressure and an osmotic pressure of which it can only be said that it is higher than the osmotic pressure of the more dilute and lower than that of the more concentrated solution.

It will be seen that the maximum height to which the meniscus will temporarily attain depends upon both the magnitude and the *rate* of the rise in temperature, while its final position is determined solely by the former. In other words, a rapid rise in temperature always produces a larger *thermometer effect* than a slow one. It will be seen also that the magnitude of the thermometer effect in question, when translated into pressure, depends in large measure upon the volume of the nitrogen in the manometer.

2. If, after a rise, the temperature, instead of becoming constant, again sinks to its original level, a more complicated series of changes in cell pressure is observed. The cause of the increased complexity of the situation is the falling temperature which may begin to operate before or after the meniscus has reached its greatest height. If it begins before, the meniscus will evidently not rise so high as it otherwise would. For present purposes, let it be supposed that the fall in temperature sets in immediately after the meniscus has reached the highest point in its ascent, i. e., when the greatest pressure has been developed in the cell. Up to this point, then, the conditions are identical with

those in the preceding case. But there is now a falling instead of a stationary temperature. The elements of the situation are (*a*) an over or mechanical pressure in the cell due to a previous rise in temperature, and (*b*) a falling temperature. The consequences of (*a*) are:

(1) An increase in osmotic pressure, due to the concentration of the solution which follows the expulsion of solvent.

(2) A decrease in mechanical pressure, due to the smaller volume of the solution after expulsion of solvent.

The consequences of (*b*) are:

(3) A decrease in mechanical pressure, due to the diminishing volume of the cell contents.

(4) A decrease in osmotic pressure, due to lower temperature.

(5) A decrease in osmotic pressure, due to dilution of the solution through intake of solvent.

(6) An increase of pressure within the cell, due to the increase in the volume of the solution through intake of solvent.

Of the effects enumerated above, (1) and (6) are positive, i. e., they tend toward the maintenance or increase of pressure in the cell. In the same sense, (2), (3), (4), and (5) are negative. The amount of *over* or *under* pressure in the cell at any given moment is, of course, the algebraic sum of all these effects. By "over" and "under" pressure is meant the difference between the actual pressure in the cell at any time and the true osmotic pressure of the solution at the original temperature, i. e., before the rise and subsequent fall of temperature. One would expect, perhaps, that the sum of the "over" and "under" pressures would become zero when the bath had recovered its original temperature. In other words, that the meniscus would stop in its descent and become stationary, when the pressure in the cell is equal to the true osmotic pressure of the solution at the original and now constant temperature. But this is by no means the case. It continues to descend, and, before coming to a rest, may go far below the level which corresponds to the osmotic pressure of the original solution at the given temperature. Here again the reason for the apparently anomalous conduct of the cell is to be found in the fact that changes in volume, due to fluctuations of temperature, are accomplished more quickly than the migrations of solvent through the membrane which follow such fluctuations. Having reached the lowest point in its descent, the meniscus rises again and finally comes to rest at its original level, i. e., at the level which corresponds to the true osmotic pressure of the original solution at the original temperature. The upward movement of the meniscus in the final return to its first position is the resultant of two opposite effects of the intake of solvent: (1) the increasing volume and (2) the decreasing osmotic pressure of the solution. To recapitulate: If, after a rise, the bath recovers its original temperature, the meniscus first ascends to a point whose elevation above the original position depends

(1) upon the magnitude and rate of the rise in temperature, and (2) upon the time at which the fall in temperature sets in and the rate of the fall. The meniscus then descends to a point below its original level. The distance between the two positions depends (1) upon the magnitude of the upward displacement and (2) the rate at which the bath recovers its original temperature. Finally, the meniscus ascends to its first place.

The third and fourth situations are not more simple than the first and second, but enough has already been said for the present purpose, which is merely to emphasize the complex nature of *thermometer effects*. Hence in the remaining cases the movements of the meniscus only will be stated.

3. The conditions are as follows: The cell contains a solution of known concentration which is exhibiting its true osmotic pressure at a given constant temperature when a fall in temperature occurs. Afterwards the temperature becomes constant at a lower level. The movements of the meniscus which are observed are : (1) A fall (usually quite rapid) to a point *below* the position which it will finally take, and (2) a rise to some intermediate point at which it becomes stationary. The final position corresponds to the true osmotic pressure, at the given lower temperature, of a *permanently diluted* solution. The difference between the lowest and final positions of the meniscus will depend upon the magnitude of the fall in temperature and upon its rate as compared with that of intake of solvent.

The movements of the meniscus are sometimes less simple than stated above, since at times one observes an *extra* excursion of the meniscus, i. e., it falls to its lowest level and then rises to a point above the position which it finally takes.

4. If, after the fall, the temperature rises and becomes constant again at the original level, which is the most frequent case, the movements observed are as follows: The meniscus falls to its lowest position, then rises to one higher than it had originally, and finally sinks to the place from which it started. Here again an *extra* excursion of the meniscus is sometimes observed, namely, a second one to a point below its final position. When the meniscus has finally recovered the position from which it first started, we have again, of course, the true osmotic pressure of the original solution at the original temperature.

The "extra" excursions of the meniscus mentioned under 3 and 4, as well as certain other anomalies not mentioned, are probably due to temporary inequalities of concentration in the solution—to the fact, namely, that when solvent is expelled or taken in, the solution in immediate contact with the membrane is, for the time being, concentrated or diluted to a greater extent than the main body of the solution. The final adjustment of the meniscus can not, of course, be reached until the whole solution has become homogeneous through diffusion

of the solvent. Evidently the magnitude of the so-called *extra* excursion will depend very much upon the rate at which the solvent can pass through the membrane in either direction.

The magnitude, and therefore the importance, and the peculiarities of *thermometer effects* depend upon several conditions which will be briefly recapitulated. They are:

1. The relative volumes of the liquids (solution and mercury) and of the gas in the cell. Since the latter is always very small as compared with the former, slight disturbances of temperature must always produce large thermometer effects.

2. The degree of the "lag" in the passage of solvent through the membrane, which, in turn, depends upon temperature and the area and age of the membrane.

3. The rapidity with which the changes in temperature are accomplished. The relation of 3 to 2 is self-evident.

4. The "lag" in the distribution of solvent through the solution by diffusion, which produces temporary conditions of non-homogeneity in respect to concentration.

It is obvious that, in one sense, we could have no *thermometer effects* if the passage of solvent through the membrane and its subsequent uniform distribution by diffusion were instantaneous, since, in that case, there could never develop in the cell a condition of *over* or *under* pressure. In other words, we should then have at all times simply the osmotic pressure of a solution whose concentration varies with the temperature. The fact that diffusion does not quite keep pace with transferences of solvent through the membrane is not a source of serious trouble, but in the lag of such transferences behind fluctuations in temperature we have a most formidable obstacle in the way of the accurate measurement of osmotic pressure. The only remedy for this unfortunate situation is to be found in the most perfect means which can be devised for the automatic maintenance of constant temperature.

It will be gathered from what has already been said that the *duration* of thermometer effects also depends principally upon the rate at which the solvent is able to diffuse through the membrane. In practice it is found that, according to the age of the membranes, they may last from 12 hours to 4 days after the bath has recovered its normal temperature. As regards the minimum temperature change which will give a sensible thermometer effect, it may be said that a fluctuation of 0.01° produces a movement of the mercury meniscus which can be detected. A change in temperature amounting to 0.05° gives a large thermometer effect, even when the membrane is new. It has not been found practicable to regulate the temperature of the large baths which are in use to within less than 0.01°; accordingly the meniscus is constantly moving within narrow limits, with the result that two successive readings, several hours apart, are rarely quite identical. Fluctuations

of 0.02° in bath temperature, if they follow one another with regularity, are tolerable, because the thermometer effects due to rise in temperature are then partially neutralized by those due to falling temperature.

Change in concentration without leakage.—It has been seen that a solution in a cell may become permanently concentrated if the temperature rises and becomes constant at a higher level; also that it may be permanently diluted if the temperature falls and becomes constant at a lower level. There are also two cases in which the concentration of the solution may be altered without any change in the temperature of the bath. Alterations of this kind occur when the cells are filled with solutions whose temperature differs from that of the bath. In such cases, concentration or dilution of the solution ensues, according as the temperature of the solutions is lower or higher than that of the bath. There is, however, no essential difference between the two modes of effecting concentration on the one hand and dilution on the other, since both depend on changes in volume due to changes in the temperature of the solutions.

Except for the maintenance of zero temperature, all the devices for regulation conform to one principle, which may be stated as follows:

> *If all the water or air in a bath is made to pass rapidly (1) over a continuously cooled surface which is capable of reducing the temperature slightly below that which it is desired to maintain, then (2) over a heated surface which is more efficient than the cooled one but which is under the control of a thermostat, and (3) again over the cooled surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set, and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the water or air. The principle is a general one and provides for the maintenance of any temperature between zero and the boiling-point of water. Moreover, any desired temperature can be maintained without regard to the temperature of the surrounding atmosphere, since the air about the bath must always aid in the work either of the cooling or the heating surface.*

The "cooling" surface is usually furnished by a series of brass pipes through which water—under a constant pressure—is circulated. If the temperature to be maintained is a moderate one, i. e., not far from that of the atmosphere but above that of the hydrant water, the latter is passed directly through the circulating system, the rate of flow being so regulated as to maintain, without the coöperation of the heating surface, a temperature which is slightly too low. This margin between the temperature which the cooling surface, acting alone, will maintain and that which it is desired to keep should, for economical reasons, be

made as small as is consistent with safety. If the temperature to be maintained in the bath is very near to or below that of the hydrant water, the latter, before entering the circulating system, is passed through coils of metallic pipes which are surrounded by ice. If the desired temperature is not much above that of the atmosphere, the cooling effect of the surrounding air upon the exterior of the bath may suffice, in which case the circulation of hydrant water is discontinued. Finally, if the temperature to be maintained is considerably above that of the atmosphere, the system within is connected with one on the outside, thus forming a closed circulating system which is partly within and partly without the bath, and through this hot water is circulated by means of a pump. The pump may be situated anywhere in the system, i. e., either within or without the bath. At some point outside, provision is made for heating the water by gas as it passes through the system.

Thus far, provision for the *cooling surface* only has been made. Notwithstanding the application of heat, and sometimes a good deal of it, the circulating system mentioned above is, essentially, a cooling device, inasmuch as its purpose is to reduce the temperature of the bath below that which is to be maintained. In this system, for economical reasons, gas is used for heating rather than electricity, but care is taken so to regulate its flow that a "cooling margin" will be maintained, whatever may be the fluctuations in the pressure upon the gas. Since the "cooling surface" is not subject to exact regulation, it must never be allowed to become, in effect, a "heating surface," for in that case the thermostat becomes useless.

The "heating surface" usually consists of one or more copper cylinders, in which are inclosed ordinary electric lamps, which serve as stoves, whose purpose is to overcome the "*cooling margin.*" If that margin is small—and it should be made as small as possible—the consumption of electricity is not large. Lamps are used rather than other forms of electric heating devices, because one can always select among them stoves whose capacity is suited to the work to be done, and because they heat up and cool down quickly, which is an important element in temperature regulation.

The circulation of water over the cooling and heating surfaces is effected by means of pumps, and it will be seen later that a single pump may be made to circulate the water over these and also through the cooling system. The air in the baths is circulated by means of rotating fans.

THE SCHEME FOR ELECTRICAL REGULATION.

The device by means of which the margin of under-temperature produced by the so-called "cooling surface" is exactly and automatically overcome is shown in Figure 29. Everything not essential to an understanding of its plan is omitted. It consists, in its simplest form, of (1)

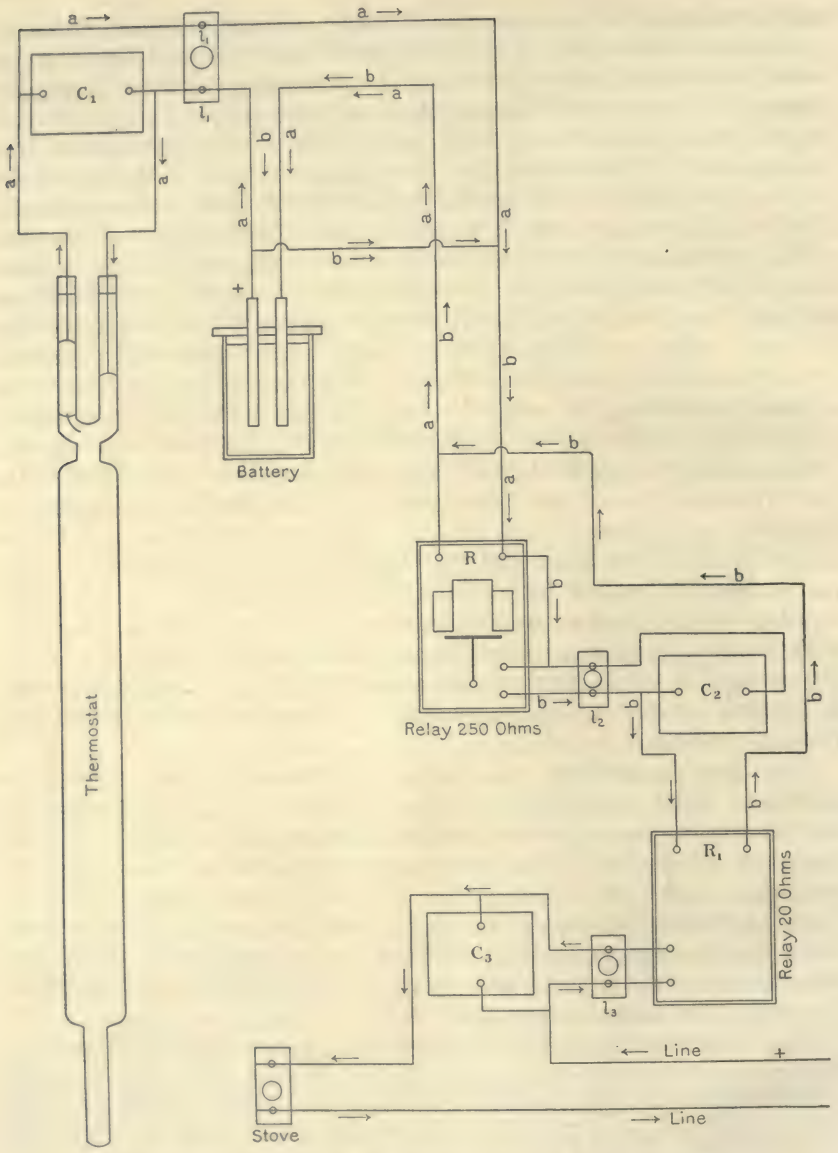


FIG. 29.—General scheme for the electric regulation of bath temperature.

(C_1), (C_2), and (C_3) condensers spanning spark-gaps of thermostat and relays; (l_1), (l_2), and (l_3) lamps spanning the same spark-gaps as the condensers; (R) the master relay (250 ohms resistance), which is operated by battery and may control any number of stoves in parallel; (R_1) stove relay operated by battery through the "local" of the master relay, (*a* with arrows) course of current through battery, thermostat and "main" of master relay, (*b* with arrows) course of current through battery, "local" of master relay and "main" of stove relay. Current of main line passes through "local" of stove relay and stove. "Stops" of all relays reversed.

a battery of one cell; (2) a thermostat; (3) two relays; (4) three lamps (*l*) and three condensers (*c*) which span the spark gaps of the thermostat and the two relays; (5) two battery circuits which operate the relays and a third one of 120 volts which passes through the stove.

1. The Battery.

For charging purposes, all the cells in use (about twenty in number) are placed in series upon a single circuit in which a lamp of appropriate resistance is also inserted. The charging is continuous. The cells themselves, though in series on a single circuit for charging, are distributed, in numbers corresponding to the amount of work to be done, at points conveniently near to the various baths. A single cell suffices to operate the system at any point, hence each cell in a local battery consisting of more than one is at work only a part of the time, i. e., every third day, if the local battery consists of three cells.

2. The Thermostat.

No single element in a system of regulation is of greater importance than the thermostat. Its efficiency depends upon a considerable number of conditions, some of which are worthy of more than a passing mention. That the mercury must be of exceptional purity, and that its volume must be so related to the diameter of the capillary as to secure a large movement of the meniscus for a small change of temperature, are facts too obvious to require discussion. The feature to which too little attention is usually given is the mechanism for adjusting the *contact point. This should be located directly over the center*, i. e., *the highest part of the meniscus*, and the mechanism should be such that it can never take any other position with reference to the surface of the meniscus. The best form of thermostat which we have in use is shown in Figure 30. The platinum rod (*a*) is finished to a smooth point at the lower end, and just above the latter is a guide (*b*) of glass, which is designed to keep the point near the center of the tube, and therefore nearly over the highest part of the meniscus. At the upper end, the platinum rod (*a*) is firmly set in the threaded brass rod (*c*). The adjustment is made by means of the nut (*e*, *e*), which is so nicely fitted into its framework that it can move in a horizontal-circular direction only. The dotted circle indicates the apertures through which the adjusting nut (*e*, *e*) is grasped between the thumb and forefinger when the contact-point is to be lowered or raised. The guide (*b*), which must fit the tube rather loosely, does not suffice to compel the contact-point to keep exactly its proper position with reference to the meniscus. The rod (*a*) is never absolutely straight, hence the point, if the rod is allowed to turn, will describe a circle over the meniscus. For this reason, having once correctly adjusted the point, its motion must be limited to the vertical direction; in other words, the threaded rod (*c*) must not be allowed to turn with the nut

(*e*, *e*). The device by which any movement of (*c*) in a horizontal direction is prevented is seen in the upper part of the figure. The two nuts—(*f*) and (*g*)—are threaded internally to fit *c*. The lower and wider one is bored at two opposite points for two rods, of which only one (*h*) is seen in the figure. Corresponding to the holes in *g*, two other holes are bored in the brass cap (*i*). Having found the correct position for the contact-point, the rods *h* and h_1 (not seen), are inserted, and the set nut (*f*) is turned down upon *g*. The rod (*c*), though still free to move in a vertical direction, can not now turn with the adjusting nut (*e*, *e*).

Sparking at the point of contact in the thermostat is effectively prevented by spanning the spark gap (Figure 29) with a lamp of high voltage (l_1) and a condenser (c_1). Since removal of the condenser has not been found to induce visible sparking at the point of contact, it is doubted whether it serves any useful purpose. As a matter of fact, it is often omitted. The lamp (l_1) which is ordinarily employed is one of 16 candle-power at 250 volts.

The water in the baths is always in rapid motion, and a thermostat which is immersed in it without protection is subject to slight but constant jarring, which results in a phenomenon which has come to be known under the name of "*frosting*." The air between the mercury in the thermostat and the glass wall collects at a multitude of points in minute bubbles, which give to the glass a frosted appearance. In the course of time, the bubbles of gas coalesce, forming aggregations so large that the true nature of the phenomenon can be discovered by the naked eye. The first indication which one usually receives that "*frosting*" has commenced is a "*chattering*" of the relays.

"*Frosting*" can be prevented by protecting the thermostats from the shock of the moving water by surrounding them with metallic tubes, or by exhausting them before introducing the mercury. The boiling-out process employed for barometers has not been found practicable for thermostats of the form used by us.

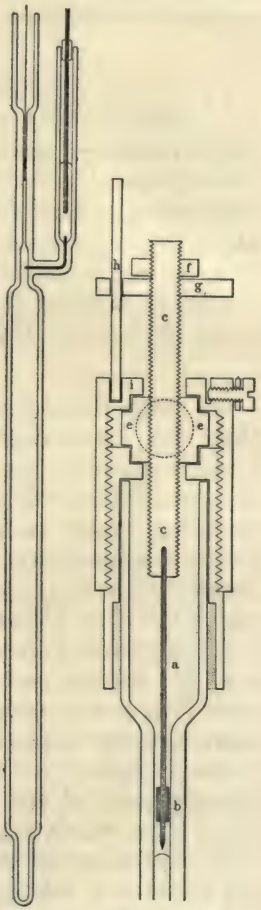


FIG. 30.—The thermostat.

(*a*) Platinum rod, pointed at lower end; (*b*) glass guide to keep (*a*) in center of tube; (*c*) threaded brass rod; (*e*) inclosed nut for adjusting contact point; (*f*), (*g*), and (*h*) arrangements for preventing all movements of the contact point, except in a vertical direction. The figure to the left shows the glass parts of the thermostat.

3. The Master Relay.

The master relay (R, Figure 29), so called because it controls all the relays connected directly with the stoves, has a resistance of 250 ohms, and is of the type commonly used in telegraph lines. High resistance in this relay is desirable in order to reduce to a minimum the current which must pass through the thermostat. The course of the only circuit which passes through the thermostat and the magnets of the master relay is indicated in Figure 29 by the letter a. The current in this circuit amounts to 8 milamperes plus, of course, what may pass through the high-resistance lamp (l_1).

4. The Minor Relay.

The "local" of the master relay is made the "line" circuit of the minor relay (R_1). The course of this circuit is indicated by the letter b. The spark-gap of the master relay, like that of the thermostat, is spanned by a lamp (l_2) and a condenser (c_2), although the latter is often dispensed with. The minor relay has a resistance of only 20 ohms. Its spark-gap is also spanned by a lamp (l_3) and a condenser (c_3). The stove circuit, as shown in the figure, passes through the "local" of the minor relay.

In all of the relays—both master and minor—the usual arrangement of the "stops" is reversed, so that the closing of the circuit through the thermostat opens the circuit through the "locals" of the relays. Obviously, what it really does is to cut down the current in these circuits by throwing into them the resistance of the lamps (l_2 and l_3). None of the three circuits employed in the system is ever fully broken. But the currents which pass continuously through the lamps (l_1 and l_2) are insufficient to operate the relays, while that which passes continuously through l_3 does not overheat the bath.

By putting the minor relays in parallel, a single master relay is made to operate any number of stoves. In some of our baths, the "*master*" controls as many as eight stoves.

For convenience in use, the system of electrical control is divided into two units, and the apparatus belonging to each is permanently installed on a portable board which may be fixed in any suitable position with reference to a bath. All connections, except the permanent ones on the boards, are made by means of flexible leads, to the ends of which are attached insertion plugs. On the "*master board*" are placed and wired together the master relay, the lamp which spans the spark-gap of its "local," and plug attachments for the battery, the condenser, and for several stove boards. On each of the minor or stove boards are placed and wired together two minor relays in parallel for as many stoves, the lamps which span their spark-gaps, and plug attachments for the master board, the condensers, and the stoves. The "*unit*" boards of each kind are uniform in arrangement and size and are therefore interchangeable.

THE BATH FOR 0°.

As previously intimated, the bath which is employed for determinations at 0° does not conform to the general principle upon which all baths for higher temperatures are constructed. The essential difference between it and the others is that in the bath for 0° there is no forced circulation of water and air. An attempt was made to construct a bath in partial conformity with the general principle in question. In this, a large mass of ice was made the "*cooling surface*," and the exterior of the bath the "*heating surface*." Water was passed rapidly over the ice, and then over the compartments in which the cells were located. It was found, however, that the lowest temperature which it was practicable to maintain in this manner was always a little above 0°; and that owing to imperfect control of the *heating surface*, the temperature was subject to considerable fluctuations which produced large *thermometer effects*.

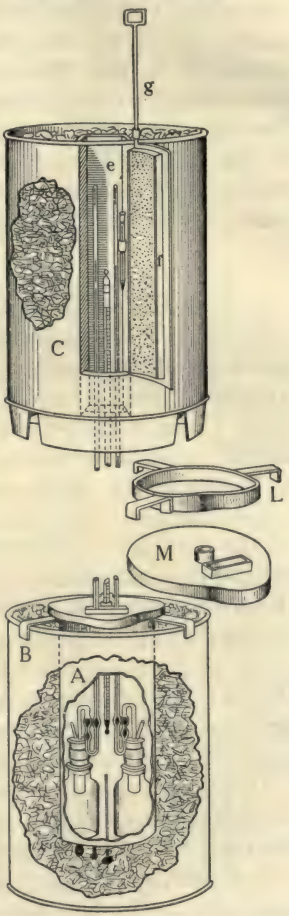


FIG. 31.—Interior ice bath for measuring osmotic pressure at 0°.

(*A*) Galvanized-iron can containing cells; (*B*) galvanized-iron ice-container surrounding (*A*); (*C*) galvanized-iron ice-container which shuts down upon (*B*); (*e*) protected compartment for manometers and thermometers; (*f*) padded door to (*e*); (*g*) arrangement for opening and closing the door from above the outer ice bath, which is not shown in the figure; (*L*) arrangement for suspending (*A*) in (*B*); (*M*) cover to (*A*).

The bath which was finally evolved for the determination of osmotic pressure at zero is seen in Figures 31, 31 *L*, and 31 *M*. The apparatus, which is made of heavy galvanized sheet iron, consists of three principal parts: First, a can (*A*), in which the cells are placed; second, a much larger one (*B*), in which *A* is suspended by means of the arrangement seen in Figure 31 *L*; and third, the cylinder (*C*), which shuts down tightly upon *B*. There is an inclosed chamber (*e*) running through the whole length of *C* and open at both ends, in which are located the upper ends of the manometers and the two thermometers which are seen in the figure. The thermometers and manometers are exposed to view, when a reading is to be made, by opening the felt-lined door (*f*). In order that the door may be opened and closed from the outside, the detachable rod (*g*) is made to pass through the top of the larger bath (to be described later) which surrounds *A*, *B*, and *C*. The bottoms of both *A* and *B* are perforated so that no water can collect in the cans.

The "larger bath" referred to above is one of those ordinarily used for measurements of pressure at higher temperatures. To prepare it for use at 0°, it is stripped of all its interior accessories, including circulating pipes and pump, leaving the copper-lined rectangular tank entirely empty. On the bottom of this, in the center, is placed a staging about 5 centimeters high, on which rests the ice-filled arrangement consisting of *A*, *B*, and *C*. All the space in the tank which is not occupied by *A*, *B*, and *C* is filled with closely packed broken ice, and the water which collects upon the bottom is removed by means of an automatic siphon. All the space in the upper part of the bath—usually designated as the "air space"—which is not occupied by the upper part of *C* is filled with ice containers of such form that they surround *C* except directly in front of the door (*f*). One of these occupies the space between the upper end of *C* and the top of the outer bath, the upper end of the chamber (*e*) being covered to prevent the entrance of water.

All of the ice-containers in the air space above are open at the lower end, so that the broken ice moves constantly downwards as it melts away underneath, keeping the tank below and also the can (*B*) always full. A little over 150 kilograms of ice are required to fill the bath properly, and the amount of fresh ice which it is necessary to introduce daily is between 25 and 30 kilograms.

The container above *C* and *C* itself, after the ice in them has been picked out, can be lifted through the opened top of the outer bath whenever cells are to be removed from *A*. If cells are to be introduced, all parts of the bath except *C* and the container above it are closely packed with ice, and, after waiting until the temperature in *A* has fallen to 0°, the cells are placed in position. *C* is brought down upon *B* and packed with ice. Finally, the container which belongs directly above *C* is placed in position and filled with ice.

The arrangement described above serves its purpose perfectly. The temperature in *A* does not deviate sensibly from 0°. There are, therefore, no appreciable thermometer effects. The temperature of the manometer space (*e*) may be affected somewhat by the lamp used in reading, unless one interposes a screen for the purpose of cutting down the heating effect of the light. We have employed for this purpose a 4 per cent solution of nickel sulphate, which—as determined by means of a thermocouple—reduces the heating effect of the lamp nearly 99 per cent.

BATHS FOR MAINTENANCE OF TEMPERATURE ABOVE ZERO.

Descriptions of the earlier forms will be omitted. The baths which were first employed in an attempt to measure osmotic pressure were found to be incapable of maintaining sufficiently exact temperatures. In other words, the thermometer effects produced by their fluctuations of temperature were intolerably large. The baths which are now used and which will be described are the products of a persistent attempt to reduce these effects to harmless proportions. They all belong to cer-

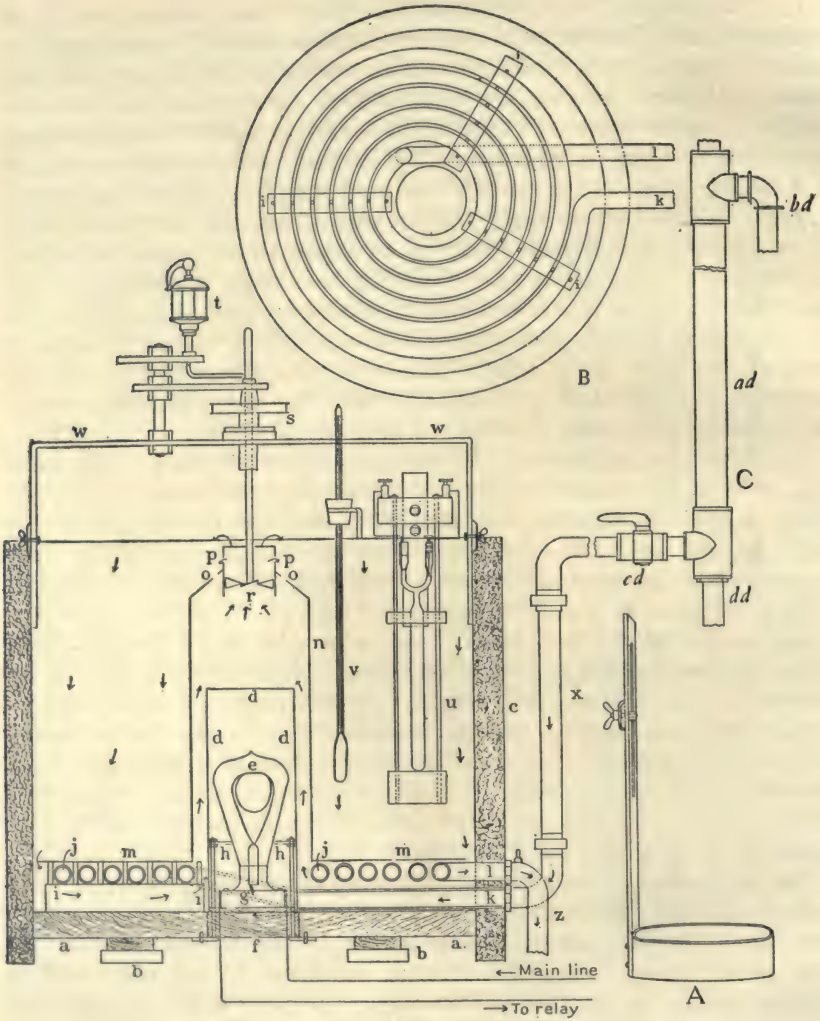


FIG. 32.—60-liter galvanized-iron bath for intermittent use.

(*a*) and (*b*) wooden base; (*c*) hair padding; (*d*) water-tight inclosure for electric stove (lamp); (*e*) electric stove; (*f*) and (*g*) removable base for lamp; (*h*) frame for lamp; (*i*) supports for circulating system; (*j*) coil of block-tin pipe for the circulation of cold or hot water (shown better in Figure 32, *B*); (*k*) and (*l*) pipes by which water enters and leaves the circulating system (*j*); (*m*) and (*n*) cylinder open at top and resting on pegs between coils of (*j*); (*o*) holes for escape of gas expelled from water; (*p*) holes for escape of water into outer bath; (*r*) propeller for pumping water over heated chamber (*d*); (*s*) pulley; (*t*) oil cup; (*u*) thermostat; (*v*) thermometer; (*w*) adjustable iron frame for fixing the propeller in place; (*x*) vertical pipe leading to pressure regulator.

A. Adjustable support for bottles, etc. *B*. Block-tin circulating system (*j* in Figure 32).

C. Constant-pressure arrangement. (*ad*) Stand-pipe; (*bd*) overflow; (*cd*) stopcock for the regulation of flow of water through circulating system in bath; (*dd*) entrance place of water-supply.

tain fairly distinct types, though differing much among themselves in respect to details. An example of each type will be given.

TYPE I.

This bath (Figures 32 and 33), which was designed for general but intermittent use in connection with the work, consists of a cylindrical tank of galvanized iron, which holds from 60 to 80 liters. It is surrounded by a thick covering of hair felt (*c*, Figure 32), and rests upon a wooden base (*a*, *a*), which is raised above the table or floor by the blocks and rubber pieces (*b*, *b*). Inverted over the hole in the center, and riveted and soldered to the bottom of the bath, is the cylinder (*d*, *d*, *d*), which serves as a receptacle for the lamp (*e*), or any other suitable kind of electrical heating device. The lamp is mounted, in the manner indicated in the figure, upon the removable block (*f*), which is held in its place by buttons screwed to the base (*a*, *a*). Resting upon the framework *i*, *i* (Figure 32) and *i*, *i*, *i* (Figure 32 *B*) is the continuous block-tin pipe (*j*, *j*, *j*, *j*), through which the hydrant water circulates. The cylinder (*d*, *d*, *d*) constitutes the "heating" surface, and the pipe (*j*, *j*, *j*, *j*) the "cooling" surface. The running water enters the bath at *k* and leaves at *l* (Figures 32 and 32 *B*). The course of the water in the pipe, after entering the bath, is continuously horizontal or upward—never downward. This arrangement is necessary in order to prevent the lodgment of air in any part of the pipe. The successive coils of pipe (six in number) are separated by the pegs seen in Figures 32 and 32 *B*, and on these rests the galvanized iron disk (*m*, *m*). The hood (*n*, *n*), of the same material, shuts down tightly over a flange on the disk (*m*, *m*) and is adjusted and secured in its place by set screws directed towards *d*, *d*. The form of the hood will be clear from the figure, and it is necessary only to call attention to the small holes for the escape of air at *o*, *o*, and to the larger holes at *p*, *p*, through which much of the water raised by the propeller (*r*) escapes into the outer bath.

The purpose of the various parts which go with the propeller—the adjustable cross-bar (*w*, *w*), which is clamped to the sides of the bath, the oil cup (*t*), the pulley (*s*), etc.—is sufficiently obvious.

It is quite essential that the hydrant water which flows through the pipe shall be under constant pressure, otherwise much water and heat are necessarily wasted. The arrangement by which the constant pressure is secured is shown in Figure 32 *C*. It consists of a large standpipe (*ad*) with an overflow (*bd*) near the top. The water from the tap enters at the bottom (*dd*) and passes to the bath through *cd*, where the flow is controlled by a stopcock. The circulating water is thus brought under an invariable pressure, and it is possible to regulate the quantity passing through the bath with considerable nicety and for any length of time. At the highest point in the waste pipe (*z*, Figure 32) is placed a vent through which any air carried along by the water may escape.

If the temperature of the hydrant water is above that at which the bath is to be maintained, the block-tin spiral pipe (Figure 33) is inserted between the tap and *dd* (Figure 32 *C*). To cool the water which enters at *a*, before it passes through *b*, *dd*, and *cd* into the bath, the large and well-protected box in which the spiral is located is packed with ice. In this manner, it is practicable to maintain a quite low temperature in the warmest weather.

The bath just described is used principally for bringing solutions to temperature and for maintaining them at temperature, for the comparison of thermometers and the adjustment of thermostats, and for other similar purposes. The various instruments and vessels are held in their places in the bath by means of adjustable supports or clamps, of which that for bottles is shown in Figure 32 *A*.

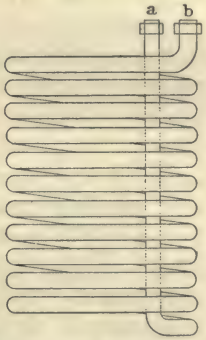


FIG. 33.—Coil of block-tin pipe for cooling or heating water before it enters the circulating system within the bath.

(*a*) Entrance; (*b*) exit.

The maintenance of any temperature from a little above 0° to that of the room can be readily accomplished by means of the hydrant water, with or without ice. If, however, a temperature above that of the room is to be maintained, the flow of the hydrant water is cut off. The outer surface of the bath and the exposed surface of the water then become the "cooling" surface, and the bath works on precisely the same principle as before. If a temperature above 50° is to be maintained, the consumption of electric energy becomes expensive in large baths, and it is well to accomplish a portion of the heating by means of gas. This is done in various ways, but most simply by removing the wooden base and mounting the bath on a large iron tripod over a ring burner of suitable diameter, taking care, of course, so to regulate the quantity of burning gas that the stove alone can not raise the temperature of the bath to the required height.

TYPE II.

Figure 34 represents one of the more recent forms of bath, in which the membranes are deposited and in which the cells and the solutions are maintained at the temperature at which osmotic pressure is to be measured.

The "*cooling*" surface is furnished by the horizontal brass pipes (1 to 8). The hydrant water, cooled by ice if necessary, enters by pipe 1 and, after circulating through all the six intervening pipes in the order in which they are numbered, it leaves the bath by pipe 8. For all temperatures below the highest temperature of the room, it is necessary to keep some water in circulation in this system of pipes. The amount to be sent through will, of course, depend on the difference between the

temperature of the hydrant water and that which is to be maintained in the bath. If the hydrant water is to be cooled before entering the bath, as when a low temperature, e. g., 5°, is to be maintained in summer, it is first passed through the coils of pipe seen in Figure 33, which are embedded in ice. The arrangement shown in Figure 32 *C* is also employed in this bath to secure a constant pressure upon the circulating water.

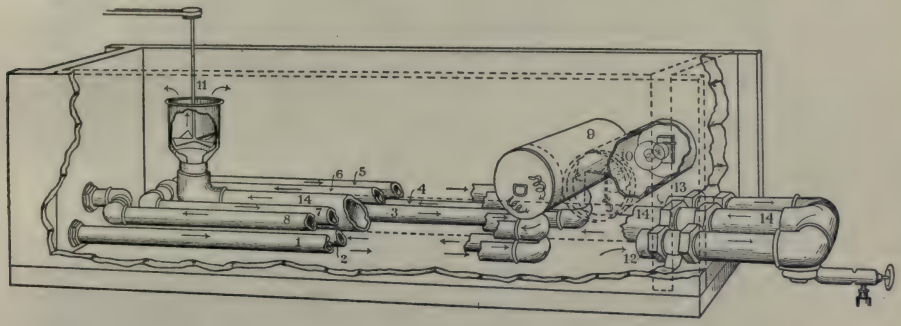


FIG. 34.—Rectangular bath for general laboratory use.

(1) to (8) Brass tubes for circulation of hydrant water; (9) and (10) copper cylinders, opening on opposite sides of the bath, for the lamps; (11) pump; (12) and (13) pipes through which water is drawn out of the bath and over the gas stoves seen at the end; (14) large pipe through which water heated by the gas stoves is drawn and delivered at (11).

A word of caution may be given regarding the valves to be used when a constant pressure on running water is to be maintained. Our first pressure arrangements were constructed in accordance with correct principles, so far as we knew, but it was found that they would not maintain constant pressures. The flow of water diminished continually, and very small streams ceased altogether after a time. After a long search, the difficulty was located in the valves. Those we were using—the so-called "gate-valves"—were found to be so constructed as to permit the accumulation of the gas which is expelled from water, when its temperature is raised, to such an extent as to impede the flow of the water, and to stop it altogether if only a little were passing through the valves. After replacing the "gate-valves" by others of the common lever variety, the difficulty disappeared.

The "*heating*" surface is furnished by the two copper cylinders (9 and 10), the latter of which is broken in order to show the location of the stoves. The large wooden box is lined with copper, and the two copper cylinders in question extend entirely through it from side to side, and are opened at both ends upon the outside of the bath. They are closed with caps, upon the inside of which are fastened the lamps. Provision is thus made for four lamps which are usually of 16 candle-power, though lamps of 8 candle-power often suffice at low temperatures. The lamps (stoves) are regulated according to the scheme already explained.

The circulation of the water in the bath over the cooling and heating surfaces is effected by means of the pump (11). It enters the pipes (12 and 13), which end just inside the rear end of the bath, and passes, in the direction of the arrows, into the large pipe (14), thence to the pump and out again into the open bath. It will be observed that the tendency is to draw the colder water upon the bottom of the bath very rapidly into the pipes (12 and 13), but that, as it enters these, it is necessarily mixed with water which has passed over the heating surfaces (9 and 10). Many positions for the heating surfaces have been tried, but that given in Figure 34 has been found most satisfactory.

The rate of pumping depends upon what is found to be necessary in order to secure identical temperatures at the two ends and the middle of the bath. Ample provision is made for any rate which may be required. A moderate rate for some of the larger baths is 400 liters per minute.

The purpose of extending the pipes (12, 13, and 14) outside of the bath, where, at their junction, the circulating water passes over a gas stove, is obviously to economize electricity. The rule here, as in all other baths, is to utilize gas for heating purposes to the utmost safe limit, leaving for the electrical appliances only so much as is indispensable for regulation.

Five baths of Type II are in use, varying in size and equipment, but all conforming in principle to that just described. Plate 3 presents their appearance, also that of the baths of Type I.

Type III.

An example of one kind of bath in which osmotic pressure is measured is shown in Figures 35 and 36. The first (Figure 35) represents the lower part, which is filled with water and in which are located circulating systems similar to those described under Type II. In the second (Figure 36) is seen the upper part of the bath, the so-called "air space." Both divisions are lined with copper and are separated by a vapor-tight brass plate (1, Figure 35 or 36), which is divided diagonally across the bath into two parts which are reunited by the brass strip (2). The brass plate (1) is screwed down upon the upper edge of the outer wooden bath, but between the two, as also between 2 and 1, strips of sheet rubber are placed to prevent the passage of water vapor from the lower part of the bath into the "air space" above. The reason for keeping the latter as dry as possible will appear later. Six lead-weighted copper cans are suspended from the brass covering plate, the flange of each resting upon a rubber collar; they serve as receptacles for the cells. During a measurement of pressure, the space in the cans above and around the cells is filled with wool. In two of the three baths of Type III, the cans have been replaced by two long, narrow troughs, whose depth is equal to that of the cans. The troughs have covers which are divided into many readily removed sections. A bath so arranged will easily accommodate 24 cells instead of 6.

View of circular and rectangular laboratory baths in use.

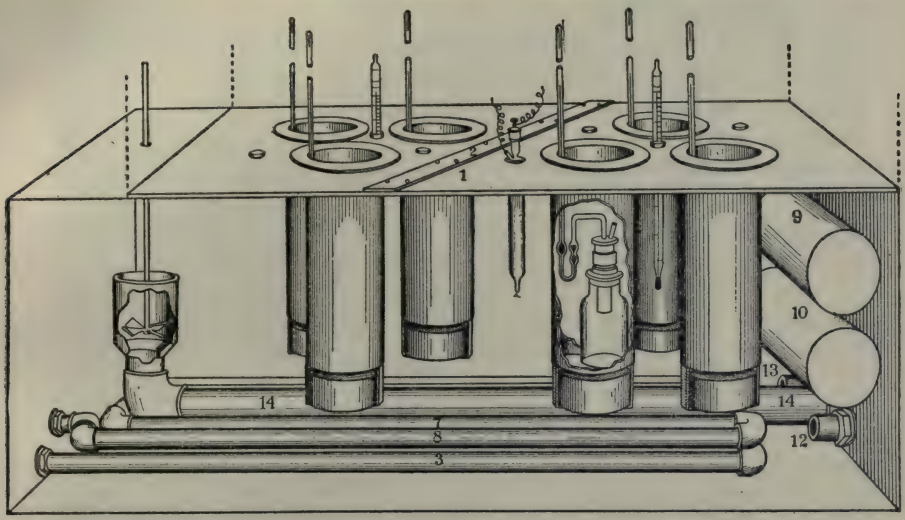


FIG. 35.—Lower half of rectangular bath for measuring osmotic pressure—the "water compartment."

(1) and (2) Brass vapor-tight cover from which are suspended the copper cans which contain the cells; (3), (7), and (8) one-half of the brass tubes belonging to the circulating system for hydrant water; (9) and (10) copper tubes which open at both ends on the outside of the bath; (12) and (13) tubes through which the water is drawn from bath and over the gas stoves; (14) large pipe through which water heated by the gas stoves is again pumped into the bath.

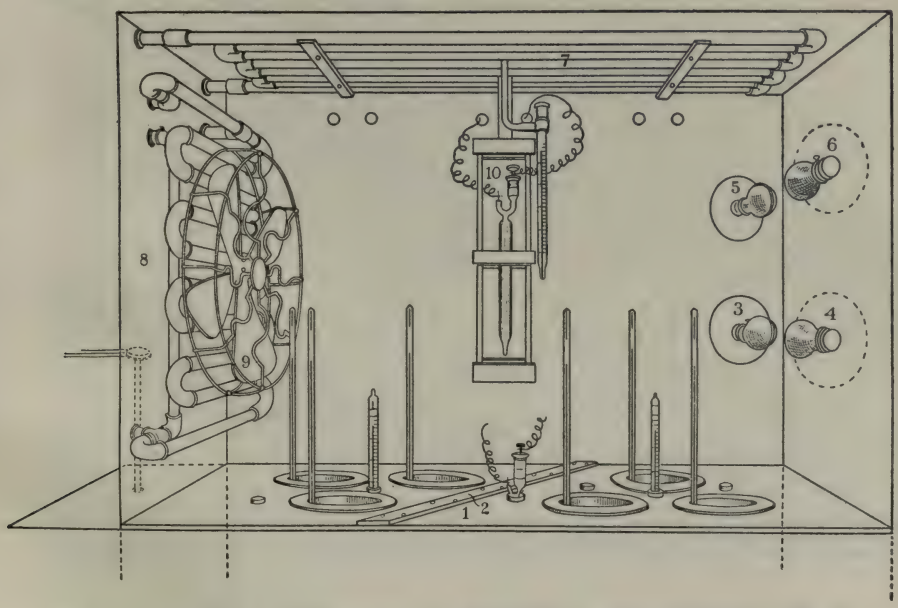


FIG. 36.—Upper half of rectangular bath for measurement of osmotic pressure—"air" or "manometer compartment."

(1) and (2) Vapor-tight cover to "water compartment;" (3), (4), (5), and (6) screened lamps; (7) brass pipes for circulation of hydrant water; (8) circulating system for hot water; (9) electric fan; (10) thermostat.

It will be seen (Figure 35) that the arrangements in the lower part of the bath are nearly identical with those of the bath described under Type II. There is the same system of brass pipes (3, 7, 8, etc.) for the circulation of hydrant water, and the same arrangement for pumping water out of the bath (through 12 and 13) to be heated by a gas stove and returned through the large pipe (14). There is also in both baths the same provision for the "heating surface," except that the copper cylinders (9 and 10), in which the lamps are located, are somewhat differently placed in the two cases.

The copper-lined upper part of the bath—the "air space"—(Figure 36) is electrically heated by means of the lamps (3, 4, 5, and 6), which are shaded for the protection of the various instruments containing mercury. There are two systems of pipes in the air space. That seen in the top (7) is for the circulation of hydrant water. It serves the same purpose in the air space as the system of pipes (3, 7, 8, etc.) in the lower part of the bath. The system of pipes situated at the end of the bath (8) is for the circulation of hot water. It may also be used for cold water. The air in the upper part of the bath is kept in circulation by means of the fan (9).

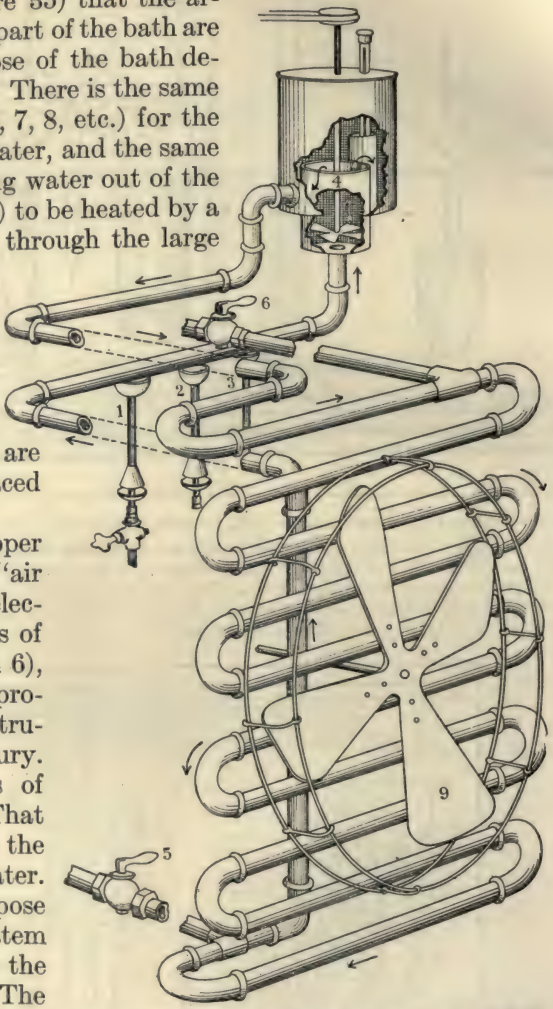
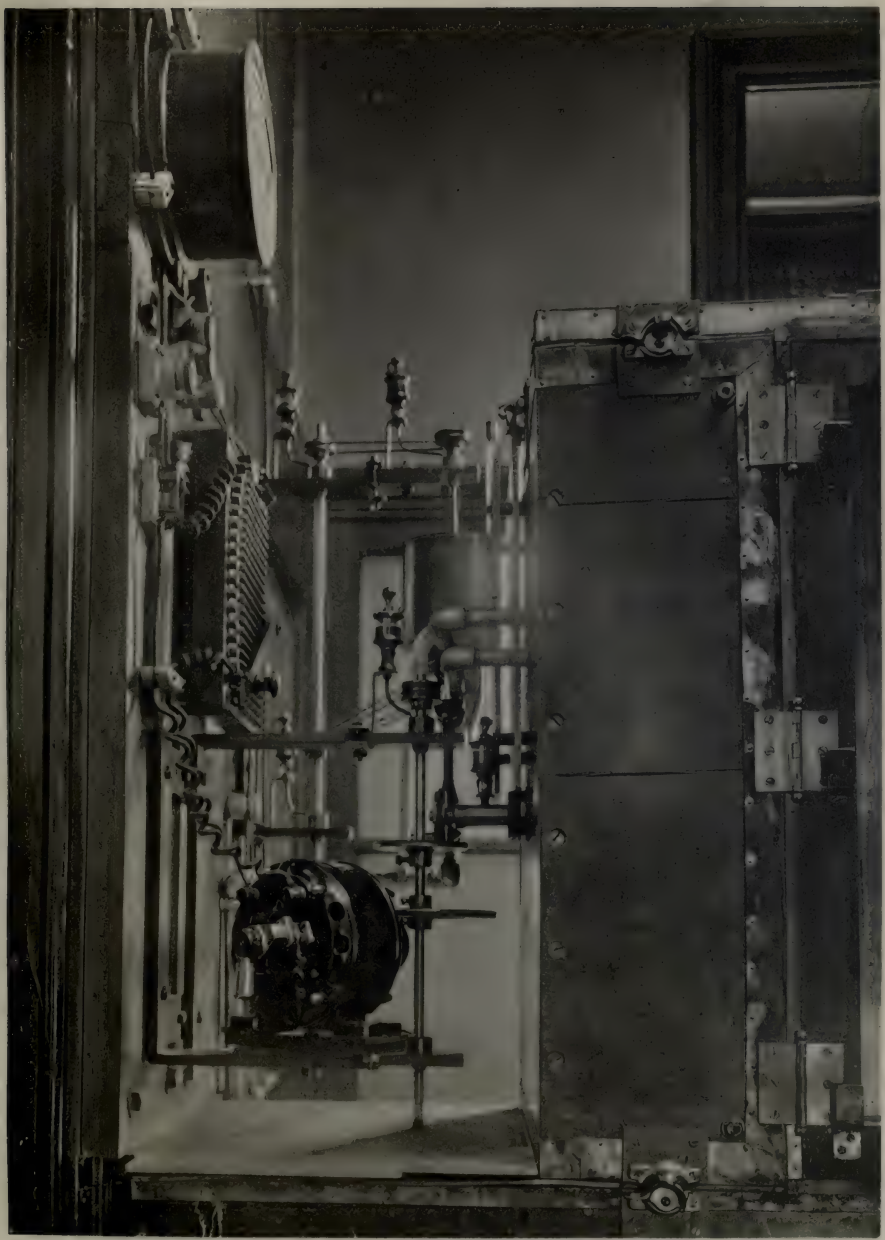


FIG. 37.—Hot-water circulating system with end of bath removed.

(1), (2), and (3) Gas lamps (outside of bath) for heating circulating water; (4) pump; (5) and (6) stopcocks which are used when hydrant water is to be circulated through the pipes.

The heating and pumping arrangements for the hot water are situated on the outside of the bath. Their relation to what is seen on the inside is shown in Figure 37. The gas burners (1, 2, and 3) heat the water on its way to the pump (4), from which it is returned in the direction of the arrows. When the system is used for the circulation of hydrant water, the water enters through 5 and leaves through 6. In one of the baths



Rectangular bath, end view.

of Type III, the interior portion of the system has been replaced by a single large pipe of ring form, which is so arranged on the inside that the hot water is returned to the upper part, while the colder water is constantly pumped out of the bottom.

The motor fan (9) is employed to keep the air in the inclosed space in circulation over the heated pipes and over the lamps; but it serves also to keep the manometers gently but constantly agitated, and thus to overcome the tendency of the mercury to lag in the tubes. This agitation is increased to any desired extent by attaching bits of stiff paper to the upper ends of the manometers.

The external appearance of the bath is seen in Plates 4 and 5. In the latter, the system of pipes for the circulation of hydrant water, which should be seen at the top of the interior, has been removed, as this bath is but little used for temperatures below that of the air.

The other baths of the same general type (two in number) were planned with reference to the measurement of osmotic pressure at low or very moderate temperatures. They differ from the bath described mainly in the care which has been taken to protect the interior from external temperature conditions. Their wooden walls are all double and the intervening space is filled with hair. Moreover, the small rooms in which they are located are made subject to temperature regulation by means of pipes covering the ceiling through which hydrant water is circulated when necessary. A further means of cooling these bath rooms consists of a chute opening upon the outside of the building, through which air is introduced into the room at any desired rate by means of a rotary fan. Formerly it was attempted—by means of a circulating system for hydrant water, by the introduction of a regulated quantity of air from the outside, and by means of gas stoves under the control of thermostats—to keep the bath room as nearly as possible at the temperature of the bath; but with the present improved facilities for the internal regulation of the baths, this is no longer necessary. The recent practice is, in general, to keep the temperature of the room 4° or 5° below that which is to be maintained in the bath. The flexibility of the system of temperature regulation, however, is such that differences of temperature amounting to 25° can be easily tolerated. At the highest temperatures at which osmotic pressures have been measured, differences of 60° were not infrequent.

Type IV.

The baths previously described, which are made partly of wood, are not adapted to the measurement of osmotic pressure at high temperatures. For this purpose, it was necessary to construct baths of different design and wholly of metals.

The baths for high temperatures, which are equally well adapted to work at low temperatures, are of two sizes and are made of heavy sheet brass and copper—mainly of the former. *A* (Figure 38) exhibits a

section of the inner compartment of one of the smaller baths. It is this compartment which is maintained at any desired constant temperature, and in which the cells are located during a measurement of pressure. It is circular in form in the smaller baths, 300 millimeters in diameter and 1 meter in height. Surrounding this is a large cylinder (*B*, *B*)

38

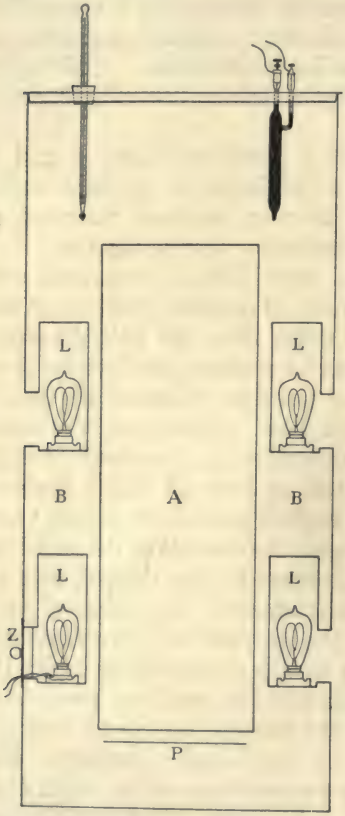


FIG. 38.—Brass and copper bath for high-temperature work. Vertical section.

(*A*) Inner bath; (*B*) outer bath; (*L*), (*L*), (*L*), and (*L*) lamps; (*P*) brass plate to prevent water rising directly from heated bottom of (*B*) to bottom of (*A*); (*Z*) caps for lamp compartments.

39

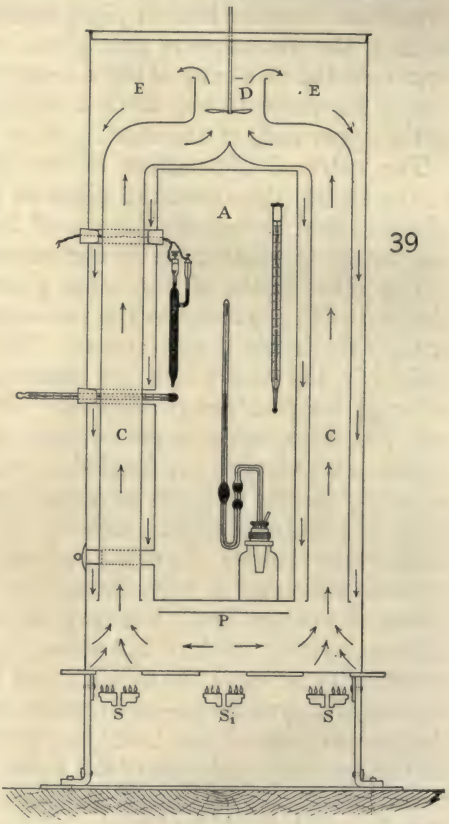
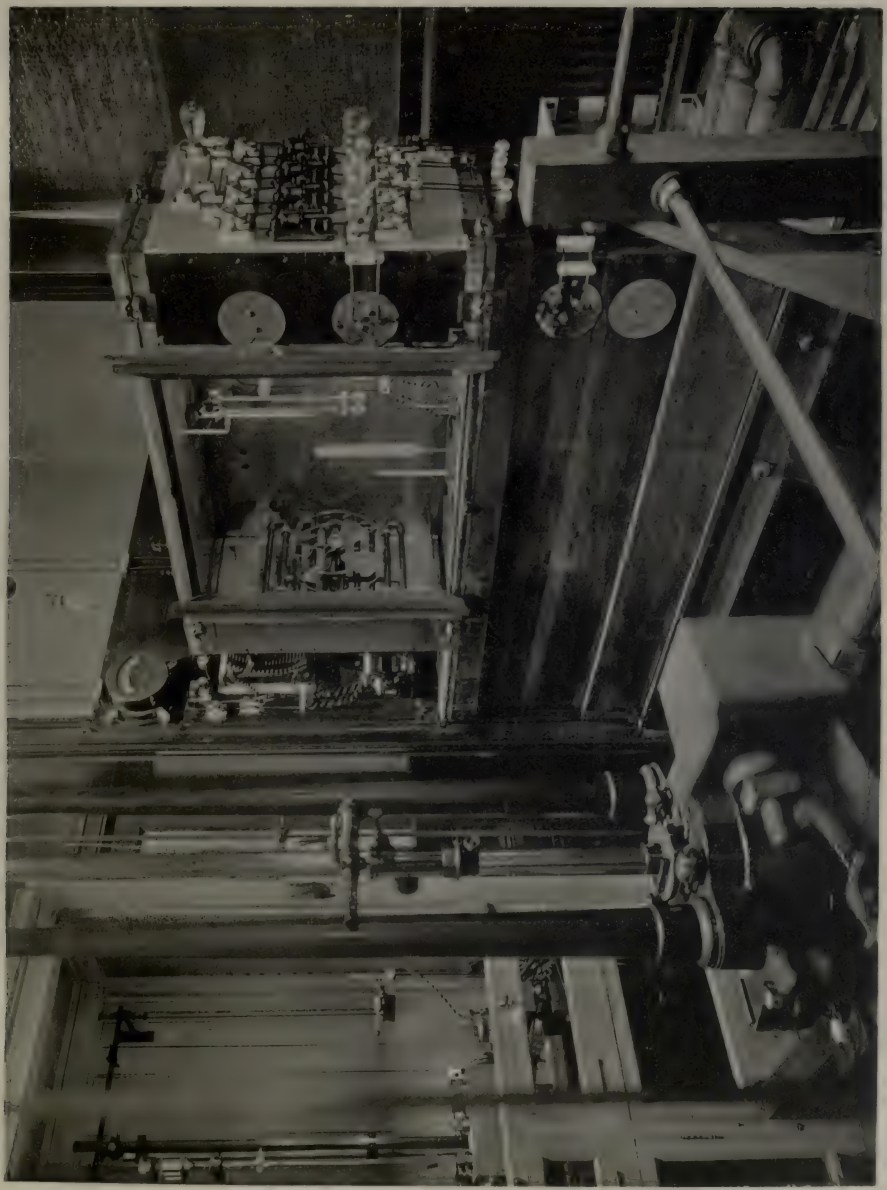


FIG. 39.—Brass and copper bath for high temperatures, second vertical section.

(*A*) Inner bath; (*C*) pumping tubes; (*E*) space into which water coming up (*C*), (*C*) is delivered; (*S*), (*S*), and (S_1) gas stoves.

which is twice as wide and much higher. In the space between the two brass cylinders, the water is heated and made to circulate rapidly over the exterior surface of the inner compartment (*A*). The circulating system and the arrangements for heating the water by gas are shown in Figure 39. *C*, *C* are the pumping tubes, 100 millimeters in diameter, which unite at the top in the short but wider tube (*D*). At the bottom, they open directly over the gas stoves (*S*, *S*). There is a third gas stove



Rectangular bath, side view.

(S_1) which is not ordinarily in use. The water, heated by the stoves (S, S), is pumped up through the tubes (C, C) at the rate of about 500 liters per minute. At the top of D it is delivered into the space (E, E), whence it returns to the bottom of the outer cylinder to be reheated by the gas stoves and again pumped up through the tubes (C, C). In its downward course the water passes over the outer surface of A and also over the lamp compartments (L, L, L, and L, Figure 38). In the smaller baths there are 6 or 8 of these lamp compartments, and in the larger ones 8 or 12. They are distributed in pairs, one in each pair being located directly over the other. The circular openings, through which the lamps are introduced from the outside, are closed by means of caps, one of which (Z) is shown in Figure 38. Below the inner compartment (A, Figures 38 and 39) is the disk (P), which prevents the water which has been heated by any of the gas stoves from rising directly against the bottom of A. In Figure 39, there are also to be seen three tubes, indicated by dotted lines, which serve as passage ways between the exterior and interior for the introduction of thermometers, wires, etc. Figure 40 is a horizontal section of one of the smaller baths, in which the positions of the pumping tubes are indicated by C, C, and those of the lamps by L, L, L, and L. The entrance to the inner bath (A, 150 millimeters in width) is closed by the plate-glass door (I, Figure 40) and by the hollow metal door (M). There are two such doors, as will be seen in Figures 41 and 42. The lower one, which is opened only when it is necessary to introduce or remove the cells, is packed with hair. The upper door, on the other hand, must be opened whenever an observation is to be made. On this account, it is provided with an independent temperature-regulating device, portions of which can be seen in Figure 43. By means of this, the door is prevented from cooling down when open. The space between the inner glass door and the outer metal doors is about 40 millimeters in width. It is occupied by a brass frame, as large as the glass door, which is filled with minute doors, any one of which can be opened independently of the others. Between this frame (which is placed close to the glass door) and the outer metal doors is a hair-filled pad, which is so divided that any small portion of the frame of brass

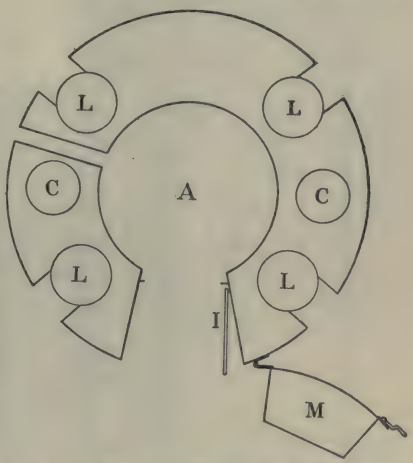
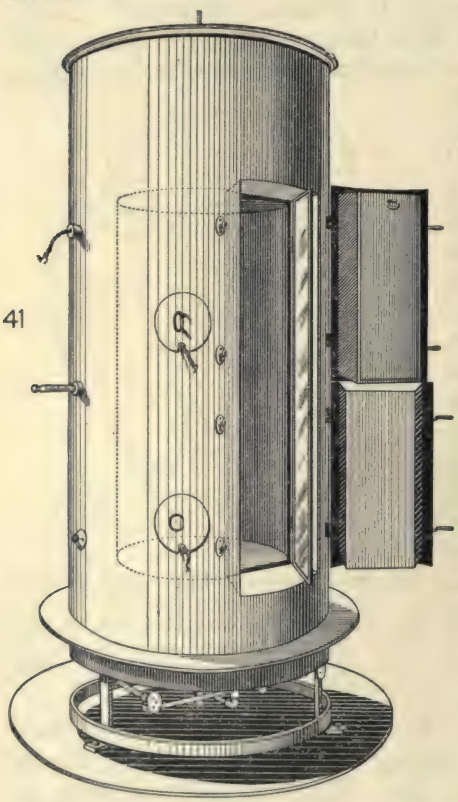


FIG. 40.—Brass-copper bath for high temperatures. Horizontal section.

(A) Inner bath; (C) and (C) pumping tubes; (L), (L), (L), and (L) lamp compartments; (I) plate-glass door; (M) lower hollow door filled with hair.

doors behind it may be exposed to view. With these arrangements, and with artificial illumination by screened lamps, it is practicable to observe objects in the bath with very little exposure of the interior.

Figure 41 shows the external appearance of the circular bath, and Figure 42 the appearance of the interior when a portion of the outside is removed.



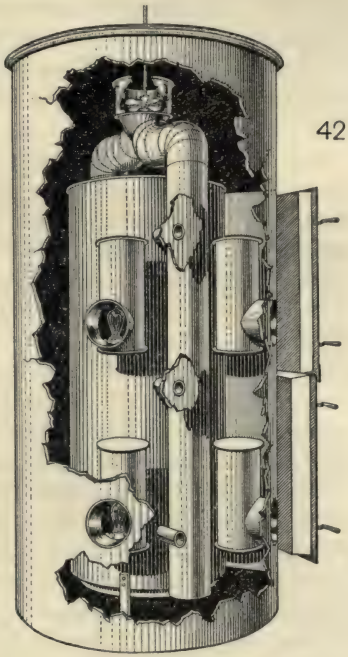


FIG. 41.—Exterior view of bath for high temperatures.
FIG. 42.—View between interior and exterior baths, i. e., of space filled with water.

Figure 44 is a horizontal section of one of the larger baths of Type IV. Like the smaller ones, they are used for the measurement of osmotic pressure, and also for all of the purposes for which the so-called "manometer house" was formerly employed—such as the determination of capillary depression, the determination of nitrogen volumes, the comparison of manometers, etc. It is elliptical in form, the longer axis being twice the diameter of the compartment (A) in the smaller baths. It is also higher than the circular baths by 100 millimeters, giving a height of 1.1 meters for A. It has three pumping tubes (C, C, and C) instead of two, and 8 or 12 lamp compartments (L, L, L, and L) instead

of 6 or 8. The two smaller metal doors of the larger bath are like the corresponding doors in the smaller bath, except that they are inserted in a larger door, which serves as a frame. The relations of the three doors will be seen in Figures 44 and 45. The largest door and the lower small one are packed with hair and are opened only when it is necessary to introduce or remove apparatus, or to make some adjustment of the instruments within. The upper of the two smaller doors, which must be opened whenever an observation is to be made, is provided with a device (Figure 43) for the independent regulation of its temperature. As regards the disposition of the space between the glass and the metal doors, there is no difference between the larger baths and the smaller ones.

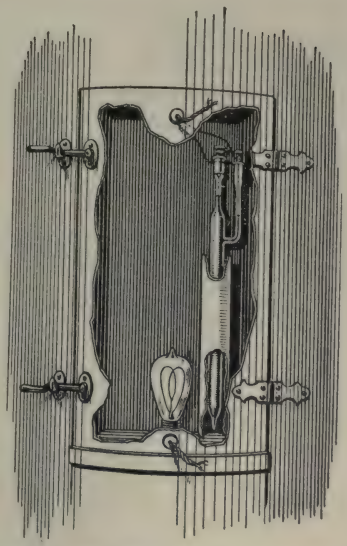


FIG. 43.—Automatic arrangements for maintaining temperature of upper door when open.

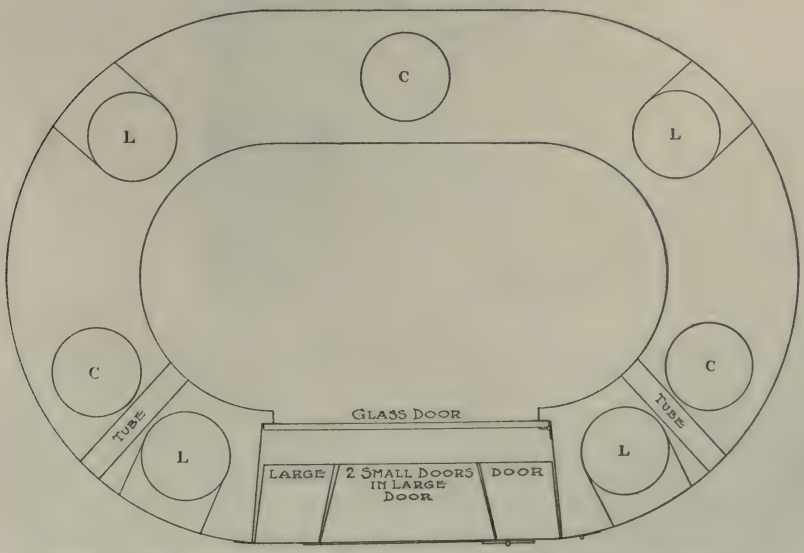


FIG. 44.—Larger (elliptical) bath for high temperatures. Horizontal section. (*C*), (*C*), and (*C*) pumping tubes; (*L*), (*L*), (*L*) lamp compartments.

No lamps of more than 16 candle-power are used in baths of Type IV, even when they are maintaining temperatures near the boiling-point of

water. For most purposes, lamps of 8 or 10 candle-power suffice. If temperatures but little above that of the room are to be maintained, the electrical appliances only are employed to heat and regulate the baths. For low temperatures, a coil of block-tin pipe is placed in the space (*E*, *E*, Figure 39), and through it there is made to circulate, under constant pressure, a current of hydrant water, which has previously been cooled with ice if necessary.

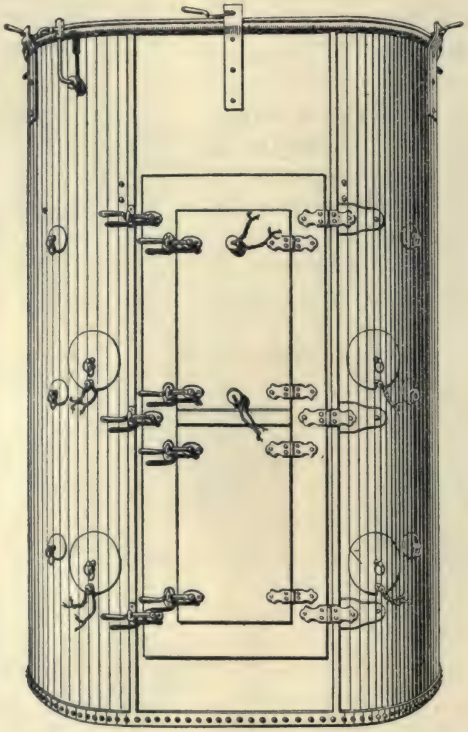


FIG. 45.—Exterior view of larger bath for high temperatures.

In Figure 39 the thermostat is shown within the compartment (*A*), while in Figure 38 it is represented as being immersed in the water of the bath. The latter has been found to be the better of the two possible positions for the instrument. The temperature of the water about the thermostat may not be precisely that of the interior compartment, and at other points it may vary slightly, but when the instrument has once been set for a given interior temperature, it is quite capable of maintaining it for any length of time to within 0.01°, which is a rather better regulation than can be secured in baths of Type III.

CHAPTER IV.

THE MEMBRANES.

Pfeffer was the first to give to artificial semi-permeable membranes the support of a rigid background, and to him, therefore, belongs the credit of having originated the only practicable method of measuring directly and correctly the osmotic pressure of solutions. But many years of persistent investigation were necessary in order to overcome the great difficulties which are inherent in the method and to reduce it to a workable form through the elimination of its sources of error.

The following is an accurate restatement, though not an entirely literal translation, of Pfeffer's description of his method of depositing membranes:

"The clay cells were first completely injected with water by means of repeated evacuations under the air pump. They were then filled with, and placed for several hours in, a 3 per cent solution of copper sulphate. Afterwards, they were several times quickly rinsed (upon the inside only) with water, and well dried internally and as expeditiously as possible with strips of filter paper. Having been dried slightly upon the outside, they were left exposed in the air until the exterior surface was still just moist to the feel. The cells were then filled with a 3 per cent solution of potassium ferrocyanide, and returned to the solution of copper sulphate.

"After standing quietly from 24 to 48 hours, the cells were filled completely with a solution of ferrocyanide and closed. The contents now developed gradually a certain over-pressure due to the superior osmotic pressure of the interior solution. After another period of from 24 to 48 hours, the apparatus was opened and refilled with a solution containing 3 per cent of potassium ferrocyanide and 1.5 per cent of saltpeter (by weight), which developed ordinarily an osmotic pressure of something more than 3 atmospheres. If the cells were to be used for higher pressures, they were tested with solutions containing more saltpeter."

Pfeffer found that a "slow increase in pressure and a certain period of low pressure" were essential to success in the preparation of his membranes. The explanation which he gives is that, at certain points, the membrane spans depressions in the cell wall, and is, therefore, more liable to rupture, if the pressure, which is to force the membrane against the wall in such unsupported places, is rapidly or suddenly increased. He also states that a somewhat prolonged period of deposition is necessary in order to give to the membrane the strength which will enable it to withstand pressure.

The attempts which were made in this laboratory many years ago to reproduce the membranes of Pfeffer with a view to *measuring* osmotic pressure, especially that of concentrated solutions, were failures, as have been all similar attempts on the part of other investigators. It was not impossible to make membranes which would yield impressive

osmotic phenomena, but when they were tested as to their sufficiency for quantitative purposes by the rule that a perfect membrane must be able to develop and maintain maximum pressures, without leakage of the solute at any time during an experiment, they were found to be wanting.

The failure of the membranes to justify the hopes which had been entertained of them could be ascribed to any one, or all, of several causes—to the want of perfect semi-permeability on the part of the copper ferrocyanide; to the faulty character of the supporting porous wall; or to the imperfect attachment of the membrane to the wall; or to all three of these possible defects. It was strongly suspected that the third cause for failure existed; in other words, that the membranes made by the method of Pfeffer are not at all points firmly attached to the supporting wall.

The ideal membrane (as regards location) is obviously one consisting of innumerable *plugs* which are driven so firmly into the mouths of the pores which open on the interior surface of the cell that no pressure can rupture or dislodge them—that is, the membrane must be firmly *embedded* in the wall and not consist of a mere (more or less detached) cover for its interior surface. Looked at from this point of view, the practice of Pfeffer of *carefully drying the interior of his cells with filter paper* was a highly rational procedure. Subsequent observations have proved it to be the vital feature of his process. Pfeffer himself recognized this in a practical way, but he appears to have regarded these membranes as "*aufgelagert*" rather than embedded, though he gives no explanations; for he says (page 9), "*während ich anfangs mit grossen Schwierigkeiten zu kämpfen hätte, und ehe ich zu partieller Abtrocknung meine Zuflucht nahm, überhaupt keine aufgelagerte Membran zu Stande brachte.*" The obvious purpose of the "*Abtrocknung*" was to empty the mouths of the pores of the solution of copper sulphate, in order that they might be filled with the solution of potassium ferrocyanide and thus force the formation of an *embedded* membrane. It seemed probable, however, that the procedure of Pfeffer failed, in some degree, to accomplish its purpose, i.e., that the embedding was emperfect; and the question arose whether it might not be possible to devise some method by means of which these "*plugs*," of which the membrane should exclusively consist, could be more firmly driven into and more securely fixed in their places than is the case when the diffusion method of Pfeffer is employed. It was in this connection that the electrolytic process for the deposition of the membranes occurred to the writer.

It should be stated, however, that the first suggestion which led up to the solution of the problem came accidentally. While the subject of measuring osmotic pressure was still uppermost in the mind of the writer, he was engaged in an attempt to procure pure aqueous solutions of permanganic acid by the electrolysis of potassium permanganate.

The process consisted in placing two porous cups, partly filled with water, side by side in a solution of the salt, and electrolyzing with the anode in one cup and the cathode in the other. At times the pores of the anode cup became filled with a deposit of peroxide, and it was noticed that whenever this occurred the volume of the contents of that cell seemed to increase more rapidly than could be accounted for by any probable "electrical endosmose" of the solvent. It was immediately suspected that the deposit of peroxide in the porous wall was playing the part of a semi-permeable membrane and, upon further investigation, the suspicion was proved to be well founded. The process by which the semi-permeable peroxide was deposited in the pores of the cell and that by which osmotic membranes are now made differ radically; but the mere fact of having formed one active membrane by electrolytic means sufficed to suggest the practicability of employing electricity for the production of all semi-permeable membranes.

The work of Pfeffer was unique and brilliant, and its consequences have been far-reaching and beneficent. The writer, after fourteen years of activity in the same difficult field, has more reason than any other to appreciate its great merit and less justification than any other for detracting from its value. This statement of attitude is made with a view to disarming any possible suspicion of careless criticism on the part of the writer, when he states, on the basis of his own experience, that *none of the pressures recorded by Pfeffer could have been the maximum pressures of his solutions.*

The final step in the preparation of Pfeffer's cells for quantitative measurements was by means of a solution containing 3 per cent of potassium ferrocyanide and 1.5 per cent of potassium nitrate. The cells were filled with this solution, closed, and placed in 3 per cent solutions of copper sulphate. Pfeffer states that the pressure subsequently developed was usually something more than 3 atmospheres. If we add the excess of the ferrocyanide's pressure (over that of the copper sulphate) to the true pressure of the nitrate, the total pressure which should have been developed is something *more than 6.5 atmospheres.* The unavoidable conclusion is that the membranes did not perfectly retain the solute, and that the subsequent measurements were undertaken with defective cells.

In order to show that the osmotic pressure of solutions obeys the law of Boyle for gases, van't Hoff cites the pressures of the 1, 2, 4, and 6 per cent solutions of cane sugar which were obtained by Pfeffer. These pressures are strikingly proportional to the concentration, which is the form of the law as applied to solutions. There was, at that time, and for many years thereafter, no reason known why this evidence should not be accepted at its face value, and its validity appears never to have been questioned; accordingly one finds it repeated and emphasized in every presentation of the subject of osmotic pressure from 1887 to the present

time. The validity of the proof depends, however, upon the question whether the pressures obtained by Pfeffer were the full (maximum) pressures of his solutions. Pfeffer believed them to be so; for he mentions having ascertained, by means of specific-gravity determinations, that the solutions did not lose appreciably in concentration while in the cells. It is questionable, however, if this method is sufficiently delicate, unless carried out with extraordinary precautions, to detect differences which, if discovered, might well have led to a verdict unfavorable to the applicability of Boyle's law. The writer and his associates have not yet exactly repeated the experiments of Pfeffer, though they expect to do so in the near future. They have, however, done enough work at temperatures and concentrations approximating to those of Pfeffer to enable them to predict with considerable confidence about what the pressures in question will be found to be. The following table gives the pressures found by Pfeffer which have been universally quoted as proof of the conformity of osmotic pressure to Boyle's law and those which the work of the writer and his associates enable them to predict:

TABLE 3.

1. Concentration. Grams of sugar per 1000 c.c. H_2O.	2. Pressures found by Pfeffer.	3. Pressures required by Boyle's law at 15°.	4. Pressures Pfeffer should have found.	5. Differences between Pfeffer's and the author's results.
10	0.71 atms.	0.69 atms.	0.75 atms.	5.6 per cent.
20	1.34	1.37	1.48	10.4
40	2.74	2.77	3.00	9.5
60	4.05	4.16	4.41	8.8

If we compare the pressures found by Pfeffer with those required by the law of Boyle at 15°—that is, columns 2 and 3—the agreement is astonishing, and it is not surprising that these data have played an important part in nearly all discussions of osmotic pressure during the last twenty-five years. If, on the other hand, we compare the pressures of Pfeffer with those calculated for the same solutions from the results of the author and his associates—that is, columns 2 and 4—it will be observed that the latter are considerably higher than the former. The differences (column 5) vary from 5.6 to 10.4 per cent. The data given in column 4, which are designated (somewhat presumptuously perhaps) as "the pressures which Pfeffer should have found," are all calculated from measurements made after the method of measuring had been brought to its highest state of perfection—that is, after the last vestige of leakage of solute had been eliminated. The inference to be drawn from the facts, as stated above, is that the smaller pressures of Pfeffer were due to some leakage of the solute. The solutions of Pfeffer which are cited in this discussion contained in 1,000 cubic meters of

water 10, 20, 40, and 60 grams of sugar; while those from whose pressures the values given in column 4 were calculated contained in the same volume of solvent 8.49, 16.98, 33.96, and 67.92 grams. They were, in fact, 0.025, 0.050, 0.100, and 0.150 "weight-normal" solutions, whose pressures were 0.64, 1.28, 2.54, and 4.99 atmospheres respectively.

To one who has had long experience in the measurement of osmotic pressure, the conformity of Pfeffer's results to the requirement of Boyle's law—stated merely as proportionality of pressure to concentration—is not surprising. It is, in fact, almost a necessary consequence of using cells which do not quite perfectly retain the solute. The leakage of solute from any series of defective, but equally good, cells is proportional to the pressures of the solutions rather than to their supposed concentrations. In other words, the pressures of cane-sugar solutions, between 0° and 25°, are for some reason not proportional to their supposed concentration. If now a series of them of varying strength are placed in defective cells, the escape of solute will be proportional to the pressures, and not to the supposed relative concentration of the solutions. The necessary consequence is that the relative pressures will gradually approach proportionality to the (supposed) relative concentrations of the solutions. In a later chapter the author will have occasion to show how membranes which *do not* leak may be the means of *appearing* to establish the applicability of Boyle's law to osmotic pressure upon evidence which is superficially convincing, but fundamentally unsound. It may be stated here that all solutions of cane sugar thus far investigated do obey the law of Gay-Lussac between 0° and 25°, while none of them *appear* to obey the law of Boyle until higher temperatures are reached. That this failure, in the latter case, may be more apparent than real will be shown elsewhere.

It is fortunate that the validity of the generalizations of van't Hoff regarding solutions does not depend exclusively upon the correctness of Pfeffer's measurements; and, in one sense, it is also fortunate that Pfeffer obtained the results which he did, rather than the correct pressures of his solutions; for, whatever may have been the relative importance assigned to them by van't Hoff, they undoubtedly contributed more than any other one of his arguments to the immediate and general acceptance of his views.

The first announcement* regarding the electrolytic method of depositing membranes was made in the following words:

"If a solution of a copper salt and one of potassium ferrocyanide are separated by a porous wall which is filled with water, and a current is passed from an electrode in the former to another electrode in the latter solution, the copper and the ferrocyanogen ions should meet within the wall and separate as copper ferrocyanide at all points of meeting, so that in the end there should be built up a continuous membrane well supported on either side by the material of the wall."

*Amer. Chem. Journal, xxvi, 81.

The electrolytic method of depositing membranes was soon successfully applied to all the usual varieties of porous vessel which accumulate in a laboratory, and to several new forms of the same. It was found, in fact, that a highly active membrane could be produced without difficulty in every kind of porous wall. The method was also employed for the deposition in porous vessels of many other compounds than copper ferrocyanide, and a large number of these (about 25) proved to be osmotically active.

The success of the new method as a means of building up membranes was placed beyond question, but the possession of it did not enable us to proceed at once to the *measurement* of osmotic pressure. The resisting power of the membranes made by the electrolytic method was much greater than that of those produced by the process of Pfeffer, but even they were unable, in the porous vessels then available, to withstand high pressures without rupture. Our attention during the succeeding four years was given almost exclusively to the *porous wall* on, or within, which the membrane is deposited.

A brief account of this part of the investigation has been given in the first chapter; but a concise restatement of those structural characteristics of the cell wall, upon which the efficiency of the membrane was found to depend, will be useful in this place. They are:

1. A great and uniform strength of wall, which was secured by employing mixtures of different clays.
2. Absence of "air blisters," which were eliminated by subjecting the clays to great pressures.
3. An exceedingly fine and uniform porosity, which was secured by the employment of the finest portions only of the clays, by subjecting the mixtures to high pressure, and by burning at high temperatures.

THE DEPOSITION OF THE MEMBRANE.

The first steps toward the formation of the membrane are the expulsion of air from the pores of the cell and its replacement by water. This has been effected from the beginning by means of the considerable volume of water transported by the cations whenever dilute aqueous solutions of salts are subjected to electrolysis. At first the salt employed was potassium sulphate, but the fact that the "atmosphere" of water which surrounds the lithium ion is much greater than that transported by the potassium ion suggested the use of lithium salts rather than those of potassium. A series of quantitative comparisons carried out by Frazer showed that the quantities of water drawn through the cell wall conform to the following rule:

The volumes of water carried through the porous wall of a cell, under identical conditions, are inversely proportional to the relative velocities of the various cations, divided by their respective valencies.

The improvement in the method which followed the replacement of the potassium salt by lithium sulphate was very striking. A 0.005 normal solution was employed. The cell is nearly filled with the solution and immersed in the same to the lower limit of the glazed portion. The electrodes are of platinum and the one within the cell is made the cathode. Provision is made for the automatic removal of the water which is drawn into the cell through the pores. At intervals the electrolysis is interrupted for the purpose of mixing the liquid which has been removed by the siphon with the solution in the outer vessel. When it is thought that all the air has been expelled from the pores, the cell is taken out, emptied, and rinsed with pure water; it is then soaked for a time in distilled water, which is frequently renewed; lastly, it is filled with, and partially immersed in, pure water, and the electrolysis is resumed. When the conductivity, after frequent renewals of the water, has fallen nearly to that which is normal for the distilled water, the cell is ready for the deposition of the membrane. If the membrane is not to be deposited immediately, the cell is placed, and kept until needed, in water in which a little thymol or formaldehyde has been dissolved. The reason for this precaution will appear later when the subject of the *infection* of the membrane is taken up. It is also well to take any other precautions against infection which suggest themselves, such as boiling all the water which comes in contact with the cells, covering the vessels in which they are kept, etc. Such precautions are by no means superfluous.

The arrangement for the deposition of the membrane is as follows: the anode, which consists of a cylinder of copper, nickel, or cobalt, according to the composition of the membrane to be deposited, is placed in an empty glass vessel, and within the cylinder is placed the cell, which is closed by a rubber stopper carrying (1) the cathode, a platinum cylinder; (2) a funnel with a stem nearly long enough to reach the bottom of the cell; and (3) an overflow tube. The circuit is closed, and, as nearly simultaneously as possible, the cell and the vessel outside of it are filled, each with its appropriate solution. The solutions, which in the majority of the experiments to be reported are potassium or lithium ferrocyanide, and copper or nickel sulphate, are made one-tenth normal. The voltage employed is 110. At first the resistance is very high, owing to the fact that the cell wall is filled with nearly pure water. Very soon, however, the current begins to increase, and within a short time it attains a maximum. It then drops steadily for two or three hours, and perhaps longer, when it reaches a minimum corresponding to the maximum resistance of the membrane which it is possible to obtain at that "running." If the electrolysis is continued very long after the current has reached a minimum, the resistance begins to fall again, and the decline persists until the circuit is broken. This strange behavior of the membrane appears to have some connection with an accumulation of alkali in the cell and perhaps in the membrane itself; accordingly,

during the electrolysis, the ferrocyanide is renewed every 2 or 3 minutes by pouring a fresh solution of it into the funnel. A temporary increase in resistance follows each renewal, but this may be due in part to a fall in the temperature of the contents of the cell. The final decline in resistance may be postponed by frequent renewals of the solution, but not indefinitely. For this reason, it is suspected that the phenomenon is possibly due to accumulation of alkali in the membrane. Having reached its maximum resistance, the membrane can not be further improved by electrolysis, without a thorough preliminary soaking in pure water—that is, water which is free from *electrolytes*. The cell is therefore placed in water in which a little thymol has been dissolved, and is allowed to soak, with frequent renewals of the water, for several days. The period of soaking is quite indefinite, but experience has shown that it should be not less than 3 days; and that, in general, the longer the soaking is the better will be the result of the succeeding electrolysis.

After soaking, not less than 3 days, the membrane-forming process is repeated. On this occasion the resistance usually rises much higher than before, but finally reaches a maximum beyond which it can not be driven, however frequently the solution of ferrocyanide may be renewed. If the electrolysis is continued beyond this point, a gradual fall in resistance sets in, which may eventually lead to the total ruin of the membrane. As in the first instance, when it is found that the resistance no longer increases, the electrolysis is interrupted and the cell is again placed in water for a period of 3 or more days. The further procedure is simply a repetition of the alternate "running" and "soaking" described above, which is persisted in until the resistance of the membrane can be forced no higher. The maximum resistance which is finally obtained varies greatly. Obviously, it varies with the effective area of the membrane; and this, in turn, varies from cell to cell, according to the porosity of the cell wall. In general, it is found that membranes in hard-burned cells have high final resistances. The temperature of deposition is also an important factor in determining resistance. In a given cell, a membrane deposited or repaired at 0° may have a resistance of more than 1,000,000 ohms, while at 80° the resistance can not be driven above 1,000 ohms. Again, the resistance of the membranes increases with age and repeated use.

Having developed the maximum resistance in the manner described, the membrane is subjected to a process of "seasoning" under pressure. For this purpose the cell is set up with a concentrated solution of cane sugar (not less than half normal) to which a small amount of ferrocyanide has been added, an osmotically equivalent quantity of copper sulphate having been dissolved in the water in which the cell is to stand during the experiment. The initial mechanical pressure which is brought upon the contents of the cell at the time of closing may be

above the known osmotic pressure of the solution or considerably below it. In the former case the mercury in the manometer falls, in the latter it rises. Eventually, in either case, the meniscus generally comes to rest at a point below the position it should have, showing that the solution has been diluted. The irregular movements of the meniscus, which often precede the assumption of its final position, are all such as can be interpreted as being due to a breaking of the membrane under pressure, and a mending of the rents by the membrane-formers. Whatever may be the result of the first trial, which usually extends over several days before the pressure becomes constant, the cell is emptied and soaked from 3 days to a week in distilled water, when it is again subjected to the membrane-forming process. Afterwards, it is again set up with a solution of cane sugar in the same manner as for the first trial. On the second trial the pressure developed is usually higher than on the first. Sometimes, but not often, the full osmotic pressure of the undiluted solution is obtained. The further procedure with the cell is simply a repetition of the steps already described. Sooner or later there is developed in this way a cell which gives maximum pressures on every occasion, and in which the solutions suffer no dilution. It is then ready for the measurement of osmotic pressure.

OBSERVATIONS ON THE MEMBRANE.

1. TEMPERATURE OF DEPOSITION.

As nearly as possible, the membrane is deposited and developed at the temperature at which it is afterwards to be employed for the measurement of pressure. The temperature rises somewhat during the deposition, but is kept within limits by the frequent renewals of the ferrocyanide solution. During the intervals of rest, i. e., while soaking, the cell is also maintained at the temperature at which its membrane was formed and at which it is to be used for the measurement of pressure.

When a cell has been prepared or used at one temperature and is to be prepared for use at another, the ease with which the change may be accomplished depends very much upon the relation of the different temperatures to one another, and whether they are, in general, high or low temperatures. It has been found that when the temperatures in question are moderate ones, e. g., between 0° and 30°, it is better to deposit the membrane and use the cell at the highest temperature first, and then to work at each of the lower temperatures in the descending order. The reverse order is, however, entirely practicable. If the membranes are to serve for measurements at high temperatures, e. g., 50° to 90°, the training of the cells for their work is quite laborious. It is then necessary to deposit and "train" the membranes at some moderate temperature, e. g., 30°, and to repeat these operations at short temperature-intervals in the ascending order.

A cell which has been used at a high temperature, and has then been allowed to cool rapidly and to stand at a considerably lower temperature, is generally ruined for use at any temperature whatsoever. An unfortunate experience of the writer and one of his associates will illustrate the point. Starting with about 25 cells at 25°, they had laboriously trained them up by short temperature-intervals, until they were measuring with perfect success at 70° and 80°. When the summer vacation arrived, the cells were put in soak in thymol water, as usual at such times, and allowed to stand through the summer months. On resuming the work in the autumn, it was found impossible to restore the cells to a usable condition at high temperatures, and only a few of them were afterwards useful at any temperature. It is not known what happened to the membranes in consequence of the large and rather rapid temperature transition. It is possible that they might have been saved by reversing the process by which they were built up for use at high temperatures, i. e., by dropping the temperature gradually and "seasoning" the cells into a usable condition at short temperature-intervals. Membranes which have been prepared and used at any ordinary temperature withstand the fluctuations of summer temperature without deterioration.

2. TREATMENT OF THE CELL WHILE IN USE.

The foregoing statements have especial reference to the preparation of the cell for the measurement of pressure. The treatment of the cell while in use has not been stated in sufficient detail. Having built up the membrane, in the manner described, until its resistance can be forced no higher, and having afterwards "seasoned" it under pressure until the solutions are proved to suffer no dilution while in the cell, the formal measurements of osmotic pressure are begun. The first statement to be made in this connection is the general one that, from the time the deposition of the membrane is commenced until the work of measuring at a given temperature is finished, the cell is maintained, as nearly as possible, *at temperature*. This makes it necessary also to maintain at temperature all the solutions which are used with it.

Following the custom of Pfeffer, there is added to the solution whose pressure is to be measured a small amount of potassium ferrocyanide. The exact quantity is 83.9 milligrams to each 100 grams of water, which gives a 0.01 weight-ion-normal solution, if the dissociation of the salt is complete. This solution is one-tenth as strong, with respect to the ferrocyanide, as that formerly used in depositing the membranes, and is of the same strength as that which is employed in developing them under pressure. An osmotically equivalent quantity of copper sulphate (123.9 milligrams per 100 grams of water) is added to the water in which the cell stands during an experiment. The solutions without and within the cell are also made 0.001 weight-normal with thymol to guard against infection. The presence of the "membrano-

gens," as they are called by Pfeffer, is undoubtedly of service while the development of the membranes under pressure is in progress; but it is still a question whether they are required after the membranes have once been perfected.

After finishing a measurement of pressure, the cell is emptied, is thoroughly washed, and is then allowed to soak three days or more in water which is 0.001 normal with respect to thymol. The water is renewed at least twice each day. The cell is then ready to be prepared for another measurement of pressure. The preparation consists in subjecting it to one or more repetitions of the membrane-forming process, until the high resistance of the membrane indicates that its condition is again satisfactory.

3. THE SOAKING OF THE CELL.

It has previously been stated that before every repetition of the membrane-forming or repairing process, the cell (whether it is being prepared for use or is in use) is soaked in distilled water for a considerable period. This treatment is of the greatest importance—in fact, it can not be dispensed with. Moreover, it may be stated, as a general proposition, that the longer the soaking is continued the better will the condition of the membrane be found to be. In accord with this statement is the fact that those membranes which have soaked through the three summer months without interruption are always found to be in excellent condition for the resumption of work in the autumn. The statement does not, of course, apply to cells which have suffered from infection, or from the effects of use with electrolytes, or from use at high temperatures followed by too rapid cooling. The observed effect of too little soaking is always an inability on the part of the membrane to maintain pressure.

The beneficial effect of water on the membranes is not fully understood, but it is believed to be due to the extraction of alkaline metals from the membrane material, and therefore to the effect which such extraction may be supposed to have in the preservation or improvement of the *colloidal* condition of the membranes. It is the purpose of the writer, while engaged upon this investigation, to confine himself, as much as possible, to the discussion of established facts, but he ventures to suggest in the present connection that all the phenomena which have come under his observation are in accord with the idea that true *semipermeability* is an attribute of colloids only, and that the passage of water through an osmotic membrane is a phenomenon of the hydration of a colloid upon one side and its partial dehydration on the other. This statement explains nothing, but it enables one to account, in a plausible manner, for the highly beneficial effect of pure water upon the semipermeability of membranes, and also for the deleterious effect of electrolytes.

The suspicion that much of the difficulty experienced in securing good membranes and in maintaining them in effective condition thereafter is due to the mischievous influence of potassium upon the colloidal state of the membrane material led to several modifications of the method of building up membranes. The first of these was a considerable dilution of the solutions which are used in forming them, a dilution from 0.1 to 0.01 weight-ion-normal. Somewhat later the concentration of the "membranogens," which are used within and without the cells while measuring pressure, was reduced from 0.01 to 0.001 normal. The effects were seemingly good, in that higher resistances could be obtained at any single "running" than before and the cells appeared to require less soaking between measurements. Still later a 0.01 weight-ion-normal solution of ferrocyanic acid was substituted for the potassium salt in all operations connected with the deposition and reinforcement of membranes. The results of the last substitution are very promising, and the acid seems likely wholly to displace the salt.

It has been found that, while potassium salts are in a marked degree injurious to the membranes and may easily ruin them, the salts of lithium are comparatively harmless. This discovery has been utilized to some extent and with advantage in the deposition of membranes by substituting the ferrocyanide of lithium for that of potassium.

4. ACTIVITY OF THE MEMBRANE.

In discussing the so-called "*thermometer effects*," which are due to fluctuations of temperature, the fact was emphasized that the passage of solvent through the membrane is by no means instantaneous, and that it may be exceedingly slow. We have, therefore, a "*barometer effect*" due to fluctuations of atmospheric pressure. Barometer effects are, however, less troublesome than thermometer effects, because, as a source of error in the measurement of osmotic pressure, their magnitude is limited to the comparatively small variations in atmospheric pressure. Moreover, the errors due to them can be eliminated by correcting the mean of all the daily observations of osmotic pressure by the mean barometric pressure for the whole period within which an experiment is in progress.

The activity of a membrane, i. e., the rate at which the solvent will pass through it, depends, of course, in the first place, upon its area. Since, however, the membrane is made up of a multitude of little "plugs," which fill the mouths of the pores opening upon the interior of the cell, the area of the membrane is equal to the aggregate area of these pores at their mouths. In other words, the size of the membrane depends, not on the area of the interior of the cell, but upon the number and the size of the pores in the cell wall. It is this fact which makes all quantitative comparisons of the membranes of different cells impossible. We can never know their relative areas. It is only known that, other things being probably equal, water passes more slowly

through a membrane in a hard-burned cell, in which the pores are presumably small, than it does through the membrane of a soft-burned one, in which the pores are presumably large.

The rate at which water will pass through a given membrane decreases with age and use. In cells with new membranes, the osmotic pressures of solutions often attain a maximum within six hours, provided the temperatures, and therefore the volumes of the solutions, remain constant; while the same cells, two years later, may require from five to ten days, or even longer, for the establishment of equilibrium pressures. In Table 4 the records of the determinations of osmotic pressure illustrate the difference, as regards the time required for the development of equilibrium, between an excellent new membrane and an old one, which, though slow, is otherwise in good condition for the measurement of osmotic pressure:

TABLE 4.—*Observed osmotic pressures.*

I. New membrane. 0.9 weight-normal solution of cane sugar. Temperature 25°.		II. Old membrane. 0.6 weight-normal solution of cane sugar. Temperature 25°.	
First day	24.127	Sixth day	15.654
Second day	24.148	Seventh day	15.612
Third day	24.125	Eighth day	15.628
Fourth day	24.102	Ninth day	15.629
Fifth day	24.125		
Mean	24.126	Mean	15.627

The maximum pressure was reached in less than six hours in the case of the new membrane cited above, while six full days were required in that of the old one. In another instance, the maximum pressure was reached on the tenth day and it remained constant for 12 days, when the cell was opened. The measurement was an excellent one, and the only defect of the cell was the excessive slowness with which the solvent passed through the membrane into the solution. It should also be noted in this place that certain cells whose membranes had suffered some deterioration through contact with electrolytes have been known to require more than 20 days for the establishment of final pressures. The measurements were, nevertheless, entirely satisfactory.

In cells with old membranes, and in those whose membranes have become slow through contact with electrolytes, "thermometer" and "barometer" effects are necessarily large; hence when small pressures, i. e., those of dilute solutions, are to be measured, cells with young and especially active membranes are selected. For such purposes, soft-burned cells have the obvious advantage that in them the areas of the membranes are relatively large. If the pressures to be measured are minute, they may be entirely masked by the thermometer and barometer effects. To illustrate this point, it is recalled that certain

small amounts of the membrane-forming compounds are employed in measuring osmotic pressure for the purpose of mending any rents which may be made in the membranes. The compounds, in the quantities used, are supposed to be osmotically equivalent, and therefore to have no effect upon the observed osmotic pressures; but this can not be proved, because the difference, if any, is less than the unavoidable thermometer and barometer effects. Similar difficulties are encountered when it is attempted to employ very small membranes. On certain occasions, in the course of the present investigation, it was desirable to employ membranes of very limited area. To obtain these, the cells were glazed over the whole surface, interior and exterior, and afterwards ground off on opposite sides of the cell over as much of the "biscuit" as it was desired to expose for the membrane. Such cells were found, however, to be quite impracticable, because of their slowness in responding to fluctuations of bath temperature and atmospheric pressure. Since, other things being equal, the time required for the establishment of equilibrium pressure and the magnitude of the thermometer and barometer effects are inversely proportional to the area of the membrane, it is obviously desirable to make the membranes as large as they may be consistently with other requirements.

"Slow cells" are kept under observation for much longer periods than "quick" ones, because of the minimizing effect of time on the magnitude of thermometer and barometer effects.

After hundreds of quantitative measurements of osmotic pressure, we are still unable to say how the rate of passage of the solvent through the membrane is affected by the concentration of the solution within the cell. The difficulty in settling a question of this kind is due to the fact that no two membranes are exactly alike in all the elements which determine the rate of transference. It has already been stated that the membranes of no two cells are of equal area; and it is also true that the membrane in any given cell is never exactly the same on two successive occasions. The effect of temperature upon the activity of the membranes is also uncertain, though the writer and his associates are under the impression that a rise in temperature increases their activity. But here again quantitative comparisons are impossible.

If a cell is set up with a solution, under a small initial mechanical pressure, it is noticed that the rise of the mercury in the manometer is very rapid at first, but that the rate of ascent decreases with great regularity and becomes exceedingly slow as the meniscus approaches its final position. This appears to indicate that the rate of passage of the solvent through the membrane depends on the difference between the pressure existing in the cell and the true osmotic pressure of the solution. There are, however, no means of determining how the whole time required for the establishment of equilibrium is related either to the concentration or to the temperature of the solution.

5. DETERIORATION OF THE MEMBRANE.

If the ferrocyanide of zinc (the membrane of Tamman) is deposited in a cell in the usual manner and is tested soon thereafter with a solution of sugar, considerable pressure is developed on the first trial, but by no means the full osmotic pressure of the solution. Moreover, the pressure does not at any time become constant, but, having reached its highest development, it falls slowly and continuously until it is in equilibrium with the pressure of the air. If the cell is now emptied and soaked in water, and the membrane is reinforced in the usual manner, and the cell is again set up with a solution of sugar, some pressure is developed, but always less than on the first trial. On each succeeding trial, a still smaller pressure is obtained, until at last the cell develops no pressure whatever. After the first trial, the solutions which are removed from the cell have a milky appearance, due to suspended ferrocyanide of zinc; and on close examination the compound is found to have lost its original structureless (colloidal) condition and to have become granular, though not distinctly crystalline. We have here a clear case of degeneration which appears to consist in a change in the membrane material from a gelatinous or colloidal condition to a granular state. From the fact that after a time no pressure can be obtained, however much the membrane may be soaked in water or reinforced by the deposition of additional material, it is inferred that during the later experiments the newly formed ferrocyanide is transformed as fast as it is deposited. A similar, but less striking, degeneration has been noticed on the part of the manganese ferrocyanide membrane. Neither the zinc nor the manganese salt has been found suitable for the measurement of osmotic pressure.

The ferrocyanide of copper membrane, when carefully treated in the prescribed manner, appears to suffer no such deterioration as long as it is used to measure the pressure of non-electrolytes only, and at moderate temperatures. It is still uncertain whether the disastrous effect of rapid cooling, after using the membrane at high temperature, is due to a similar transformation, or not. The membrane becomes less active with age, but not ineffective. In fact, old membranes are preferred for the measurement of high pressures, because of their great strength and reliability; and old cells are discarded only when the passage of solvent through their membranes becomes intolerably slow, and never because they will not measure correctly, if given time enough. Some cells have been in use more than four years. The decreased activity of old membranes may be due, in part at least, to the thickening effect of the frequent reinforcement with new material to which they are subjected.

The conduct of the ferrocyanides of nickel and cobalt resembles that of the ferrocyanide of copper. Both of them give membranes which do not appear to degenerate under the influence of non-electrolytes.

The same is probably true of a number of the cobalticyanides, but the experimental evidence with regard to the last class of salts is still too meager to warrant any positive statements concerning their durability. A ferrocyanide of copper membrane can be satisfactorily reinforced with the nickel or the cobalt salt, and vice versa.

6. THE EFFECT OF ELECTROLYTES.

It has been shown that the effect on the membranes of the alkali which is liberated during their deposition is undoubtedly injurious; and the impossibility of building up good membranes and of maintaining them thereafter in good condition, without repeated and prolonged soaking in pure water, has been ascribed to the accumulation of potassium in the membranes. It was therefore apprehended that the measurement of the osmotic pressure of potassium salts, and perhaps of other electrolytes, would be attended with great difficulties. These fears have been partially, but not fully, realized. Our experience with the electrolytes will be given in Chapter XI, which describes our efforts to measure the osmotic pressures of potassium and lithium salts.

7. THE SEMIPERMEABILITY OF MEMBRANES.

It is often asserted that no membrane is truly semipermeable; in other words, it is frequently affirmed that all membranes are permeable to the solute as well as to the solvent—that the difference is one of degree only. Such statements appear to be without justification. They are certainly not founded on any reliable information in the possession of those who make them. The question is one of fundamental importance and is to be decided only by experiment. The fact that all the solutions of cane sugar and glucose which are taken from good cells, after a measurement of osmotic pressure, are found to have maintained their concentration perfectly, is evidence enough that membranes may be made sufficiently semipermeable for quantitative purposes. But, though many of our cells had maintained, without evidence of weakness, the maximum pressures of the solutions for 10, 15, and even 20 days, it was decided to test the soundness of the membranes by means of an experiment of much longer duration. For this purpose, a cell containing a 0.5 weight-normal solution of cane sugar was selected at random and allowed to remain in the bath at 15° for *two full months*. The record of the cell is given in Table 5 in atmospheres of osmotic pressure.

At the end of the two months, the solution was removed from the cell and compared in the polariscope with a reserved portion of the original solution. The rotations of the two were identical, showing that no leakage of the solute had occurred.

The cell employed in this experiment is a good example of what came to be known as "*quick cells*." In less than 24 hours after setting

it up, the osmotic pressure which it registered was 12.522 atmospheres, the barometric pressure being 1.013. On the sixtieth day thereafter, the osmotic pressure was also 12.522 atmospheres and the barometric pressure was 1.016. The lowest osmotic pressure observed during the two months was 12.517; the highest was 12.552. The extreme (apparent) fluctuation in osmotic pressure was therefore 0.035 atmosphere, or 0.28 per cent of the mean (12.533 atmospheres) of all observations. The extreme fluctuation in atmospheric pressure during the same period was 0.035 atmosphere. In other words, the extremes of variation were the same for osmotic and barometric pressures. The highest (apparent) osmotic pressures were contemporaneous throughout with the lowest atmospheric pressures, and vice versa. This is due, of course, to the fact that, owing to the slowness with which the solvent passes through the membrane, the pressure within the cell can not immediately adjust itself to changes in atmospheric pressure.

TABLE 5.—*Observed osmotic pressures.*

Day.	Atmospheres.	Day.	Atmospheres.	Day.	Atmospheres.	Day.	Atmospheres.
2d.....	12.522	17th....	12.539	32d.....	12.537	47th....	12.534
3d.....	12.535	18th....	12.533	33d.....	12.531	48th....	12.544
4th....	12.544	19th....	12.527	34th....	12.536	49th....	12.533
5th.....	12.534	20th....	12.530	35th....	12.533	50th....	12.532
6th.....	12.536	21st....	12.527	36th....	12.532	51st....	12.552
7th.....	12.552	22d.....	12.536	37th....	12.537	52d.....	12.533
8th.....	12.535	23d.....	12.525	38th....	12.517	53d.....	12.532
9th.....	12.536	24th....	12.526	39th....	12.517	54th....	12.535
10th.....	12.538	25th....	12.536	40th....	12.524	55th....	12.533
11th.....	12.524	26th....	12.534	41st....	12.529	56th....	12.540
12th.....	12.541	27th....	12.524	42d.....	12.533	57th....	12.536
13th.....	12.537	28th....	12.537	43d.....	12.523	58th....	12.545
14th.....	12.529	29th....	12.524	44th....	12.528	59th....	12.539
15th.....	12.532	30th....	12.535	45th....	12.530	60th....	12.527
16th.....	12.531	31st....	12.535	46th....	12.546	61st....	12.522

8. REMOVAL OF THE MEMBRANE.

When, through age and frequent reinforcement, or through the deterioration due to contact with electrolytes, a membrane has become intolerably "slow" or otherwise unserviceable, it is desirable to replace it by a new one. According to Pfeffer,* an old membrane of copper ferrocyanide can be removed and successfully replaced by a new one. For the removal, he recommends soaking the cell in a dilute solution of potassium hydroxide, to which has been added a little Rochelle salt, and afterwards in water, in hydrochloric acid, and again in water. The removal of the membrane by this method is easy, but we have never been able, after such treatment of a cell, to build up in it a thoroughly good new membrane. The process has been modified in

*"Osmotische Untersuchungen," 12.

various ways, but without entirely satisfactory results. One of the modifications consisted in the omission of both the caustic potash and the hydrochloric acid, and in the removal, by electrolysis, of the soluble salts which were left in the wall after soaking the cell in water. The best results were obtained by a simple electrolysis of the membranes in the presence of water, but the removal of membranes by this method is exceedingly slow. Fairly good results were also obtained by grinding off the interior wall of the cells with a carborundum wheel running at high speed, and afterwards reburning them. In whatever manner the membranes may be removed, the reburning is essential. It is suspected that the walls of the pores, near their mouths, are in some way modified (perhaps made more smooth) by the reagents which are employed to remove the membranes, with the result that the "plugs" of the new membranes do not fit so firmly into their places. It is now preferred to discard cells with old or defective membranes rather than attempt to restore them to use by replacing their membranes.

9. INFECTION OF THE MEMBRANES.

The ready infection of the membranes by voracious nitrogen-consuming fungi has been one of the serious obstacles to the progress of the present investigation. The particular fungus known to have produced a large amount of mischief is a strain of *Penicillium glaucum*. Others are believed to have contributed to the frequent destruction of the membranes, but they have not been identified with certainty.

The first announcement* regarding this pest was as follows:

"Soon after beginning the measurement of osmotic pressure, there appeared upon one of our cells an abundant growth of a fungus, which upon examination was found to be penicillium. Within the next few days, it appeared upon one after another of the remaining cells, until all were affected in the same manner as the first. We then exposed several solutions of glucose to the air of the laboratory, and the fungus appeared in all of them in a short time. We had had no similar experience previously, though we had worked with solutions containing invert sugar more than two years, and the conditions under which we were working were in general unfavorable to the fungus. The sudden prevalence of penicillium spores in the atmosphere of the laboratory could, however, be accounted for, though it had not been anticipated. At the time, certain changes were in progress in the lower part of the building which involved the tearing away of old walls, and the atmosphere of all parts of the laboratory was, in consequence, in a somewhat dusty condition."

A search was immediately instituted for some poison which would kill the fungus without injuring the membranes. Of the numerous substances which were tested, hydrocyanic acid in gaseous form and thymol were found to be quite effective and entirely harmless to the membranes. Formaldehyde has also been extensively employed, especially for the disinfection of the baths.

*Amer. Chem. Journal, xxxvi, 34.

The first intimation of infection is, of course, the fact that the cells will not develop maximum pressures. On removing the solutions, they are found always to have a more or less greenish color, and the absence of this color is a sure sign that the membrane has not been attacked by the fungus. If the destruction of the membrane by the penicillium is far advanced, there are also found, upon the bottom of the cell, minute grains of a substance whose color varies from green to blue. When the fungus is allowed to grow in a solution of sugar to which some membrane material (copper ferrocyanide) has been added, the solution becomes green, then blue, and finally brown from suspended iron hydroxide, as if the whole of the nitrogen of the ferrocyanide had been appropriated.

The restoration to a usable condition of a membrane which has been attacked by this penicillium is a work of some months. The quickest method of killing the fungus is to place the wet cell under a bell jar and to develop in the inclosed space gaseous hydrocyanic acid by dripping dilute hydrochloric acid into a dish containing potassium cyanide. Though it grows vigorously in dilute solutions of copper sulphate which are exposed to the air, it soon dies in a saturated solution of thymol. It is quickly killed by formaldehyde in dilute solution. Phenol and salicylic acid appear to be less poisonous to it than thymol.

After destroying the penicillium, it is necessary to begin anew and to repeat in every detail the series of operations employed in building up and seasoning membranes.

Because of the laborious character of the measures which must be resorted to for the restoration of the membranes, every possible precaution is taken to prevent infection. Some of these preventives have already been mentioned incidentally—for example, the boiling of all water which comes in contact with the cells, the careful covering of all vessels, the soaking of the cells in thymol water, and the addition of minute quantities of thymol to the liquids within and without the cell when a measurement of pressure is to be made. Another precaution consists in the occasional disinfection of the baths at high temperature (from 70° to 80°) with the vapors of formaldehyde, which are circulated within the inclosed spaces by means of fans. The interior walls of the baths, together with all their fittings, such as wires, etc., are frequently washed with a solution of formaldehyde. In the older form of "rectangular" bath the water and air spaces were not carefully separated. The upper or air space was therefore always saturated for the given temperature with water vapor, producing a condition which was especially favorable to the growth of the penicillium. It was found impossible to rid these baths of infection for any length of time. They were, therefore, all reconstructed with vapor-tight partitions between the two compartments. It was afterwards practicable to keep the air spaces so dry (by means of desiccating agents) that the fungus could not grow.

CHAPTER V.

THE WEIGHT-NORMAL SYSTEM FOR SOLUTIONS.

The solutions employed in this investigation have been made, from the beginning, by dissolving a gram-molecular weight of the substance, or a decimal part of the same, in 1,000 grams of water. Moreover, in calculating the theoretical gas pressure of the solute at any temperature the volume of the *solvent* in the pure state, and not that of the *solution*, has been adopted as the standard. The solutions so made have been called "*weight-normal*" to distinguish them from "*volume-normal*" solutions, or those made by dissolving the same quantities of substance and diluting the solutions to a volume of 1,000 cubic centimeters. Perhaps a better name for such solutions would have been "*solvent-normal.*"

There have existed a widespread and persistent misapprehension of the reasons which led to the adoption of the *weight-normal* system for osmotic-pressure measurements and a quite general misunderstanding of the nature of the advantages which were expected from its employment. Unfortunately, but perhaps not altogether unnaturally, it has been inferred by many that the preference shown for this system has somehow committed the author and his associates to the view that under it the osmotic pressure of aqueous solutions will be found to conform necessarily to the gas laws. This appears to be the interpretation of Findlay, who, in his recent excellent work* on osmotic pressure, has reduced the weight-normal system, as employed by the writer and his co-workers, to the form of a general equation which he calls the "equation of Morse," and has then proceeded to show—though by evidence which is not entirely convincing to the writer—that it must fail in the case of highly concentrated solutions. It is hoped that the following somewhat discursive presentation of the subject will serve to clear up some of the misunderstandings which have arisen.

The fact that van't Hoff expressly limited his deductions concerning osmotic pressure to extremely dilute solutions, in which neither the aggregate volume of the solute molecules nor their mutual attractions are of moment, has been—certainly until recently—too often ignored or too feebly emphasized. That he had a clear vision of some of the complications which must arise when it was attempted to deal with the osmotic pressure of concentrated solutions, and that he, on that account, deliberately excluded these as something for which the simple equation $PV = KT$ is inadequate, is convincingly shown by the follow-

*"Osmotic Pressure," by Alexander Findlay. Longmans, Green & Co., 1913.

ing quotations from van't Hoff's memorable paper.* At the conclusion of Section I, entitled "Der Osmotische Druck, Art der Analogie, welche durch dessen Einführung entsteht," he says (page 483):

"Von diesem praktischen Vorteil werden wir in Nachfolgenden Nutzen ziehen, speziell zur Erforschung der für *ideale Lösungen giltigen Gesetze, für Lösungen also, die derartig verdünnt sind, dass sie den idealen Gasen an die Seite zu stellen sind, und in denen somit die gegenseitige Wirkung der gelösten Moleküle zu vernachlässigen ist, wie auch der von diesen Molekülen eingenommene Raum bei Vergleich mit dem Volum der Lösung selbst.*"

The succeeding three sections, namely, II, III, and IV, are entitled:

II. "Boyle's Gesetz *für verdünnte* Lösungen."
III. "Gay-Lussac's Gesetz *für verdünnte* Lösungen."
IV. "Avogadro's Gesetz *für verdünnte* Lösungen."

Again, he says (page 498):

"Noch trefflicher ist dass der so allgemein auch für Lösungen angenommene Guldberg und Waagesche Satz thatsächlich als einfache Schlussfolgerung aus den *oben für verdünnte Lösungen aufgestellten Gesetzen* entwickelt werden kann."

It is equally certain that some of those who were foremost in adopting the new views concerning osmotic pressure, and who became the most effective agents in promoting their publicity and general acceptance, failed to make clear the full significance of van't Hoff's reservations; for we find stated, without due qualification, and thereafter constantly repeated as models of concise yet comprehensive definition, propositions like the following:

"*Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified at the same temperature without change of volume.*" [Again] * * * "d. h. *der osmotische Druck gelösten Rohrzucker ist gerade so gross wie der Gasdruck den man beobachten würde, wenn man das Lösungsmittel entfernte, und die gelöste Substanz den gleichen Raume bei gleicher Temperatur in Gasform erfüllend zurückliesse.*"

Much confusion and futile discussion would have been saved if it had been clearly explained in connection with all such statements:

1. That van't Hoff intended to apply the equation $PV = KT$ only to "*ideal solutions*," i. e., to solutions so dilute that neither the volume nor the mutual attractions of the solute molecules are of importance.

2. That when more concentrated solutions are to be dealt with, it will obviously be necessary to modify the simple equation for "*ideal*" solutions in a manner analogous to the modification by van der Waals of the equation for "ideal gases."

3. That, because of the *solvent*, the case of solutions is more complex than that of gases, and that, for this reason, the general equation for them may be more complex than the equation of van der Waals for gases.

*Zeitschrift für physikalische Chemie, 1, 479.

Apparently the confusion of mind which prevailed for several years after the publication of van't Hoff's paper—and of which one sees many evidences, even at the present time—was due, in great part, to the persistence of the habit of regarding the simple equations which apply to so-called "ideal" conditions as the embodiments of the general laws for gases and solutions. The really comprehensive equation for gases is, of course, that of van der Waals $\left(P+\frac{a}{V^2}\right)(V-b)=RT$; while the equation for so-called "*ideal*" gases, $PV=RT$, covers only a special, and, in fact, a purely imaginary and impossible case, that, namely, in which the $\frac{a}{V^2}$ and the b of van der Waal's equation have become zero.

It is conceivable that in the course of time an approximately comprehensive equation will be developed for osmotic pressure, but, in the opinion of the writer, it will be the fruit of extensive and painstaking experimental research rather than of ingenious speculation. In other words, it will be the embodiment of the general rule which is finally formulated for the purpose of correlating a great variety of *authenticated* facts concerning osmotic pressure. The equation of van't Hoff will, of course, stand in much the same relation to it as does the expression $PV=RT$ to the more general equation of van der Waals. It is doubtful, however, if any proposed general equation for osmotic pressure, although containing suitable terms for all the factors which must be taken into account, would be of any present utility in the case of aqueous solutions, since the value of at least some of these terms—e. g., that covering hydration—must still be experimentally determined for every solute and at every temperature and in each individual concentration of solution. If it is true that the value of an equation is to be measured by its competence to foretell the truth in any case to which it may appropriately be applied, then every general equation for osmotic pressure is bound to disappoint one who attempts to apply it to aqueous solutions. To illustrate: There is no equation conceivable which could foretell, in the case of cane-sugar solutions, that the value of the hydration term is constant for each concentration between 0° and 25°, or that it soon thereafter begins to decline in value to become zero at some definite higher temperature; or further, how what may be called the idiosyncrasies of hydration may be expected to vary from one solute to another. In view of the necessary limitations of its usefulness as a means of discovering truth, the author does not regard a general equation as the *ultimum bonum* in the field of osmotic pressure or (in the present meager and inexact state of our knowledge of the subject) as even highly desirable. The osmotic pressure of solutions—especially of aqueous solutions—depends upon such a variety of still unmeasured and imperfectly understood conditions that any attempted comprehensive expression for it at the

present time must fail to convince, and is bound to absorb in futile discussion much energy which might be more profitably employed in finding out what the *facts* of osmotic pressure really are.

It has been intimated by some of our friendly colleagues that the adoption at the beginning of our investigation (1) of the *weight-normal* system for the solutions; (2) of the practice of referring the gas pressure of the solute to the volume of the solvent; and (3) of the custom of always stating the ratio of observed osmotic pressure to the calculated gas pressure of the solute are all inconsistent with the general attitude toward the subject which is professed above—that, in fact, all three of the itemized practices are indicative of preformed judgments in a case which we were professedly attempting to investigate without prejudice. This plausible indictment calls for some defense on each of its specifications.

Long before taking up the investigation of osmotic pressure, the author had been accustomed to point out certain defects of the usual "*volume-normal*" system of making up solutions, and to maintain that, while it was advantageous and correct for merely analytical purposes, it was both disadvantageous and illogical whenever any phenomenon was to be studied in which the influence of the solvent upon the solute was involved. It was maintained that, in cases of the latter kind, the true concentration of a solution is determined by the numerical ratio of the molecules of the solute to those of the solvent rather than by the number of solute molecules in a given space. An illustration frequently used for the purpose was the case of cane sugar and glucose. In a *volume-normal* solution of cane sugar at 0°, the numerical ratio of solute to solvent molecules is about 1 to 44.1, while in a *volume-normal* solution of glucose at the same temperature the ratio is about 1 to 49.2. In other words, with respect to the solvent, the cane-sugar solution is 11.5 per cent more concentrated than that of glucose. When stated in terms of osmotic pressure, the difference is about 3.7 atmospheres, notwithstanding the fact that equal volumes of the two solutions contain the same number of solute molecules.

Another illustration of the difficulties which are encountered when *volume-normal* solutions are employed was the following example of the effect of what may be called *decimal* dilution. Suppose a 0.1 volume-normal solution of cane sugar to be made up by diluting 100 cubic centimeters of a normal solution to 1,000 cubic centimeters. With respect to the relative numbers of solute molecules contained in equal volumes, the new solution is one-tenth as concentrated as that from which it was made, but with respect to ratios of solute to solvent molecules, namely, 1: 44.1 and 1: 544.1, the concentration of the diluted solution is *not 0.1, but 0.081* normal.

When it came to a choice of systems, it was concluded by the author and his colleague, Frazer, that the only justification for the use of the

volume-normal system was based on the presumption—already extensively abandoned—that the phenomenon of pressure in the osmotic cell is due simply to the bombardment of the membrane by the solute molecules. If we *had* employed the *volume-normal* system for solutions, our colleagues could have convicted us, by circumstantial evidence, of being under the dominion of a discarded conception of the cause (and therefore of the proper magnitude) of osmotic pressure. Inasmuch as the obviously immediate cause of the pressure observed in the cell is a *dilution* of the solution within by solvent acquired from without, the *weight-normal* appeared to involve less of hypothesis and to be more rational than the *volume-normal* system.

As to the part which is played by the membrane in bringing about this dilution of the imprisoned solution, upon which the existence of the pressure in the cell depends, the original idea of Graham—that the passage of the aqueous solvent through it is due to some sort of hydration of the colloidal material of the membrane on the side bathed by the more dilute solution, and a dehydration on the side covered by the more concentrated solution—has always appealed to us as more simple than and quite as satisfactory as any of the numerous other explanations which have been offered. It is certainly in accordance with the observed fact that the amount of water which a colloid can acquire and retain depends on the concentration of the solution to which it is exposed. If Graham's view concerning the *modus operandi* of the transmission of water is correct, the real problem to be studied in this connection would seem to be the dependence of the hydration of the colloidal membrane upon the concentration of the solutions and upon pressure.

The course of reasoning which led to the adoption of the *volume of the solvent* as the standard for the computation of the gas pressure of the solute is quite elementary and appears to involve very little of hypothesis.

The essential difference between a substance in gas form and in solution, which strikes one at once and first of all, is the fact that the molecules of a gas are moving through space otherwise unoccupied, while in a solution the molecules of the solute are moving through space occupied by the solvent. The analogy of the "*free space*," in the case of a gas, to the *free* or pure solvent in a solution is, in this particular, obvious and unmistakable. Moreover, it was to be presumed that the *space occupied by the solute molecules* would bear, in general, somewhat the same relation to osmotic pressure that the aggregate volume of the gas molecules bears to the pressure of a gas—in other words, that a *correction* would have to be employed for osmotic pressure which is equivalent to the correction symbolized by the term b in the equation of van der Waals for gases. It was also clear that, if the pressure of a gas could always be computed on the basis of, or referred to, the volume

of the free space, instead of the total volume of the gas, the correction term *b* in the equation of van der Waals would be automatically eliminated. Such a course is impracticable in the case of gases, but easy in that of solutions. The obviously equivalent procedure in the case of solutions was to compute the gas pressure of the solute—with which osmotic pressure was to be compared—on the basis of the volume of the solvent, which is known approximately wherever the weight-normal system of solutions is employed. The correction for the volume of the solute, which is effected by adopting the weight-normal system and by the practice of referring the gas pressure of the solute to the volume of the solvent, is, however, somewhat uncertain, because the volume of the solvent in a solution is not exactly known. The volume of a solution is not equal to the sum of the volumes of the solvent and solute in their separate states. Moreover, the volume of the free solvent is liable to diminution through combination of solvent with solute molecules, as in *hydration*. When a weight-normal solution of cane sugar is made up at 0° by dissolving a gram-molecular weight of the substance in 1,000 grams of water, the volume of the solution is less than the sum of the volumes of the separate components by about 6.7 cubic centimeters. The shrinkage in the case of glucose under identical conditions is about 6 cubic centimeters. It is uncertain how much of this shrinkage is to be ascribed to each of the apparently possible causes, i. e., to change in the volume of the solvent itself, to change in the state of aggregation of the solute, and to the formation of hydrates. It appears probable, however, that the observed shrinkage in volume is principally due to one or both of the last two causes; but only one of these, namely, hydration, is known to affect the volume of the solvent.

In regard to the adoption of the volume of the solvent at the temperature of maximum density, as the standard for the computation of the gas pressure of the solute, it can only be said that the practice is based on the observation that the results appear to be slightly more harmonious among themselves, when this is done, than when the gas pressure is referred to the supposed volumes of the solvent at the temperature at which the measurements of osmotic pressure are made.

The most amazing judgment upon the work of the author and his collaborators is that pronounced by Professor W. D. Bancroft,* who says, in regard to the practices elaborated above:

"Quite recently Morse and Frazer have shown that their direct measurements of osmotic pressure came out better when the concentrations are referred to a constant volume of solvent. They consider this a discovery of their own, quite overlooking the fact that they have simply gone back to van't Hoff's original formulation. Having reached their conclusion empirically, Morse and Frazer have also overlooked that their method of expressing concentration contains the tacit assumption that there is neither expansion nor contraction when the two components are mixed."

*Jour. Phys. Chem., x, 320.

In view of the fact that van't Hoff had in mind *volume-normal* solutions only, and referred the gas pressure of the solute always to the *volume of the solution*, the author is unable to understand just how the adoption of the *weight-normal* system and the practice of referring the gas pressure of the solute to the *volume of the solvent* constituted a return to "*van't Hoff's original formulation.*"

Furthermore, it is not clear what Professor Bancroft has in mind when he says that Morse and Frazer have overlooked the fact that their procedure "*contains the tacit assumption that there is neither expansion nor contraction when the two components are mixed.*" If he means that the assumption in question is to the effect that the volume of the solution is neither greater nor smaller than that of the solvent, he has apparently again failed to apprehend the clear distinctions between the *weight-normal* and the *volume-normal* systems for solutions, and has imputed to Morse and Frazer an equal confusion of ideas. If he means, on the other hand, that Morse and Frazer have overlooked or ignored the fact that the volume of the solution is not exactly equal to the sum of the volumes of solvent and solute separately, he is quite misinformed as to the state of their knowledge of solutions, and as to their attitude of mind toward the volume relations in question.

It was realized in the beginning that the volume relations of solvent, solute, and solution constitute an important phase of the subject under investigation, and that they should be determined with the utmost practicable precision. Accordingly, almost simultaneously with the measurement of the osmotic pressure of cane-sugar and glucose, there was begun a very careful parallel investigation of the *volumes* of the various *weight-normal* solutions of those substances. The work at 0° was finished, but that at the higher temperatures is still incomplete.

An example of the kind of information which was sought is given in Tables 6 and 7.

The important question—considered in its bearing upon the practice of referring the gas volume of the solute to the volume of the solvent—is not what is the *total* contraction which is observed when the components of a solution are brought together, but *to what extent does the contraction modify the volume of the solvent itself?* Any shrinkage or expansion which may be due to the fact that the solute monopolizes less or more space in the solution than in its previous separate state does not necessarily involve the volume of the solvent. Contraction due to the formation of hydrates in solution does involve the solvent, and it undoubtedly diminishes its volume and concentrates the solution in what may be called the *weight-normal sense.* This concentration of the solution through hydration of the solute must express itself in the form of an equivalent increase in osmotic pressure. An "*ideal*" solution, in the "*weight-normal sense,*" is one in which the solvent has the same volume as in the separate state and is otherwise uninvolved.

If it can once be determined what rule or law governs the magnitude of the osmotic pressure of the solute in such "ideal" solutions, it will be practicable to study effectively the subject of hydration in aqueous solutions. No other method of equal comprehensiveness and promise is available, except perhaps the *vapor pressure* method, and that, in its present imperfect condition, is not adapted to the investigation of hydration. It is to be hoped that the study of solutions at *high temperatures*—at temperatures so high as to preclude the existence of hydrates—will

TABLE 6.—*Volume of weight-normal solutions of glucose at 0°.*

[Sp. gr. glucose at 0° =1.5567.]

Concentration.	Volume of solvent.	Volume of solute.	Sum.	Volume of solution.	Difference.	Contraction.
	c.c.	*c.c.*	*c.c.*	*c.c.*	*c.c.*	*p.ct.*
0.1	1000.13	11.48	1011.61	1010.93	0.68	0.07
0.2	"	22.96	1023.09	1021.70	1.39	0.14
0.3	"	34.45	1034.58	1032.55	2.03	0.20
0.4	"	45.93	1046.06	1043.42	2.64	0.25
0.5	"	57.41	1057.54	1054.29	3.25	0.31
0.6	"	68.89	1069.02	1065.22	3.80	0.36
0.7	"	80.37	1080.50	1076.14	4.36	0.40
0.8	"	91.81	1091.99	1087.06	4.93	0.45
0.9	"	103.34	1103.47	1097.94	5.53	0.50
1.0	"	114.82	1114.95	1108.92	6.03	0.54

TABLE 7.—*Volume of weight-normal solutions of cane sugar at 0°.*

[Sp. gr. cane-sugar at 0° =1.59231.]

Concentration.	Volume of solvent.	Volume of solute.	Sum.	Volume of solution.	Difference.	Contraction.
	c.c.	*c.c.*	*c.c.*	*c.c.*	*c.c.*	*p. ct.*
0.1	1000.13	21.328	1021.458	1020.73	0.728	0.07
0.2	"	42.656	1042.786	1041.25	1.536	0.15
0.3	"	63.984	1064.114	1061.80	2.314	0.22
0.4	"	85.312	1085.442	1082.38	3.062	0.28
0.5	"	106.640	1106.770	1103.01	3.760	0.34
0.6	"	127.968	1128.098	1123.70	4.398	0.39
0.7	"	149.296	1149.426	1144.39	5.036	0.44
0.8	"	170.624	1170.754	1165.13	5.624	0.48
0.9	"	191.952	1192.082	1185.91	6.172	0.52
1.0	"	213.280	1213.410	1206.69	6.720	0.55

eventually reveal the simplest forms of the laws governing the osmotic pressure in aqueous solutions. If these are once established, we can then measure hydration at lower temperatures by the *apparent abnormalities* of the osmotic pressure. It is not to be ignored, of course, that other factors than hydration may assert themselves at the lower temperatures and obscure, to some extent, the results.

The reasons given or implied in the foregoing statement are those which decided the author and his collaborators to adopt, in the beginning, the *weight-normal* system of solutions for the measurement of

osmotic pressure. They have never made any claim to the *discovery* of this system, as has been intimated by one critic of their work. Such a claim would have been absurd in the light of the fact that the "*weight-normal*" system was the obvious and the already known alternative of the "*volume-normal*," or more usual, system of making up solutions.

The question now to be answered is whether the *experimental* data, as far as they have been acquired up to the present time, *do*, or *do not*, appear to justify the wisdom of the choice which was made and to call for its continuance in use. The strongest evidence which could be adduced in favor of any system would be the fact that, under it, the osmotic pressures of the solutions appear to conform to a definite temperature coefficient and to bear some definite relation to concentration. It is not at all necessary, in order to give weight to the evidence, that the relations in question shall be found to conform to the laws of Gay-Lussac and of Boyle for gases. Evidence pointing equally clearly to the existence of other laws than these would be quite as convincing. The facts are, however, that, under the weight-normal system, all the reliable osmotic evidence thus far gathered points emphatically either to a substantial conformity with the laws of Gay-Lussac and of Boyle for gases, or to a species of non-conformity which is rationally and adequately explainable on the supposition that, at moderate temperatures, some of the solutes are hydrated. A brief résumé is given below of the established facts which bear upon the question of the obedience of osmotic pressure in aqueous solutions to the laws of Gay-Lussac and of Boyle.

(1) It has been shown that in all solutions of cane sugar, from 0.1 to 1.0 weight-normal, the ratio of the observed osmotic to the estimated gas pressure of the solute *is constant for each concentration* between 0° and 25°. This *proves* that, between the specified limits of concentration and temperature, the osmotic pressure of cane-sugar solutions obeys the law of Gay-Lussac for gases.

(2) The ratio in question *exceeds unity* in every instance. This suggests, of course, a concentration of the solutions through a withdrawal of some of the solvent for the purpose of hydrating the solute. If hydration exists, it must be constant in quantity for each concentration of solution within the given limits of temperature; for, otherwise, the law of Gay-Lussac could not hold.

(3) The osmotic pressure of cane-sugar solutions, between 0° and 25°, *are not proportional to the quantities of the solute*. In other words, the ratio of osmotic to gas pressure varies from concentration to concentration, though, as stated under (1), it is strictly constant for any given concentration. This leaves the applicability of Boyle's law in doubt, but does not demonstrate its inapplicability; for the phenomenon may be due to differences among the various concentrations of solution in respect to the degree of hydration which they have severally suffered.

(4) When solutions of cane sugar are heated to a temperature above 25°, the ratios of osmotic to gas pressure—which are all above unity and are constant for each concentration at lower temperatures—begin to decline. The decrease in the ratio with rising temperature is relatively more rapid in dilute solutions than in concentrated ones. Such conduct on the part of solutions is indicative of the presence in them of dissociating hydrates.

(5) The decline in the ratio of osmotic to gas pressure, which begins a little above 25°, continues until, at some temperature which is characteristic for each concentration, *it becomes unity*. This shows that, at these temperatures, the osmotic pressures of all the solutions conform both to the law of Gay-Lussac and to that of Boyle.

(6) The work upon solutions of cane sugar, between the boiling-point of the solvent and the temperatures at which the ratio of osmotic to gas pressure becomes unity for the several concentrations, has not been finished, but there is already in hand considerable evidence to the effect that a ratio, having once become unity at some temperature, does not further decline at still higher temperatures.

(7) The conduct of glucose solutions differs somewhat but not wholly from that of cane-sugar solutions: (*a*) At 0° the ratio of osmotic to gas pressure is greater than unity, which again suggests hydration. The ratio is, however, *the same for all concentrations of solution*. In other words, the osmotic pressures are *proportional to concentration*. This means that they conform to the law of Boyle. (*b*) At some temperature above 0°, but below 10°, the ratio begins to decline, which suggests the presence of dissociating hydrates. At 10°, half the difference between the observed ratio at 0° and unity has already disappeared. But the ratio *is still the same for all concentrations*, showing that the law of Boyle holds at 10°, as well as at 0°. (*c*) At 25° and also at 30°, 40°, and 50° the ratio of osmotic to gas pressure is unity for all concentrations from 0.1 to 1.0 weight-normal, proving that at these temperatures the osmotic pressure of glucose solutions obeys both of the gas laws.

(8) The ratio of osmotic to gas pressure in all solutions of mannite is *unity* at 10°, 20°, 30°, and 40°. Its value at other temperatures has not been ascertained.

The mistaken impression that the author and his collaborators are engaged in an endeavor to demonstrate that the gas laws apply generally to osmotic pressure is probably due to the emphasis which has frequently been laid upon the relations pointed out above. The truth is, however, that they have limited their discussions to the few facts established by themselves, and have only sought to formulate the more obvious relations of their own experimental data. If any rule proposed by them as apparently fitting their experimentally acquired facts has been found susceptible of a concise mathematical expression, it has not thereby acquired, in their estimation, any additional merit

or utility, or, least of all, the character of a general equation. It has still remained—despite its more impressive appearance in mathematical dress—simply a rule, the question of whose validity was to be strictly limited to the already known and fully accredited facts, and which, therefore, was subject to modification as the number of established facts increased. The direct measurement of osmotic pressure is a task of supreme difficulty, and those who would undertake it effectively should qualify themselves for the enterprise by discarding all convictions as to whither their labors may lead them.

Probably it will be generally conceded that the weight-normal is the simpler and more rational system for the statements of the freezing-point depressions of aqueous solutions. We have determined these in all of the concentrations of solution of cane sugar and glucose which have been employed for the measurement of osmotic pressure, and they are given in Table 8, together with the corresponding molecular depressions of the freezing-points.

TABLE 8.—*Cane sugar and glucose.—Depression of the freezing-points of weight-normal solutions.*

Concentration.	Cane-sugar.		Glucose.	
	Depression.	Molecular depression.	Depression.	Molecular depression.
	degrees.	*degrees.*	*degrees.*	*degrees.*
0.1	0.195	1.95	0.192	1.92
0.2	0.393	1.96	0.386	1.92
0.3	0.584	1.95	0.576	1.92
0.4	0.784	1.96	0.762	1.91
0.5	0.983	1.97	0.952	1.91
0.6	1.190	1.98	1.147	1.91
0.7	1.390	1.99	1.337	1.91
0.8	1.621	2.02	1.528	1.91
0.9	1.829	2.03	1.720	1.91
1.0	2.066	2.07	1.918	1.92

Table 9 is added in order to illustrate and emphasize the limitations of the freezing-point method as a means for the determination of osmotic pressure in aqueous solutions.

The direct measurement of osmotic pressure is often deprecated on account of the great difficulties which are encountered; and it is frequently asserted, with an air of thorough conviction, that there are other methods available which are more accurate and much easier. If this were really true, we should have emerged long ago from our present lamentable state of ignorance with regard to the osmotic pressure of solutions. The very fact that we can not yet make a safe prediction as to the magnitude of osmotic pressure in any aqueous solution which has not been extensively investigated by the direct method is proof enough that these other "*more accurate and easier methods*" have failed to render the service of which they are said to be capable.

The methods which are always cited in this connection are three in number—namely, the *freezing-point*, the *boiling-point*, and the *vapor-tension* methods. It is known that the depression of the freezing-point of an aqueous solution will give us approximately its osmotic pressure within a very limited region of temperature which includes the freezing-point itself. So much has been experimentally proved. It is probably true also—though it has not yet been demonstrated by direct measurements—that the osmotic pressure of an aqueous solution in the immediate vicinity of its boiling-point can be derived from the elevation of the boiling-point. But how about the osmotic pressures of the solution throughout that relatively much larger temperature area, between the freezing and boiling points, within which a variable hydration may exist, or other molecular influences than those concerned in the formation of hydrates may come into play and modify osmotic pressure?

TABLE 9.—*Cane sugar. Comparison of osmotic pressures calculated from freezing-points with those directly determined.*

Conc.	0°		5°		10°		15°		20°		25°	
	Calc.	Det.	Calc.	Det.	Calc.	Det.	Calc.	Det.	Calc.	Det.	Calc.	Det.
0.1	2.35	2.46	2.39	2.45	2.43	2.50	2.48	2.54	2.52	2.59	2.56	2.63
0.2	4.72	4.72	4.81	4.82	4.89	4.89	4.98	4.99	5.06	5.06	5.15	5.15
0.3	7.04	7.09	7.17	7.20	7.30	7.33	7.43	7.48	7.56	7.61	7.69	7.73
0.4	9.44	9.44	9.61	9.61	9.78	9.79	9.95	9.95	10.13	10.14	10.30	10.30
0.5	11.86	11.90	12.08	12.10	12.29	12.30	12.51	12.55	12.73	12.75	12.94	12.94
0.6	14.30	14.38	14.56	14.61	14.82	14.86	15.08	15.14	15.35	15.39	15.61	15.63
0.7	16.77	16.89	17.07	17.21	17.37	17.50	17.69	17.82	17.99	18.13	18.30	18.44
0.8	19.45	19.48	19.81	19.82	20.16	20.16	20.52	20.54	20.88	20.91	21.23	21.25
0.9	21.99	22.13	22.39	22.48	22.80	22.88	23.20	23.31	23.60	23.72	24.01	24.13
1.0	24.91	24.83	25.37	25.28	25.82	25.69	26.28	26.19	26.74	26.64	27.20	27.05

Conc.	30°		40°		50°		60°		70°		80°	
	Calc.	Det.	Calc.	Det.	Calc.	Det.	Calc.	Det.	Calc.	Det.	Calc.	Det.
0.1	2.61	2.47	2.69	2.56	2.78	2.64	2.86	2.72	.....	.....	.....	.....
0.2	5.24	5.04	5.41	5.16	5.58	5.28	5.76	5.44	.....	.....	.....	.....
0.3	7.82	7.65	8.07	7.84	8.33	7.97	8.59	8.14	.....	.....	.....	.....
0.4	10.47	10.30	10.82	10.60	11.17	10.72	11.51	10.87	.....	.....	.....	.....
0.5	13.16	12.98	13.60	13.36	14.03	13.50	14.47	13.66	14.90	13.99	.....	.....
0.6	15.87	15.71	16.40	16.15	16.92	16.32	17.45	16.54	17.91	16.82	.....	.....
0.7	18.61	18.50	19.23	18.93	19.84	19.20	20.46	19.40	21.07	19.57	.....	.....
0.8	21.59	21.38	22.30	21.80	23.02	22.12	23.73	22.33	24.44	22.57	25.16	23.06
0.9	24.41	24.23	25.22	24.74	26.02	25.12	26.83	25.27	27.64	25.56	28.44	25.92
1.0	27.66	27.22	28.57	27.70	29.48	28.21	30.40	28.37	31.31	28.62	32.23	28.82

The osmotic pressures given for cane sugar in Table 9 have been calculated from the depressions of the freezing-points of the solutions (Table 8), and they are there compared with the pressures which were obtained by direct measurement. As seen in Table 9, the agreement is satisfactory at all temperatures not exceeding 25°; but the two sets of values are thoroughly and increasingly discordant at all higher temperatures. It appears, therefore, that the osmotic pressure of cane-sugar solutions *can* be calculated up to 25° from the depressions of the freezing-

points, *but not at higher temperatures.* In other words, they can be calculated correctly up to the temperature above which the *previously constant* ratios of osmotic to gas pressure were found to begin to decline in value, *and no further.* So far as known at the present time, all the osmotic pressures of cane-sugar solutions *at and above the temperatures at which the various ratios of osmotic to gas pressure become unity,* can be correctly calculated from a *normal molecular depression* of the freezing-points, i. e., from a supposed molecular depression of about 1.85°. The temperature area within which the depressions of the freezing-points can be employed for the determination of osmotic pressure is much smaller in the case of glucose than in that of cane sugar. The boiling-point method of determining osmotic pressure is also hampered by restrictions. It is limited in its applicability to a wholly unknown temperature area—"*unknown*" because no one can predict at what lower temperature hydration, or some equivalent phenomenon, will manifest itself. If the freezing and boiling points of a solution were both *normal,* it would probably be practicable to calculate from either of them the osmotic pressure at any intermediate temperature. But if one of them is *abnormal*—and one or the other is usually abnormal in the case of aqueous solutions—this can not be done.

But the vapor-tension method of determining osmotic pressure—unlike the freezing and boiling point methods—is not of restricted applicability. It can be employed at all temperatures between the freezing and boiling points of solutions. All that has been said in praise of the comprehensive character of the vapor-tension method is true enough—theoretically; but if anyone who is enthusiastic for it will once attempt to apply it, he will soon discover for himself some of the reasons why it has not come into general use for the measurement of osmotic pressure. The most needed agent for the investigation of solutions at the present time is a really practicable precision-method for the measurement of vapor pressure at all temperatures.

In the foregoing pages, the author has frequently spoken of "*hydration*" as something which may account for apparently abnormal conduct on the part of solutions. He has employed this explanation of *excessive-constant* and *excessive-declining* ratios of osmotic to gas pressure because it is the simplest and most satisfactory one at hand, and not because he is fully convinced of its entire correctness.

CHAPTER VI.

CANE SUGAR.

PRELIMINARY DETERMINATIONS OF OSMOTIC PRESSURE.

The numerous determinations of the osmotic pressure of cane sugar which are to be presented in this report will be classified as *preliminary* or *final*, according as they were made before or after the method of measuring the force had been developed to a point where, in the author's judgment, full credence was to be given to the results.

The final arrangements for the measurement of osmotic pressure which have been described in the earlier chapters, and the methods of manipulation which will be discussed to some extent hereafter, were, as a rule, the products of a slow growth. In a general way, the whole history of the investigation may be divided into three periods, as follows: First, a period of four years, in which the attention of the writer and his co-workers was given almost exclusively to the task of perfecting the porous wall of the cell; second, a period of nearly equal duration, in which they were measuring osmotic pressure with a view to discovering and eliminating the sources of error in the method; third, the period within which—owing to the absence of any large sources of error—the results are regarded as reliable in a high degree.

During the second or evolutionary period, eight series of quantitative measurements of the osmotic pressure of cane sugar were made, and three series of measurements on solutions of glucose. The present chapter gives an account of the work upon cane sugar.

The value of the results increases quite continuously from the first to the last series in the proportion in which it was found practicable to diminish or suppress sources of error. Two sources of error—*thermometer effects*, and *dilution* of the cell contents during or after a measurement of pressure—were found to exceed all others in importance and to vitiate the results more than all other defects of the method. They were also the most difficult to deal with. In fact, the whole four years may be said to have been devoted to their elimination.

The "thermometer effects" have been sufficiently discussed in a former chapter. They were due, of course, to the imperfections of the earlier arrangements for the maintenance of temperature.

The dilution of the cell contents (which, at first sight, would naturally be ascribed to leakage of the membranes) was found to be due to two causes: First, to an acquisition of solvent during the closing and the opening of the cells; and second, to an enlargement of cell capacity under pressure. Accordingly, during the whole of the period within

which the so-called *preliminary measurements* fall, the chief concern of the writer and of his collaborators was to perfect the means of maintaining constant temperature, to lessen the time required for the opening and closing of the cells, and to develop a cell whose capacity could not increase under pressure. Minor sources of error, of which there are many, were not neglected, but the attention given them was strictly proportional to the relative magnitude of their effects upon the precision of the results. After *thermometer effects* and *dilution*, more attention was given to the improvement of the manometers than to any other feature of the method.

The second period begins with Series I, in which the fluctuations in bath temperature amounted, in some instances, to whole degrees, and in which the dilution of the cell contents, though unknown, must have been very large; and it closes with Series VIII, which was carried through without any material variation in bath temperature and without any dilution of the cell contents which could be detected by the polariscope.

The part played by the first eight series in the *evolution of the method* gives them great importance in the history of the investigation, but the actual results of the measurements are to be considered and appraised merely as *tests of progress* in the development of the method. They will be treated as such throughout by the writer, and not discussed, to any considerable extent, with reference to the light which they throw upon the true osmotic pressure of cane-sugar solutions.

Series I.*

The cell employed in this series was that seen in Figure 7, page 19. The closing and the opening of such a cell are difficult and strenuous performances, which require the cooperation of two experienced persons. Both operations will be briefly described because of the bearing they have upon the dilution of the cell contents which it was so difficult to suppress.

In closing, one of the operators (No. 1) holds in one hand the filled cell, which is covered with a piece of very thin rubber tubing to prevent any soiling of the outside of the cell by the overflow of the solution or by the hand. With the other hand he holds and manipulates the manometer, the nut (*h*, Figure 7) resting upon the back of the hand which grips the manometer by the rubber stopper (*k*). The duty of operator No. 2 is to manipulate the "*fang*" (Figure 8), by means of which the rubber is worked into the cell and an equal amount of the solution is let out of it; and afterwards to wrap and tie with twisted and waxed shoemakers' thread the exposed part of the stopper when it has been forced to a sufficient depth into the glass tube (*B*).

*Measurements by H. N. Morse and J. C. W. Frazer. Am. Chem, Jour., xxxiv, 1.

No. 1 places the stopper in position for entrance over the mouth of the glass tube and pushes forward with all his strength. Since the tube at the mouth is considerably constricted, the stopper does not enter. No. 2 now introduces the *fang* and works the rubber little by little through the narrow opening until enough of it has been buried in the glass tube. In the meantime, No. 1 turns and twists the stopper in any direction which seems likely to promote the progress of No. 2.

From the time when the rubber stopper first enters the glass tube until the nut (*h*) is brought down upon it and secured by the brass collar (*g*), there must be no relaxation of the pressure exerted by No. 1. Otherwise air will enter the cell through the groove on the under side of the fang; or if, as in the earlier work, no safety reservoir has been provided for the gas in the manometer, some of it may escape from the calibrated portion of the instrument. When, therefore, the stopper has been introduced and the fang withdrawn, and it is necessary for No. 1 to remove his fingers from the sides to the top of the stopper in order to make room for the winding operations of No. 2, the stopper is seized and held by the latter until the former has his fingers firmly fixed in their new position. Similar aid is required from No. 2 when, with the winding of the exposed part of the stopper completed, it is necessary for No. 1 to remove his fingers from the top of the stopper to the top of the nut (*h*). After this change of position has been effected, any desired initial pressure is brought upon the contents of the cell by turning up the brass collar (*g*) on the nut (*h*).

When a cell is to be opened, No. 1 holds the apparatus as in closing and attempts to withdraw the stopper by pulling, while No. 2 admits air to the contents of the cell by inserting the *fang* between the rubber and the glass tube. But the simple admission of air by No. 2 and the simultaneous efforts of No. 1 do not suffice for the removal of the stopper. It is necessary for No. 2 to work the rubber, little by little, out of the glass tube with the fang, while No. 1 maintains a steady pull upon the stopper.

It will be seen that both the closing and the opening of the cells required considerable time. In the beginning, each operation consumed about 15 minutes.

The first arrangements for the maintenance of temperature were crude and wholly inadequate. The bath employed in the measurements of Series I is shown in Figure 46. It consisted of a double-walled box with two front doors (*a* and *c*). The former (*a*) had a narrow plate-glass window (*b*), through which the height of the mercury in the manometers and thermometers could be read without opening the inner door. The outer door (*c*) had in its central part a smaller door (*d*), which was of the same size as the window (*b*). The spaces between the outer and inner walls of the box were filled with hair. Between the doors (*a* and *c*) a hair pad was placed, which exactly

filled the space except over the window (*b*). The window was covered by a separate pad, which could be introduced or withdrawn through the small outer door (*d*). The top of the box was removable.

The cell—with a long thermometer whose bulb was immersed in the water surrounding the cell—was placed in the box and packed with hair, except where it was necessary to leave vacant spaces for the purpose of reading the instruments. The exterior of the box was protected, during an experiment, by coverings of thick hair-felt, by woolen cloths, and even by sheepskins. Care was also taken to mod-

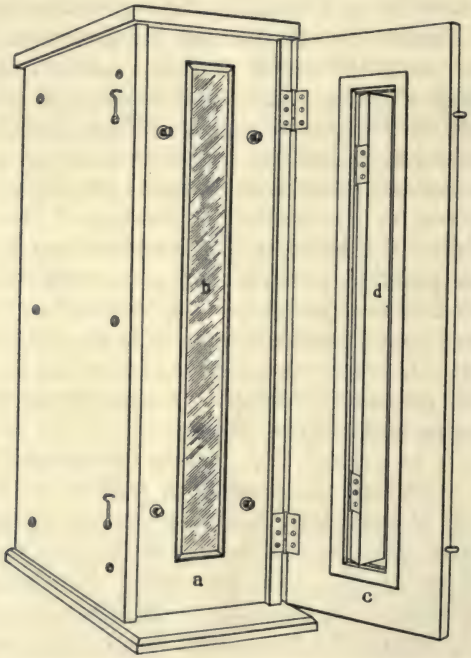


FIG. 46.—First bath employed for measurement of osmotic pressure. Double-walled, and filled between with hair.

(*a*) Inner door; (*b*) glass window; (*c*) outer door; (*d*) door of size of (*b*).

erate somewhat the extremes of temperature in the room in which the bath was located. No attempt was made to maintain some precise temperature, e. g., 20°. The cell was filled and placed in the bath, and was protected in the manner described, at the temperature of the room. In a general way, the origin and the *modus operandi* of *thermometer effects* were understood, but it was foreseen that their existence depends on the *rate* at which the solvent can pass in either direction through the membrane to compensate the changes in the volume of the inclosed solution which are due to fluctuations of temperature. It was believed, moreover, that, in solutions protected as

were ours, the changes in temperature would be so moderate and gradual that *thermometer effects* were not to be apprehended; in other words, that the solutions would at all times exhibit their true osmotic pressure, whatever their temperatures might be. It was soon discovered, however, that the speed with which the membrane is accustomed to compensate changes in volume through dilution or concentration of the solution had been greatly overestimated. There is no doubt, therefore, that the *thermometer effects* in Series I were very large.

The material employed in Series I to VIII, inclusive, was the purest obtainable "rock candy." It was not recrystallized, but was analyzed and examined by the polariscope, and was judged to be sufficiently pure for preliminary experiments.

TABLE 10.—*Cane sugar, Series I.*

Concentration.	Temperature.	Observed osmotic pressure.	Mean osmotic pressure.	Gas pressure.	Calculated molecular weight.
	degrees.				
0.05	20.36 to 21.24	1.28	1.27	1.21	327.50
"	20.20 20.90	1.25			
0.10	15.62 20.10	2.37	2.41	2.41	337.30
"	18.50 19.86	2.44			
0.20	19.64 21.75	4.77	4.80	4.84	344.85
"	20.80 21.22	4.83			
0.25	22.40 24.20	6.13	6.06	6.08	343.90
"	20.90 21.90	5.98			
0.30	18.50 19.94	7.23	7.23	7.20	341.10
"	16.82 18.42	7.23			
0.40	18.70 19.10	9.51	9.62	9.65	343.45
"	20.80 21.20	9.72			
0.50	20.78 20.94	12.02	12.10	12.10	342.50
"	20.02 20.90	12.17			
0.60	21.10 21.80	14.34	14.46	14.63	347.60
"	23.70 24.80	14.57			
0.70	19.70 20.60	16.79	16.91	17.03	344.90
"	23.20 25.10	17.02			
0.80	17.50 18.42	19.39	19.47	19.20	338.75
"	19.20 20.20	19.54			
0.891	17.50 20.20	21.19	21.19	21.46	346.50
0.90	19.10 20.20	21.89	21.89	21.71	340.10
1.00	22.20 24.00	24.80			
"	21.90 23.00	24.39	24.56	24.35	339.84
"	20.80 21.90	24.50			
				Mean....	341.41

All the solutions except one were made up on the "*weight-normal*" basis—that is, by dissolving a gram-molecular weight of the sugar, or some decimal part of the same, in 1,000 grams of water.

Table 10 gives, for Series I, the weight-normal concentrations of the solutions; the extreme temperature of the bath during each experiment; the observed osmotic pressure; the mean osmotic pressure for each concentration; the mean calculated gas pressures of the solute if its volume is reduced to that of the *solvent*; and, finally, the molecular weights which are calculated from the mean osmotic pressures by the

formula $M = W\frac{22.488+0.0824t}{P}$, in which oxygen is assigned an atomic weight of 16.

The use of O = 16 as a standard for the calculation of molecular weights was continued only through the first series of measurements. In this series, cane sugar is considered to have a molecular weight of 342.22. In all later work, $H = 1$ was employed as the standard, and the molecular weight of sugar is 339.60. Accordingly, the formula given above becomes, in subsequent computations, $M = W\frac{22.265+0.0817t}{P}$, in which M is the molecular weight; P the observed osmotic pressure; W the weight of the substance which is dissolved in 1,000 grams of water; 22.265 the theoretical pressure (at 0°) of a gram-molecular weight of a gas when its volume is 1 liter; and 0.0817 is the temperature coefficient, either of a gas or of osmotic pressure. The values are based on the weight of a liter of hydrogen as given by Morley, and corrected to the latitude and altitude of the place of work.

TABLE 11.—*Cane sugar, Series I. Variations in the temperature of the bath.*

Concentration.	Variation.	Concentration.	Variation.	Concentration.	Variation.
	degrees.		*degrees.*		*degrees.*
0.05	0.88	0.30	1.44	0.70	0.90
"	0.70	"	1.60	"	1.90
0.10	4.48	0.40	0.40	0.80	0.92
"	1.36	"	0.40	"	1.00
0.20	2.11	0.50	0.16	0.891	2.70
"	0.42	"	0.88	0.90	1.10
0.25	1.80	0.60	0.70	1.00	1.80
"	1.00	"	1.10	"	1.10
				"	1.10

The difference between the highest and lowest temperature of the bath is given for each experiment in Table 11. At the present time, when a variation of 0.05° in bath temperature is regarded as vitiating a reading of pressure, these differences appear appallingly large.

Judging by the non-appearance of solute in the water surrounding the cells, and the ability of the cells to sustain considerable pressure, it was concluded that the membrane had not leaked. Other possible sources of dilution—of which much will be said hereafter—did not at that time impress us as likely to affect materially the pressures developed in the cells. It was suspected, however, in the beginning that the sugar might be subject to some *inversion*, for which it would be necessary to correct the observed pressures. All the solutions, when taken from the cells, were therefore examined for invert sugar by the then most approved form of Fehling's method. Evidence of its presence was found in all the solutions, but it was only in the more

concentrated of them that the amount sufficed for even an approximate quantitative estimation. The osmotic-pressure correction equivalents of the quantities found are given in Table 12.

TABLE 12.—*Cane sugar, Series I. Correction for inversion found by Fehling's method.*

Concentration.	Correction.	Concentration.	Correction.	Concentration.	Correction.
	atmos.		*atmos.*		*atmos.*
0.05	0.00	0.30	0.00	0.70	0.02
"	0.00	"	0.00	"	0.02
0.10	0.00	0.40	0.00	0.80	0.04
"	0.00	"	0.00	"	0.04
0.20	0.00	0.50	0.00	0.891	0.04
"	0.00	"	0.02	0.90	0.05
0.25	0.00	0.60	0.02	1.00	0.05
"	0.00	"	0.05	"	0.04
				"	0.04

The quantities given in the table are not the *full* osmotic equivalents of the invert sugar. They are equal to *one-half* the pressure which is exerted by the products of inversion, since that is the proportion which is to be deducted from the observed pressures in correcting sucrose for the presence of hexoses.

A very noteworthy feature of Series I was the close agreement between the known molecular weight of cane sugar and that calculated from the observed pressures, on the presumption that the osmotic pressure of solutions obeys the laws of Gay-Lussac and Boyle. It will be seen, in Table 10, that the mean molecular weight derived from 25 determinations, on 13 different concentrations of solution, was 341.41; while the theoretical value (if oxygen = 16) is 342.22. The coincidence is better expressed in the form of the ratio of osmotic to theoretical gas pressure, as in Table 13. The disagreement appears

TABLE 13.—*Cane sugar, Series I. Ratio of osmotic to calculated gas pressure.*

Concentration.	Osmotic pressure.	Gas pressure.	Ratio.	Concentration.	Osmotic pressure.	Gas pressure.	Ratio.
0.05	1.27	1.21	1.050	0.60	14.46	14.63	0.989
0.10	2.41	2.41	1.000	0.70	16.91	17.03	0.993
0.20	4.80	4.84	0.992	0.80	19.47	19.20	1.001
0.25	6.06	6.08	0.997	0.891	21.19	21.46	0.987
0.30	7.23	7.20	1.004	0.90	21.89	21.71	1.008
0.40	9.62	9.65	0.997	1.00	24.56	24.35	1.009
0.50	12.10	12.10	1.000				
						Mean....	1.002

to be large in the case of the most dilute solution, but of this it is to be said that an experimental error of 0.1 atmosphere in the measurement of the osmotic pressure of the 0.05 weight-normal solution leads to an error of 30.4 units in the estimated molecular weight, or of 0.09 in

the ratio of osmotic to gas pressure. In all other concentrations the ratio approaches unity.

The striking agreement between the observed osmotic and theoretical gas pressure, which is seen in Tables 10 and 13, gave the author, for a time, much more confidence in the trustworthiness of these first results than they were afterwards found to deserve. The evidence furnished by them appeared to confirm the conclusions of van't Hoff regarding the measurements of Pfeffer. The solutions employed were, in general, much more concentrated than those of Pfeffer, and more concentrated also than those to which van't Hoff restricted his deductions regarding osmotic pressure; but it was believed that, by the adoption of the "*weight-normal*" system, the term *b* in the van der Waals equation had been practically eliminated for osmotic pressure. There was, therefore, no apparent inconsistency in the seeming conformity of *concentrated* as well as dilute solutions to the formula of van't Hoff. The correctness of this view of the function of the *weight-normal* system will be maintained later by means of data whose validity can not be questioned. The real ground for suspecting the trustworthiness of the results of Series I was revealed by the polariscope in connection with the work of Series II.

Series II.*

The measurements of Series II were made under more favorable conditions than those of Series I. Some of the improvements which were introduced will be enumerated:

1. In the earlier work there had been much uncertainty as to the exact capacity of the upper end of the manometer, where the form of the tube had been altered in closing the instrument in the flame. The original calibration could not hold for this part of the manometer, and there was no obvious method of ascertaining its capacity directly. It had been customary, therefore, to measure the height of the affected part and to assign to it a spherical, or a conical, or a conico-spherical form, according to its appearance. The diameter of the bore at the base was known from the calibration. This method would have sufficed if the form had been strictly spherical or purely conical; but, as a rule, it was neither the one nor the other, but a mixture of the two, and it was necessary, in estimating capacity, to *guess* in what proportion each form was represented. It could be easily proved, by examples of the effects of minute errors in manometric work, that the problem was one of great importance. It was solved satisfactorily by filling the upper end of the manometer with mercury in the manner described in a previous chapter.

*Measurements by H. N. Morse, J. C. W. Frazer, E. J. Hoffman, and W. L. Kennon. Am. Chem. Jour., xxxvi, 39.

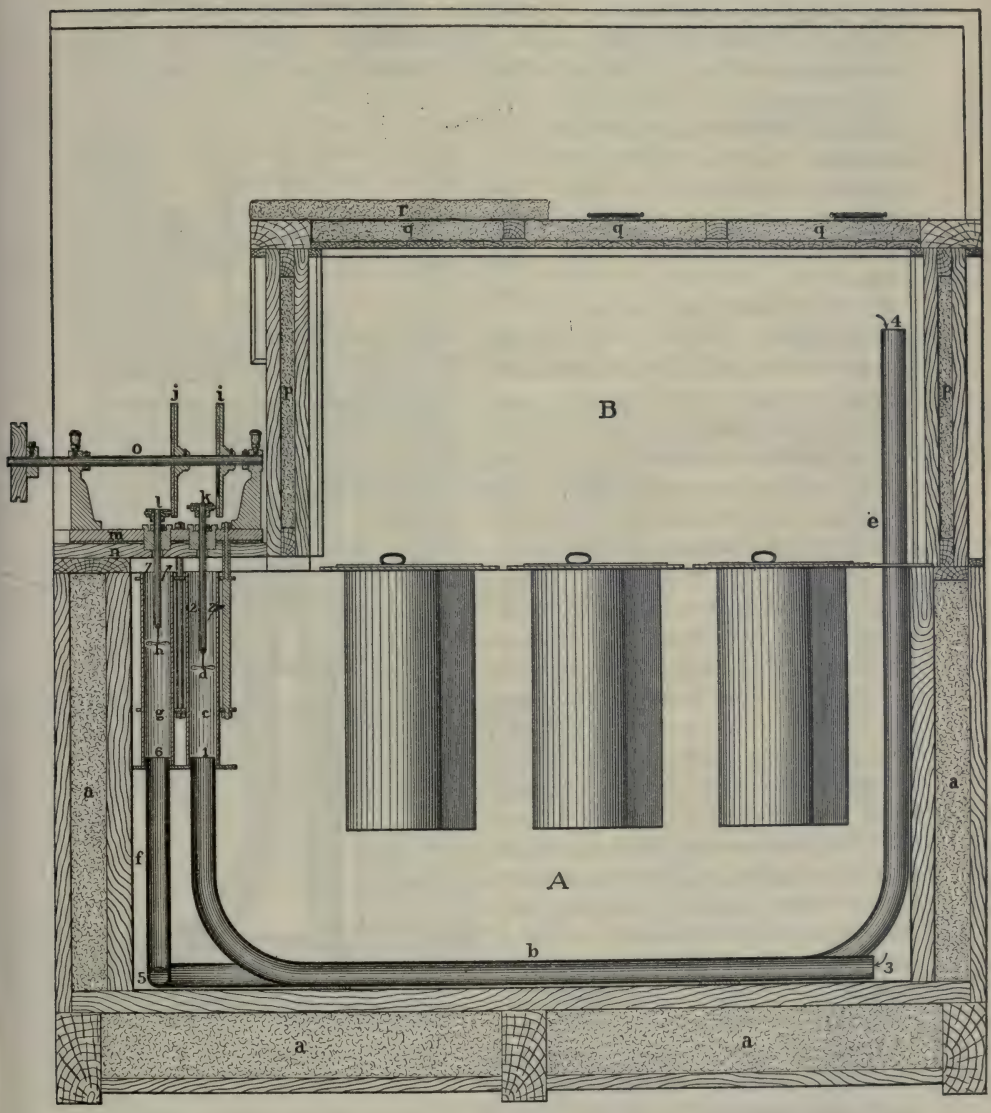


FIG. 47.—First bath in which water and air were circulated.

(*A*) Water compartment; (*B*) air compartment; (*a*), (*p*), (*q*), and (*r*) hair packing; (*b*) tube through which the water in (*A*) was pumped; (*f*) tube through which air in (*B*) was pumped; (*d*) and (*h*) propellers; (*l*) and (*k*) friction pulleys; (*i*) and (*j*) friction disks; (2) and (2) holes for escape of water into bath.

Another improvement in manometers which was made before beginning Series II was the introduction of the "safety bulb," which is blown in the tube just below the calibrated portion, and which prevents an escape of the gas when it is under diminished pressure.

The methods of calibration were also improved, and more attention—although by no means so much as at a later period — was given to the irregularities of capillary depression.

2. The greatest improvement in apparatus, however, was in the devices for maintaining temperature, though gas and electric stoves, regulated by thermostats, were not introduced for the control of bath and room temperatures until later. The first bath so furnished was the crude forerunner of that seen in Figures 35, 36, and 37, pages 69 and 70. It was a large rectangular affair (Figure 47) consisting of two superimposed compartments. The lower one contained water, which was kept in circulation by means of a pump (Figure 48). The air in the upper, or manometer, compartment was drawn continuously through pipes (Figures 48 and 49) lying in the water below by means of a second pump. The temperature of the water in which the cells were suspended was regulated, as best it could be at that time, by means of immersed electric stoves, which were controlled by a thermostat; while that of the air in the manometer space was kept approximately the same by passing it uninterruptedly through the pipes in the water. The walls were all double and were packed with hair.

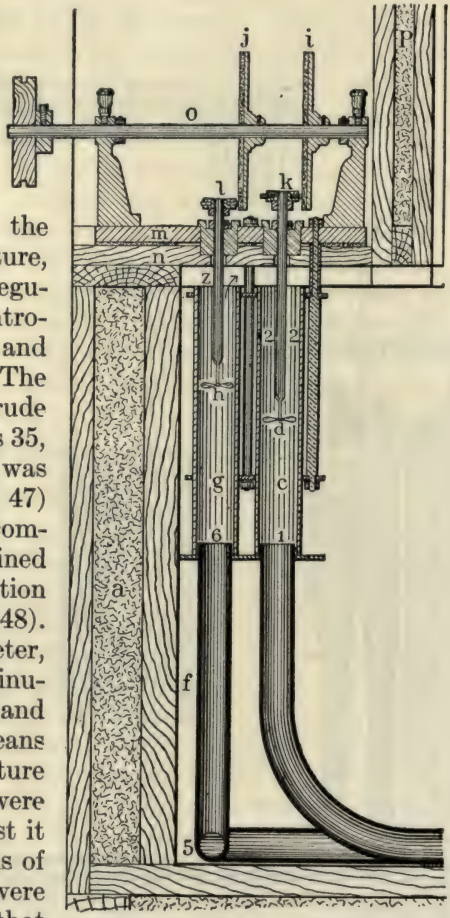


FIG. 48.—Pumping arrangements on larger scale than in Figure 47.

It will be shown later that a system of bath regulation such as that described is exceedingly imperfect. Nevertheless, it was a great improvement on that employed in Series I.

3. The improvement in the cathetometer (Figure 25, page 44) which enabled us to dispense with the micrometer eye-piece of the telescope,

and which remedied the "*lurching*" effects of the older method of adjustment, was introduced.

4. The addition to our equipment which gave the most satisfaction, and which proved to be the most indispensable of all our instruments—if comparisons are legitimate in a work whose success depends on the perfection of every one of a multitude of conditions—was a Schimdt and Hänsch saccharimeter of the best construction.

It is to be remembered in this connection that, in Series I, we had no means of ascertaining what had occurred in the solutions while in the cells except the test of Fehling and the examination of the solvent in which the porous part of the cells was immersed; also that, having found no solute in the latter, and but little invert sugar by the former, we were obliged to conclude, from the evidence available, that the solutions had maintained their concentration without much altera-

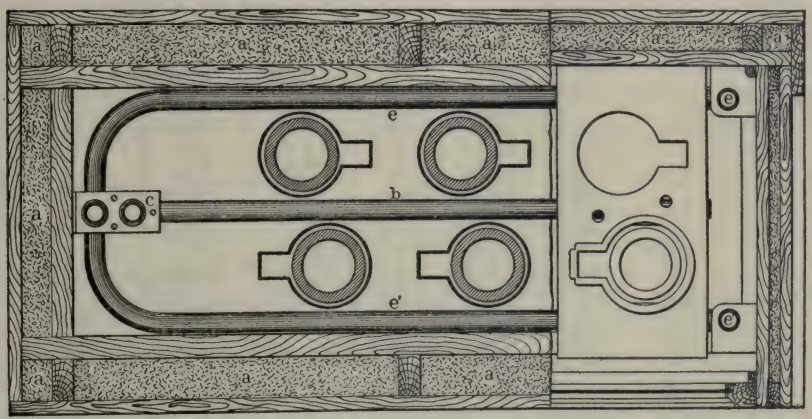


FIG. 49.—Interior view of water compartment with covers partly removed.

(*e*) and (*e'*) air tubes; (*b*) tube for circulating water. No devices for heating or cooling the water.

tion of the solute. If this conclusion were correct, and it was believed to be so in the main, the results of the measurements of Series I were trustworthy and furnished strong experimental evidence in support of the deductions of van't Hoff.

It had been suspected, however, that the inversion occurring in the cells was somewhat larger than it had been found to be by the method of Fehling, and the object sought by the introduction of the polariscope into the investigation was to measure this supposed greater inversion by the more accurate optical method. The quantity of invert sugar was to be measured by the *loss in rotation*, and one-half the pressure-equivalent of the invert sugar so found was to be deducted from the observed pressure, in order to arrive at the correct *osmotic pressure* of the original solution of cane sugar.

The loss in rotation was ascertained to be *very much larger* than had been anticipated. For the time being, however, it was all ascribed to *inversion*, notwithstanding certain suspicions which will be discussed a little later. Accordingly, in a paper which was published soon after the completion of Series II, corrections for inversion were applied to the observed pressures, which were proportional and equivalent to the losses in rotation.

The uncorrected pressures of this series are given in Table 14:

TABLE 14.—*Cane Sugar, Series II. Extreme temperatures of the bath; loss in rotation; observed osmotic pressures; calculated gas pressures.*

Concentration.	Temperature.	Loss in rotation.	Observed osmotic pressure.	Gas pressure.	Ratios.
	degrees.	*degrees.*			
0.1	24.00 to 24.10	0.50	2.58	2.41	1.077
"	24.15 24.25	0.50	2.62	2.42	
0.2	20.00 20.95	0.70	4.75	4.79	1.003
"	20.90 21.35	0.70	4.82	4.80	
"	21.50 21.85	0.50	4.88	4.81	
0.3	19.65 20.10	0.60	7.28	7.16	1.015
"	21.55 21.70	0.50	7.31	7.21	
0.4	21.45 21.75	0.80	9.76	9.61	1.012
"	22.10 22.20	1.30	9.71	9.63	
0.5	22.50 22.70	1.40	12.28	12.06	1.022
"	23.70 23.70	1.20	12.41	12.10	
0.6	24.30 24.40	2.80	14.82	14.55	1.028
"	24.15 24.30	1.90	15.00	14.55	
"	24.10 24.10	1.80	15.06	14.54	
0.7	23.35 24.00	2.60	17.38	16.94	1.025
"	23.74 24.30	2.20	17.32	16.93	
0.8	23.57 23.60	3.20	19.83	19.35	1.023
"	23.65 23.70	3.90	19.77	19.36	
0.9	24.65 24.90	2.50	22.25	21.86	1.020
"	24.65 24.90	2.40	22.32	21.86	
1.0	23.55 23.60	2.40	24.83	24.19	1.024
"	24.50 24.60	4.00	24.78	24.28	
		Total = 38.40 = 9.37 atmospheres.			Mean = 1.025

No attempt was made in Series II to keep the bath at a particular temperature throughout. It was endeavored simply to maintain it through each experiment at whatever temperature the solution was found to have when the cell was filled and closed—both solution and cell having stood for some time previously in the bath.

That the fluctuations in Series II were much smaller than in Series I will be seen in Table 15.

The most surprising, and at the same time the most perplexing, feature of the results was the large *loss in rotation.* It amounted, as will be seen by Table 14, to a total of 38.4°, which was equivalent to about 9.37 atmospheres of osmotic pressure. Expressed in another way, the total loss in rotation amounted to 2.86 per cent of the sum of all the original rotations of the solutions whose pressure had been

determined. We were strongly inclined to ascribe it in the main, if not altogether, to *inversion*. But why should so much *inversion* occur in Series II when so little of it had been detected in Series I by the method of Fehling? Admitting the greater accuracy of the optical method, it was not possible that so much invert sugar should have escaped detection in Series I, especially since the fault of Fehling's method is its liability to overestimate rather than underestimate the products of inversion.

TABLE 15.—*Cane sugar, Series I and II. Extreme variations in bath temperature.*

Concentration.	Series I.	Series II.	Concentration.	Series I.	Series II.
	degrees.	*degree.*		*degrees.*	*degree.*
0.1	4.48	0.10	0.6	0.70	0.10
"	1.36	0.10	"	1.10	0.15
0.2	2.11	0.95	"	....	0.00
"	0.42	0.45	0.7	0.90	0.65
"	....	0.35	"	1.90	0.56
0.3	1.44	0.45	0.8	0.92	0.03
"	1.60	0.15	"	1.00	0.05
0.4	0.40	0.30	0.9	2.70	0.25
"	0.40	0.10	"	1.10	0.25
0.5	0.16	0.20	1.0	1.80	0.05
"	0.88	0.00	"	1.10	0.10
			"	1.10	....
			Means =	1.31	0.24

The explanation which sufficed for a time was plausible. It was at the beginning of the work in Series II that the penicillium pest made its appearance, and it was reasonable, as we then thought, to ascribe the apparently greater inversion in Series II to an *infection of the membranes* by penicillium. The mistake in practice which was made was, of course, in wholly discontinuing for a time the use of Fehling's test as soon as the polariscope became available. An examination of the solutions of Series II by both methods would have shown at once the inconsistency of our interpretation of the loss in rotation. It was probably true, however, that the penicillium did cause some inversion in the solutions of Series II, though by no means enough to account for the whole, or any larger part, of the loss in rotation; for it was found in later series—where the Fehling test was again applied, and after the solutions and cells had been habitually treated with all the care necessary for the suppression of penicillium—that the evidences of inversion had nearly disappeared.

A circumstance which at the time tended to strengthen the impression that the loss in rotation was due to inversion was the *molecular weight* which was derived from the osmotic pressures after correcting them for inversion proportional to the observed losses. The mean molecular weight thus obtained was 337.59 (H = 1) instead of 339.60, the theoretical value. The mean molecular weight derived from Series I was 341.41 (O = 16) instead of 342.22.

The seeming adequacy of the interpretation of the loss in rotation which is given above, and the attractive concordance which the results of Series I and II acquired through its application were afterwards proved to be wholly illusive.

It was realized from the beginning that the diminished rotation could also be produced by *dilution*. Indeed, this would have been the most obvious interpretation of the phenomenon if the membranes had failed to retain perfectly the solute. But, in the absence of leakage, it was difficult to explain, as due to dilution, a loss in rotation which amounted to an average of 2.86 per cent, or to an average surreptitious introduction into the cells of nearly 0.5 cubic centimeter of the solvent.

There were, nevertheless, three sources of dilution which were apparent enough, but it was not believed that these could account for more than a small fraction of the loss. However much their aggregate effect may have been underestimated in the beginning, they were not at any time ignored or neglected. It was recognized that, in order to settle definitely the question of loss in rotation, all sources of dilution must be suppressed by improvement in the method and in the manipulation.

In discussing the three obvious sources of dilution which have been referred to, it will be necessary to introduce observations and facts which belong to later periods in the history of the investigation. If this is not done, it will be difficult to place the results of Series II in the light in which the author now sees them.

1. It has already been intimated that the closing of the cell was a difficult performance which required considerable time—in the beginning, about 15 minutes. During the whole operation, the cell contents were under a pressure which was less than the true osmotic pressure of the solution. Throughout the whole of the closing period, therefore, the solutions were undergoing a dilution by solvent taken in through the membranes. If the impression is correct that the rate at which the solvent is taken in, under such conditions, is proportional to the difference between the existing and the true osmotic pressure of the solution, the amount of dilution accomplished during the closing period must have varied considerably from cell to cell. Operator "No. 1" endeavored to maintain the highest possible "*existing pressure*" throughout the operation, but was never able to equal the osmotic pressure. Moreover, the pressure was constantly fluctuating in consequence of the manipulations of "No. 2" with the "*fang*."

It was evident that, in order to suppress this initial dilution of the cell contents, "No. 1" and "No. 2" must coöperate in such a way as to maintain the highest possible pressure upon the solution throughout the closing period; also, and above all, that the time required for closing must be greatly shortened. The first improvement in the latter direction was accomplished by tightly wrapping and tying the lower end of the rubber stopper—just above the enlargement on the manometer—

with twisted shoemakers' thread. The lower end of the stopper, whose introduction through the constricted mouth of the glass tube had previously been so slow and difficult, was thus made much smaller. The effect of the improvement was to reduce, by more than one-half, the time required for closing the cells. It was still further reduced by gradual improvement in the coöperative manipulation of "No. 1" and "No. 2" until finally a cell could be closed in less than one-fifth of the time which was required in the beginning. The effect of rapid and judicious manipulation in diminishing the total loss in rotation was so marked that "*quick closing*" soon became, and continued to be, one of the principal items in all schemes for the improvement of the method.

Another method of diminishing initial dilution, which was resorted to in the latter half of the work, consisted in dipping the cells—after filling and before closing them—in a solution of sugar. The concentration of the solutions so employed was at first equal to that of the solutions in the cells. Afterward they were made more concentrated. The purpose of the dipping process was, of course, to force the solvent which filled the porous wall outside the membrane to distribute itself between the solution within the cell and that upon the exterior surface. The solution upon the outside of the cell was afterward removed as completely as possible by rinsing, and by soaking the cell, before locating it finally in the bath, in fresh water which was repeatedly renewed. The diminution in the total loss in rotation which followed the introduction of the custom of "dipping" was also considerable.

The combined effect of shortening the time required for closing the cells, and of the process of dipping them, upon the total loss in rotation sufficed to prove that considerable dilution *must* have occurred at this period in the case of the earlier series.

2. The practice of wrapping and tying with twisted and waxed shoemakers' thread all that portion of the rubber stopper which remained outside the glass tube was followed from the beginning. The object was to confine the exposed part of the stopper within a rigid shell, so that none of the rubber within the glass tube could be forced out of it under pressure. This seemingly simple operation proved to be exceedingly difficult. In fact, it was performed with perfect success only in the last four of the eight preliminary series of measurements. The upper part of the stopper suffered, despite the careful winding, considerable distortion through a forcing out of some of the rubber between the successive turns of the thread. All such displacements of material represented, of course, an equivalent enlargement of the capacity of the cells and a corresponding dilution of the solutions. A phenonenon which always attended a distortion of the stopper was an upward displacement of the manometer while the cell was in the bath. Such displacements were recorded in the second and succeeding series and were regarded as a test of some value of the progress which had been made in

the effort to secure a cell of fixed capacity. The upward displacements of the manometer in Series II are given, as an illustration, in Table 16.

TABLE 16.—*Cane sugar, Series II. Upward displacements of the manometers (mm.).*

Concentration.	Displacement.	Concentration.	Displacement.	Concentration.	Displacement.
0.1	0.07	0.4	0.30	0.7	0.24
"	0.54	"	1.18	"	0.07
0.2	2.78	0.5	0.16	0.8	0.32
"	1.44	"	0.32	"	1.80
"	0.19	0.6	3.78	0.9	1.21
0.3	0.12	"	0.83	1.0	0.88
"	0.10	"	0.64	"	2.97

In Series I there was much actual *slipping* of the manometer in the rubber stopper, in consequence of which the enlarged part of the manometer—the bulb blown near the end—was frequently forced out of sight into the stopper. It usually stopped, in such cases, just below the constricted mouth of the glass tube. The principal purpose of the constricted mouth of the tube and of the enlargement on the end of the manometer was, originally, to prevent the instrument from being pushed out of the cell. The slipping of the manometer in the stopper was remedied by wrapping and tying the lower end of the latter in the manner already described.

The upward displacement of the manometer disappeared after the fourth series. There was therefore some dilution in the first four series, which was due to an enlargement of the capacity of the cells.

3. The opening of the cell, after a measurement, like the closing of it, was originally a process which required about 15 minutes. During this time, the contents of the cell were again under a pressure which was less than the osmotic pressure, and dilution of the solution necessarily ensued. For reasons which will be given hereafter, dilution occurring at this period was a much more serious matter than that which took place during the closing of the cells or through an increase in their capacity under pressure. It was necessary, therefore, to suppress it as expeditiously as possible. Several remedial measures were resorted to: (1) Every effort was made to increase the rapidity of the necessary manipulation; (2) the rubber stopper was pierced with a hollow needle before attempting to withdraw it; (3) "dipping" the cells before opening them was practiced; (4) a method was devised for slitting the stopper throughout its whole length, which made it possible eventually to remove the manometer in less than a minute, and without reducing the pressure upon the cell contents below that of the atmosphere.

The final result of all the measures taken to eliminate the three known sources of dilution was *the complete disappearance of loss in rota-*

tion. In other words, it was proved at last that the observed loss in rotation was due to *dilution* and not to *inversion.*

Having found that the uncertainty regarding the osmotic pressures of the solutions was due to *dilution,* and knowing the *extent* of the dilution, the question arises whether it is legitimate to correct the observed pressures of Series II for dilution as they were originally corrected for *inversion.* The author is of the opinion that, with certain reservations, this may be done, and that the results will thereby acquire a new standing in the history of the investigation which is more in accordance with their merits.

The absolute futility of attempting to correct observed pressures for dilution which is due to *leakage* of the membranes has been emphasized in another chapter. The reason given was that one has no means of ascertaining the magnitude of the *counter* pressure which is exerted by the escaped solute, even when one knows how much of it has passed through the membrane, since the lost material does not distribute itself quickly and uniformly throughout the whole body of solvent which is exterior to the membrane, but remains, for the greater part, in the pores of the cell, giving a solution next to the membrane whose concentration is unknown and can not be determined.

The dilution in the case under consideration was effected *without the loss of solute,* and solely through the acquisition of solvent at three different periods. Moreover, the concentration of the solutions was determined by the polariscope *after* the dilution had ceased. There can be no question as to the propriety of correcting for the dilution which occurred during the closing of the cells or for that which occurred while they were in the bath, since both were finished *before* the observations on the osmotic pressures of the solutions were taken. The dilution of the third or opening period is of a different order, in that it occurred *after* the measurements of pressure and *previous* to the determinations of concentration by the polariscope. It had not, therefore, affected the pressures in the cells, and it should be *deducted* from the total before correcting the observed pressures for dilution. There are, however, no means of ascertaining how much of the known total dilution occurred during the opening of the cells. It is probable, therefore, that pressures which are corrected for the total dilution will be slightly *over-corrected.* The excess can not be large, because the dilution occurring when the cells were opened was brought under control quite early in the investigation.

With this intimation that the results are somewhat, but probably not largely, overcorrected, the observed pressures of Series II, which are recorded in Table 14, are given in Table 17 as corrected for *dilution* instead of *inversion,* yet no higher degree of accuracy can be claimed for these corrected pressures; the uncertainty pertaining to the correction for dilution, the large thermometer effects which must have followed the considerable fluctuations in bath temperature, and the generally

undeveloped state of the method at the time, all conspire to diminish confidence in their precision. Nevertheless, they are doubtless much more nearly correct than were the values obtained by correcting the observed pressures for inversion. The ratios of osmotic to gas pressure are all considerably above unity and are somewhat irregular, which suggests—but does not prove—that osmotic pressure does not conform to the laws of Gay-Lussac and Boyle for gases. In a rough way, the corrected pressures in Table 17 approach those which were obtained later, after the method had been perfected; and they foreshadow much that was afterwards found to be true upon evidence which can not be questioned. One of the more obvious conclusions to be drawn from them—if they are credited with approximate accuracy—is that the excellent molecular weights derived from Series I, and also from Series II, by ascribing all loss in rotation to inversion, were entirely fallacious.

TABLE 17.—*Cane sugar, Series II. Observed osmotic pressures corrected for dilution and the ratios of osmotic to the calculated gas pressures of the solute.*

Concentration.	Observed osmotic pressure.	Corrected osmotic pressure.	Ratio.	Mean ratio.
0.1	2.58	2.69	1.114	1.119
"	2.62	2.73	1.124	
0.2	4.75	4.89	1.021	1.025
"	4.82	4.96	1.033	
"	4.88	4.98	1.021	
0.3	7.28	7.38	1.031	1.031
"	7.31	7.43	1.031	
0.4	9.76	9.92	1.032	1.034
"	9.71	9.98	1.036	
0.5	12.28	12.58	1.043	1.045
"	12.41	12.67	1.047	
0.6	14.82	15.44	1.061	1.061
"	15.00	15.42	1.060	
"	15.06	15.46	1.063	
0.7	17.38	17.96	1.060	1.056
"	17.32	17.81	1.052	
0.8	19.83	20.57	1.063	1.066
"	19.77	20.68	1.068	
0.9	22.25	22.83	1.044	1.041
"	22.32	22.67	1.037	
1.0	24.83	25.43	1.051	1.056
"	24.78	25.74	1.060	

SERIES III.*

It has already been stated that in Series I and II no effort was made to maintain specific temperatures throughout—that it was merely sought to keep as constant as possible, for the time being, whatever temperature the bath might have at the beginning of each experiment. This was a necessary course as long as the means of regulating temperature continued to be crude and to a high degree ineffective.

*Measurements by H. N. Morse, J. C. W. Frazer, and W. W. Holland. Am. Chem. Jour., XXXVII, 425.

In Series III, on the other hand, an attempt was made to maintain a specific temperature, namely, that of melting ice. It was not entirely successful, but the fluctuations were much smaller than in Series I and II. The bath which was employed was the large rectangular one previously described. To prepare it for use in Series III, all the machinery was removed except that concerned in the circulation of the water, and all the space in both compartments, except that actually required for the cells and manometers, was filled with crates for the storage of ice,

TABLE 18.—*Cane sugar, Series III. Temperatures of bath; loss in rotation; observed osmotic pressures; and calculated gas pressures of the solute.*

Concentration.	Temperature.	Loss in rotation.	Observed osmotic pressure.	Calculated gas pressure.	Ratio.
	degrees.	*degrees.*			
0.1	0.18 to 0.36	0.20	2.45	2.23	
"	0.14 0.26	0.10	2.45	"	
"	0.14 0.38	0.05	2.37	"	1.083
"	0.14 0.38	0.10	2.39	"	
0.2	0.16 0.26	0.15	4.78	4.46	
"	0.28 0.31	0.15	4.77	"	1.071
0.3	0.18 0.34	0.50	7.09	6.69	
"	0.14 0.18	0.60	7.11	6.68	1.061
0.4	0.16 0.22	0.55	9.37	8.91	
"	0.22 0.33	0.60	9.34	8.92	
"	0.26 0.34	0.40	9.36	"	1.048
"	0.12 0.16	0.40	9.31	8.91	
0.5	0.14 0.38	0.90	11.66	11.14	
"	0.20 0.26	1.00	11.73	"	
"	0.12 0.18	1.05	11.89	"	1.054
"	0.16 0.28	0.75	11.79	"	
0.6	0.16 0.28	1.20	14.12	13.37	
"	0.20 0.25	1.30	14.11	"	1.056
0.7	0.16 0.32	1.20	16.65	15.60	
"	0.14 0.16	1.10	16.71	"	1.069
0.8	0.16 0.26	1.55	19.16	17.82	
"	0.16 0.26	1.60	19.13	"	1.075
0.9	0.30 0.33	1.85	21.92	20.06	
"	0.15 0.25	1.95	21.86	20.05	1.091
1.0	0.16 0.30	2.90	24.53	22.28	
"	0.20 0.34	3.50	24.54	"	
"	0.26 0.26	2.00	24.27	22.29	1.092
		Sum = 27.65 = 6.75 atmospheres.			Mean=1.070

which, when full, contained about 150 kilograms. The water in which the ice in the lower half of the crates was immersed was kept in circulation in the usual manner, and its level was maintained by means of an automatic siphon. It was hoped to secure, by this arrangement, a temperature very close to 0°, but the table will show that the temperatures actually maintained were all higher than that.

The fluctuations in bath temperature were much smaller in Series III than in Series II. This, however, does not prove that any progress had

been made in the general improvement of the facilities for the maintenance of temperature; since it is easier, by means of circulating ice water, to maintain a temperature near 0° than to secure a fair degree of constancy by means of regulating devices at any higher temperature.

That some progress had been made in the direction of securing constant cell capacity is shown in Table 19, in which the two series are compared with respect to the upward displacement of the manometers.

TABLE 19.—*Cane sugar, Series II and III. Upward displacements of the manometers (mm.)*

Concentration.	Series II.	Series III.	Concentration.	Series II.	Series III.
0.1	0.07	0.07	0.5	0.16	0.24
"	0.54	0.07	"	0.32	0.22
"	....	0.09	"	....	0.07
"	....	0.09	"	....	0.38
0.2	2.78	0.05	0.6	3.78	0.48
"	1.44	0.05	"	0.83	0.10
"	0.19	....	"	0.64	....
0.3	0.12	0.06	0.7	0.24	0.61
"	0.10	0.06	"	0.07	0.45
0.4	0.30	0.08	0.8	0.32	0.01
"	1.18	0.07	"	1.80	0.34
"	....	0.22	0.9	1.21	0.44
"	....	0.04	"	....	0.05
			1.0	0.88	0.20
			"	2.97	0.59
			"	....	0.91
Average upward displacements: Series II = 0.94 mm., Series III, 0.22 mm					

TABLE 20.—*Cane sugar, Series II and III. Losses in rotation.*

Concentration.	Series II.	Series III.	Concentration.	Series II.	Series III.
	degrees.	*degrees.*		*degrees.*	*degrees.*
0.1	0.50	0.20	0.6	2.80	1.20
"	0.50	0.10	"	1.90	1.30
"	....	0.05	"	1.80	....
"	....	0.10	0.7	2.60	1.20
0.2	0.70	0.15	"	2.20	1.10
"	0.70	0.15	0.8	3.20	1.55
"	0.50	....	"	3.90	1.60
0.3	0.50	0.50	0.9	2.50	1.85
"	0.60	0.60	"	2.40	1.95
0.4	0.80	0.55	1.0	2.40	2.90
"	1.30	0.60	"	4.00	3.50
"	....	0.40	"	....	2.00
"	....	0.40			
0.5	1.40	0.90	Totals.....	38.40	27.65
"	1.20	1.00	Per cent.....	2.86	1.73
"	....	1.05	Pressure.....	9.37	6.75
"	....	0.75			

Further evidence of progress in the improvement of the method is to be found in Table 20, in which the losses in rotation of Series II and III are compared.

The evidence presented in Table 20 relates to the progress which had been made in the effort to suppress dilution from any or all sources,

while that in Table 19 bears upon one particular source of dilution. The reduction of the total loss in rotation from 38.40° in 22 determinations to 27.65° in 27 experiments, signified considerable improvement, especially in manipulation. Expressed in pressure, the loss was reduced from 9.37 atmospheres in Series II to 6.75 in Series III. The comparison is better made by means of percentages. The sum of all rotations of the solutions of Series II was 1342.30° and the sum of all the losses was 38.40°, or 2.86 per cent. The corresponding numbers for Series III were 1598.27°, 27.65°, and 1.73 per cent.

TABLE 21.—*Cane sugar, Series III. Observed osmotic pressures corrected for dilution, and the ratios of osmotic to calculated gas pressure of the solute.*

Concentration.	Observed osmotic pressure.	Corrected osmotic pressure.	Calculated gas pressure.	Ratio.	Mean ratio.
0.1	2.45	2.49	2.23	1.117	
"	2.45	2.47	"	1.108	1.093
"	2.37	2.38	"	1.067	
"	2.39	2.41	"	1.081	
0.2	4.78	4.81	4.46	1.078	1.077
"	4.77	4.80	"	1.076	
0.3	7.09	7.19	6.69	1.076	1.071
"	7.11	7.13	6.68	1.067	
0.4	9.37	9.48	8.91	1.064	
"	9.34	9.46	8.92	1.061	1.059
"	9.36	9.44	8.92	1.058	
"	9.31	9.39	8.91	1.054	
0.5	11.66	11.84	11.14	1.063	
"	11.73	11.93	"	1.071	1.071
"	11.89	12.02	"	1.079	
"	11.79	11.94	"	1.072	
0.6	14.12	14.37	13.37	1.075	1.076
"	14.11	14.38	"	1.076	
0.7	16.65	16.91	15.60	1.084	1.086
"	16.71	16.96	"	1.087	
0.8	19.16	19.50	17.82	1.094	1.094
"	19.13	19.48	17.83	1.093	
0.9	21.92	22.34	20.06	1.114	1.113
"	21.86	22.29	20.05	1.111	
1.0	24.53	25.21	22.28	1.132	
"	24.54	25.37	"	1.139	1.127
"	24.27	24.73	22.29	1.109	

The osmotic pressures which are given in Table 18 are those which were actually observed, that is, they have not been corrected for *inversion* or *dilution*. When the first account of the work in Series III was published, it was still imagined that *inversion* might be responsible for a portion of the loss in rotation, though it was conceded that a considerable part of it must be due to *dilution*. Accordingly, three tentative tables of "*corrected*" results were given. In one of them the whole loss in rotation was ascribed to *inversion;* and in another, to *dilution*. In the third table, one-half of the loss was ascribed to inversion and one-half to dilution. The difference between the corresponding values in the first and second tables was called the "*limit of uncertainty*" as to the true

osmotic pressure of the solutions, and a preference was expressed for the third table, in which a compromise had been attempted.

When, at a later period, it was proved that the *whole* loss in rotation had been due to *dilution*, it was necessary wholly to discard the first and third tables.

Table 21 gives the results of Series III corrected for dilution only. It is comparable with Table 17 for Series II. The corrected pressures are probably somewhat more reliable in the former than in the latter.

Series IV.*

In Series IV it was attempted to maintain a bath temperature of 5°, but the temperature varied as a rule between 4° and 5°. On two occasions it exceeded 6° for a short time. Both compartments of the bath were furnished with an extensive and continuous system of brass pipes for the circulation of hydrant water. One-half of the pipes were immersed in the water in the lower part of the bath, while the other half were suspended from the top of the upper, or manometer, compartment. The hydrant water entered at the bottom, and, after circulating through the whole length of the pipes in the water, it ascended and traveled through the whole length of the system in the air space before escaping from the bath. It was fed to the bath system from the bottom of a standpipe, 4 meters in height, and its rate of flow was regulated by means of a valve placed between the standpipe and the bath. In order that the pressure upon the water circulating in the bath might remain constant, also that it might have, at the time of entering, the temperature of the water in the street mains, the standpipe was provided with an overflow at the top, and the water was fed into it as directly as possible from the main source of supply for the building, and at a comparatively high rate. The water in the bath in which the lower half of the cooling system was submerged was kept in constant circulation by means of a pump.

The mean mid-winter temperature of the water in the street mains is about 4°, and no difficulty was apprehended in maintaining a temperature of 5° in the bath. But long before the series was completed, the temperature of the hydrant water rose above 5°, and it was necessary to insert a system of pipes, cooled by ice, between the standpipe and the bath.

The cooling system described above is essentially the same as that now employed in all baths for temperatures above 0° and below the highest temperature of the atmosphere, only it has been found better to employ two independent systems—one for the lower part of the bath, where the cells are located, and another for the air or manometer space.

During the work upon Series IV, the cooling system was in the experimental stage, and it failed to operate as satisfactorily as it afterwards did when all its details had been perfected. This accounts, in part, for

*Measurements by H. N. Morse, J. C. W. Frazer, and P. B. Dunbar. Am. Chem. Jour., xxxviii, 175.

the variations in bath temperature, which ranged between 0.2° and 0.9°. The principal difficulty, however, was due to the fluctuating external temperature conditions, which, at that time, were not under good control.

The observed osmotic pressures are given, in the customary form, in Table 22.

TABLE 22.—*Cane sugar, Series IV. Extreme bath temperatures; losses in rotation; observed osmotic pressures; calculated gas pressures of the solute.*

Concentration.	Temperature.		Loss in rotation.	Observed osmotic pressure.	Calculated gas pressure.	Ratio.
	degrees.		*degrees.*			
0.1	4.50 to 5.30		0.10	2.40	2.27	1.053
"	4.50	5.30	0.10	2.40	"	
0.2	4.40	5.00	0.30	4.74	4.53	1.045
"	5.75	6.45	0.05	4.76	4.56	
0.3	4.40	4.60	0.30	7.10	6.79	1.041
"	4.40	4.60	0.30	7.04	"	
0.4	4.20	5.10	0.40	9.44	9.05	1.041
"	4.30	5.00	0.90	9.41	"	
0.5	4.20	4.70	0.75	11.79	11.31	1.043
"	5.00	5.50	0.75	11.85	11.35	
0.6	4.70	5.20	0.50	14.41	13.60	1.059
"	5.75	6.45	0.70	14.45	13.66	
0.7	4.20	4.50	1.00	16.73	15.84	1.059
"	4.40	4.75	1.40	16.85	15.85	
0.8	4.15	4.90	1.55	19.27	18.10	1.066
"	4.25	4.40	1.40	19.34	18.09	
0.9	4.30	4.40	1.60	22.07	20.36	1.086
"	5.00	5.50	1.65	22.22	20.42	
1.0	4.30	5.00	1.70	24.52	22.65	1.084
"	4.20	4.55	2.10	24.53	22.62	
			Total = 17.55 = 4.30 atmospheres.			Mean = 1.058

TABLE 23.—*Cane sugar, Series II and IV. Fluctuations in bath temperature.*

Concentration.	Series II.	Series IV.	Concentration.	Series II.	Series IV.
	degree.	*degree.*		*degree.*	*degree.*
0.1	0.10	0.80	0.6	0.10	0.50
"	0.10	0.80	"	0.15	0.70
0.2	0.95	0.60	"	0.00	....
"	0.45	0.70	0.7	0.65	0.30
"	0.35	....	"	0.56	0.35
0.3	0.45	0.20	0.8	0.03	0.75
"	0.15	0.20	"	0.05	0.15
0.4	0.30	0.90	0.9	0.25	0.10
"	0.10	0.70	"	0.25	0.50
0.5	0.20	0.50	1.0	0.05	0.70
"	0.00	0.50	"	0.10	0.35
			Means....	0.24	0.52

The variations in bath temperature were greater in Series IV than in Series III. But since circulating ice water, whose temperature is more constant than that of hydrant water, was used in the latter, it is fairer to compare Series IV with Series II, if with any other, in order to ascertain whether any substantial progress had been made in bath

regulation. This is done in Table 23, from which it appears that the mean variation in bath temperature in Series IV was more than double that in Series II, as if the means of bath control had decreased, instead of increasing in efficiency. It is easy to show, however, that the conditions to be met in the case of Series IV were more difficult than in that of Series II, and that, on this account, the comparison is less unfavorable to the former than it appears to be. Nevertheless, it was considered necessary to revise radically the system of bath regulation before beginning the next series.

If Series III and IV are compared with respect to the upward displacements of the manometers, no evidence of progress is to be detected. It will be seen in Table 24 that the mean displacements were about equal in the two series, which signifies that little or no progress had been made in the direction of fixing the capacity of the cells.

TABLE 24.—*Cane sugar, Series III and IV. Upward displacements of the manometers (mm.).*

Concentration.	Series III.	Series IV.	Concentration.	Series III.	Series IV.
	mm.	*mm.*		*mm.*	*mm.*
0.1	0.07	0.40	0.6	0.48	0.26
"	0.07	0.34	"	0.10	0.05
"	0.09	....	0.7	0.61	0.23
"	0.09	....	"	0.45	0.49
0.2	0.05	0.22	0.8	0.01	0.32
"	0.05	0.04	"	0.34	0.19
0.3	0.06	0.07	0.9	0.44	0.19
"	0.06	0.07	"	0.05	0.40
0.4	0.08	0.03	1.0	0.23	0.41
"	0.07	0.15	"	0.59	0.59
"	0.22	....	"	0.91	....
"	0.04	....			
0.5	0.24	0.30	Means....	0.22	0.24
"	0.22	0.17			
"	0.07	....			
"	0.38	....			

If, on the other hand, as in Table 25, Series III and IV are compared with respect to loss in rotation, which is the measure of the total dilution which the solutions suffered while in the cells, some improvement is apparent. The relatively smaller loss in Series IV was due to improvements in manipulation at the time of closing and opening the cells, particularly during the latter period.

The sum of the rotations of all the 20 solutions used in Series IV was 1249.00°. The loss in rotation was 17.55°, or 1.41 per cent. The loss in rotation in Series III was 1.73 per cent. Expressed in terms of osmotic pressure, the dilution in Series IV was equivalent to 4.3 atmospheres, and that in Series III to 6.74 atmospheres.

Table 26 gives the results of Series IV as corrected for dilution, that is, for the observed losses in rotation. It stands in the same relation to Series IV as Table 17 to Series II, and Table 21 to Series III. On the whole, the corrected osmotic pressures of Series IV are probably a little more trustworthy than those of Series III.

TABLE 25.—*Cane sugar, Series III and IV. Losses in rotation.*

Concentration.	Series III.	Series IV.	Concentration.	Series III.	Series IV.
	degrees.	*degrees.*		*degrees.*	*degrees.*
0.1	0.20	0.10	0.6	1.20	0.50
"	0.10	0.10	"	1.30	0.70
"	0.05	....	0.7	1.20	1.00
"	0.10	....	"	1.10	1.40
0.2	0.15	0.30	0.8	1.55	1.55
"	0.15	0.05	"	1.60	1.40
0.3	0.50	0.30	0.9	1.85	1.60
"	0.60	0.30	"	1.95	1.65
0.4	0.55	0.40	1.0	2.90	1.70
"	0.60	0.90	"	3.50	2.10
"	0.40	....	"	2.00	....
"	0.40	....			
0.5	0.90	0.75	Totals.....	27.65	17.55
"	1.00	0.75			
"	1.05	....	Per cent.....	1.78	1.41
"	0.75	....	Pressure.....	6.75	4.30

TABLE 26.—*Cane sugar, Series IV. Observed osmotic pressures corrected for dilution, and ratios of osmotic to calculated gas pressures of the solute.*

Concentration.	Observed osmotic pressure.	Corrected osmotic pressure.	Calculated gas pressure.	Ratio.	Mean ratio.
0.1	2.40	2.42	2.27	1.066	1.066
"	2.40	2.42	"	1.066	
0.2	4.74	4.80	4.53	1.060	1.053
"	4.76	4.77	4.56	1.046	
0.3	7.10	7.16	6.79	1.055	1.051
"	7.04	7.10	"	1.046	
0.4	9.44	9.50	9.05	1.049	1.055
"	9.41	9.59	"	1.060	
0.5	11.79	11.94	11.31	1.056	1.057
"	11.85	12.00	11.35	1.057	
0.6	14.41	14.51	13.60	1.067	1.068
"	14.45	14.60	13.66	1.069	
0.7	16.73	16.94	15.84	1.070	1.077
"	16.85	17.15	15.85	1.083	
0.8	19.27	19.61	18.10	1.084	1.085
"	19.34	19.65	18.09	1.086	
0.9	22.07	22.44	20.36	1.102	1.104
"	22.22	22.59	20.42	1.106	
1.0	24.52	24.91	22.65	1.100	1.103
"	24.53	25.02	22.62	1.106	
				Mean =	1.072

SERIES V.*

The comparison of Series II and IV with respect to temperature control and of III and IV with respect to dilution of cell contents was, on the whole, unsatisfactory. There was to be found in the results no evidence of any progress in the improvement of devices for the regulation of the baths, and the reduction of dilution, from 1.73 per cent in Series III to 1.41 per cent in Series IV, did not betoken an early suppression of all dilution. It was evident that, in order to

*Measurements by H. N. Morse and H. V. Morse. Am. Chem. Jour., XXXIV, 667.

accomplish the main purposes immediately in view—namely, the complete suppression of *thermometer effects* and *dilution*—the whole method must be extensively improved.

The revision which followed, previous to beginning Series V, was a radical one, which affected nearly every detail of the procedure. The more important of the measures taken at that time for the elimination of dilution have already been mentioned. The method of wrapping the exposed part of the stopper was changed, with the result that in Series V and in the succeeding series there were no upward displacements of the manometers. In other words, the capacity of the cells no longer increased under pressure, and one of the three sources of dilution—though probably, in the beginning, the smallest—had at last been eradicated. The practice of "dipping" the cells, before closing and opening them, was followed systematically, and the method of piercing and "*slitting*" the stopper, before removing the manometer, was greatly improved. It was at this time also that nitrogen was substituted for air in the manometers, and that more attention began to be given to the errors in measurement which are due to the irregularities of capillary depression in narrow tubes.

The improvements in the devices for bath regulation had in view the bringing of the whole system of temperature control into harmony with the general scheme which has been formulated in a previous chapter in the following words:

> "If all the water or air in a bath is made to pass rapidly (1) over a continuously cooled surface which is capable of reducing the temperature slightly below that which it is desired to maintain, then (2) over a heated surface which is more effective than the cooled one, but which is under the control of a thermostat, and (3) again over the cooled surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set, and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the water or air."

The essential features of this scheme—the cooling and heating surfaces and the circulation of the air or water between them—are not novel. They are exemplified in part or fully, and more or less perfectly, in nearly all baths. But perfect success in temperature regulation depends upon the simultaneous and harmonious coöperation of all three. In principle, it makes no difference whether the heating or cooling agent is subjected to exact regulation by a thermostat.

In Series I, the maintenance of temperature was by insulation. There was no *thermostat* in the system—unless the insulation can be considered in that light—and the walls of the bath became therefore an *uncontrolled* heating or cooling surface according to the temperature of the surrounding air.

In Series II, the heating surface was provided by the electric stoves, which were regulated by a thermostat. The other essential—the *cooling* surface—was furnished by the walls of the bath; but these became an

additional but *uncontrolled heating surface* whenever the temperature of the air rose above that which it was sought to maintain in the bath.

In Series III, the ice water was the cooling agent and the walls of the bath were the heating surface. In this case *the cooling agent was regulated* and the melting ice was the thermostat. The system was perfect in principle, but failed because of the too slow circulation of the water between the heating and refrigerating surfaces.

In Series IV, the hydrant water was the cooling agent and the bath walls were the heating surface. As in Series III, the cooling agent, instead of the heating surface, was regulated. In Series III, the thermostat was melting ice, while in Series IV, it was the *valve* between the stand-pipe and the bath.

Considered as a thermostat for one temperature only, nothing is more perfect, of course, than melting ice, except a liquid of constant boiling-point, while a valve regulating the flow of water of constant temperature is obviously ineffective unless the external heat supply is constant in quantity. The system of cooling employed in Series IV was excellent. The failure to regulate satisfactorily the temperature of the bath was due to the fact that the thermostat (the valve) was not sufficiently automatic in its action to overcome the inconstant external temperature conditions. The remedy which suggested itself and was immediately applied was the reinstallation in the bath of an electric heating system controlled by a mercury thermostat. The effect of this was, of course, to give the regulation of the bath to the heating instead of the cooling system, which should always be done unless the external temperature conditions are constant, or one can employ melting ice or a boiling liquid.

The valve did not become useless when it lost its character as a thermostat, for it was still necessary as an economizer of water and heat, that is, for the purpose of keeping the so-called "*margin of under-cooling*" as small as practicable.

The beneficial effect of the improvement in manipulation and apparatus was immediate and large. In Series V, the loss in rotation was small and was confined to the solutions of higher concentration, and the fluctuations in bath temperature were less frequent and smaller than in any previous series.

The sum of the rotations of all the solutions in Series V was 1249.6°. A loss of 2.50° amounts to 0.20 per cent. Expressed in osmotic pressure, the dilution was equivalent to about 0.64 atmosphere. The corresponding values in the preceding series were 1249.00°, 17.55°, 1.41 per cent, and 4.30 atmospheres. The sum of all aberrations in bath temperature was 1.40° in Series V and 10.30° in Series IV. There were no upward displacements of the manometers.

In Table 28 the results are corrected for dilution corresponding to the observed losses in rotation.

TABLE 27.—*Cane sugar, Series V. Temperature of the bath; losses in rotation; observed osmotic pressures; and calculated gas pressures of the solute.*

Concentration.	Temperature.	Loss in rotation.	Observed osmotic pressure.	Calculated gas pressure.	Ratio.
	degrees.	*degrees.*			
0.1	10.00 to 10.00	0.00	2.43	2.31	1.054
"	10.00 10.00	0.00	2.44	"	
0.2	10.00 10.20	0.00	4.81	4.62	1.043
"	10.00 10.20	0.00	4.83	"	
0.3	10.00 10.00	0.00	7.22	6.92	1.038
"	10.00 10.10	0.00	7.15	"	
0.4	10.00 10.10	0.00	9.53	9.24	1.036
"	10.00 10.10	0.00	9.61	"	
0.5	10.00 10.00	0.00	11.96	11.54	1.039
"	10.00 10.00	0.10	12.02	"	
0.6	10.10 10.10	0.00	14.53	13.85	1.051
"	10.10 10.10	0.00	14.55	"	
0.7	10.30 10.10	0.10	17.10	16.16	1.058
"	10.00 10.10	0.00	17.08	"	
0.8	9.90 10.00	0.20	19.73	18.47	1.069
"	10.00 10.00	0.10	19.77	"	
0.9	10.00 10.00	0.40	22.28	20.77	1.073
"	10.00 10.00	0.40	22.28	"	
1.0	10.00 10.30	0.60	25.08	23.10	1.085
"	10.00 10.20	0.60	25.03	"	
		Total = 2.50			Mean = 1.055

TABLE 28.—*Cane sugar, Series V. Observed osmotic pressures corrected for dilution, and ratios of osmotic to calculated gas pressures of the solute.*

Concentration.	Observed osmotic pressure.	Corrected osmotic pressure.	Calculated gas pressure.	Ratio.	Mean ratio.
0.1	2.43	2.43	2.31	1.052	1.054
"	2.44	2.44	"	1.056	
0.2	4.81	4.81	4.62	1.041	1.043
"	4.83	4.83	"	1.045	
0.3	7.22	7.22	6.92	1.043	1.038
"	7.15	7.15	"	1.033	
0.4	9.53	9.53	9.24	1.031	1.036
"	9.61	9.61	"	1.040	
0.5	11.96	11.96	11.54	1.036	1.040
"	12.02	12.04	"	1.043	
0.6	14.53	14.53	13.85	1.050	1.051
"	14.55	14.55	"	1.051	
0.7	17.10	17.13	16.16	1.060	1.058
"	17.08	17.08	"	1.057	
0.8	19.73	19.77	18.47	1.070	1.071
"	19.77	19.80	"	1.072	
0.9	22.28	22.37	20.77	1.077	1.077
"	22.28	22.37	"	1.077	
1.0	25.08	25.23	23.10	1.092	1.091
"	25.03	25.18	"	1.090	
				Mean = 1.056	

SERIES VI.*

The conditions under which the measurements of Series VI were made were essentially the same as in Series V. Some improvements had been made in the interval between the two in both the cooling and heating systems, and the circulation of the bath water surrounding the lower half of the cooling system had been made more effective. Some slight improvements had also been made in the manipulation. The beneficial effect of the alterations is shown in the smaller fluctuations of bath temperature and in the diminished loss in rotation. Except in one case, the dilution was confined to the solutions of higher concentration.

TABLE 29.—*Cane sugar, Series VI. Bath temperatures; losses in rotation; observed osmotic pressures; and calculated gas pressures of the solute.*

Concentration.	Temperature.	Loss in rotation.	Observed osmotic pressure.	Calculated gas pressure.	Ratio.
	degrees.	*degrees.*			
0.1	15.00 to 15.00	0.00	2.47	2.35	1.054
"	15.00 15.00	0.00	2.48	"	
0.2	15.00 15.00	0.10	4.92	4.70	1.045
"	15.00 15.00	0.00	4.90	"	
0.3	15.00 15.00	0.00	7.31	7.05	1.040
"	15.00 15.00	0.00	7.35	"	
0.4	15.00 15.10	0.00	9.77	9.40	1.040
"	15.00 15.10	0.00	9.78	"	
0.5	15.00 15.00	0.00	12.29	11.75	1.046
"	15.00 15.10	0.00	12.29	"	
0.6	15.00 15.00	0.00	14.91	14.09	1.055
"	15.00 15.00	0.00	14.81	"	
0.7	15.00 15.00	0.10	17.42	16.44	1.058
"	15.00 15.10	0.05	17.36	"	
0.8	15.00 15.00	0.20	20.07	18.79	1.069
"	15.00 15.00	0.15	20.11	"	
0.9	15.00 15.00	0.30	22.97	21.14	1.085
"	15.00 15.00	0.15	22.91	"	
1.0	15.00 15.00	0.00	25.39	23.49	1.082
"	15.00 15.00	0.30	25.44	"	
		Sum = 1.35			Mean = 1.057

Table 29 gives the temperatures, the losses in rotation, the observed osmotic pressures of the solutions, and the calculated gas pressures of the solute.

In Series VI, the sum of all the original rotations was 1249.59°. A loss of 1.35° amounts to 0.11 per cent, or a dilution equivalent to 0.34 atmosphere for the whole series. The corresponding values for Series V were 1249.60°, 2.50°, 0.20 per cent, and 0.64 atmosphere. The sum of all the fluctuations in bath temperature was 0.4° in Series VI, and 1.4° in Series V. There were no upward displacements of the manometer.

In Table 30 the observed pressures are corrected for the small losses in rotation.

*Measurements by H. N. Morse and B. Mears. Am. Chem. Jour., XL, 194.

TABLE 30.—*Cane sugar, Series VI. Observed osmotic pressures corrected for dilution, and ratios of osmotic to calculated gas pressure of the solute.*

Concentration.	Observed osmotic pressure.	Corrected osmotic pressure.	Calculated gas pressure.	Ratio.	Mean ratio.
0.1	2.47	2.47	2.35	1.052	1.054
"	2.48	2.48	"	1.055	
0.2	4.92	4.94	4.70	1.051	1.047
"	4.90	4.90	"	1.043	
0.3	7.31	7.31	7.05	1.037	1.040
"	7.35	7.35	"	1.043	
0.4	9.77	9.77	9.40	1.039	1.040
"	9.78	9.78	"	1.040	
0.5	12.29	12.29	11.75	1.046	1.046
"	12.29	12.29	"	1.046	
0.6	14.91	14.91	14.09	1.058	1.055
"	14.81	14.81	"	1.051	
0.7	17.42	17.44	16.44	1.061	1.059
"	17.36	17.37	"	1.057	
0.8	20.07	20.11	18.79	1.070	1.071
"	20.11	20.14	"	1.072	
0.9	22.97	23.04	21.14	1.090	1.089
"	22.91	22.98	"	1.087	
1.0	25.39	25.39	23.49	1.081	1.083
"	25.44	25.51	"	1.086	
				Mean =	1.058

SERIES VII.*

While the work in Series V and VI was in progress, certain defects of construction in the cooling system manifested themselves. The principal difficulty experienced in this connection was with the gas which was expelled from the hydrant water while passing through the cooling system. Provision had been made in the beginning for the easy escape of this gas by giving all the pipes in the cooling system a slight upward inclination in the direction in which the water was to run. It was found, however, that, despite the inclined position of the pipes and the arrangement for constant pressure, no perfectly steady flow of water could be secured when the stream passing through the system was small. When it was very small, the flow of water would cease altogether in a few hours. It was necessary, therefore, at stated intervals throughout the day and night, to open wide for a few seconds the regulating valve and flush the system. The cause of the difficulty was finally located in the valve itself, which was found to be of such construction that gas could accumulate in it and eventually stop the flow of water whenever the stream passing through the system was small. The valve was replaced by one of different construction, and no further difficulty was experienced in securing a constant flow of water.

There was no material variation in the temperature of the bath during any experiment in Series VII, and it was apparent, therefore, that one of the two great objects of the preliminary investigation had been accomplished. The system of bath regulation had been improved to the point where *thermometer effects* were no longer to be feared. Dilution, on the other hand, had not been entirely suppressed. In a total

*Measurements by H. N. Morse and W. W. Holland. Am. Chem. Jour., XLI, 1.

rotation of 1246.85°, the loss was 1.30°, or 0.10 per cent, which was equivalent in terms of osmotic pressure to a dilution of 0.31 atmosphere. In Series VI, the dilution amounted to 0.11 per cent, or 0.34 atmosphere.

The observed pressures of Series VII are given in Table 31:

TABLE 31.—*Cane sugar, Series VII. Temperature; observed osmotic pressures; losses in rotation; and calculated gas pressures of the solute.*

Concentration.	Temperature.	Loss in rotation.	Observed osmotic pressure.	Calculated gas pressure.	Ratio.
	degrees.	*degrees.*			
0.1	25.00	0.00	2.56	2.43	1.053
"	"	"	2.56	"	
0.2	"	"	5.09	4.86	1.048
"	"	"	5.10	"	
0.3	"	"	7.58	7.29	1.038
"	"	"	7.55	"	
0.4	"	"	10.10	9.72	1.041
"	"	"	10.13	"	
0.5	"	"	12.75	12.15	1.048
"	"	"	12.71	"	
0.6	"	"	15.43	14.58	1.058
"	"	"	15.41	"	
0.7	"	0.10	18.03	17.02	1.059
"	"	0.10	18.02	"	
0.8	"	0.00	20.75	19.45	1.066
"	"	0.20	20.71	"	
0.9	"	0.15	23.71	21.88	1.082
"	"	0.25	23.67	"	
1.0	"	0.10	26.33	24.31	1.084
"	"	0.40	26.39	"	
		Sum = 1.30			Mean = 1.058

Table 32 gives the observed pressures as corrected for dilution:

TABLE 32.—*Cane sugar, Series VII. Observed osmotic pressures corrected for dilution, and ratios of osmotic to calculated gas pressures of the solute.*

Concentration.	Observed osmotic pressure.	Corrected osmotic pressure.	Calculated gas pressure.	Ratio.	Mean ratio.
0.1	2.56	2.56	2.43	1.053	1.053
"	2.56	2.56	"	1.053	
0.2	5.09	5.09	4.86	1.047	1.048
"	5.10	5.10	"	1.049	
0.3	7.58	7.58	7.29	1.040	1.038
"	7.55	7.55	"	1.036	
0.4	10.10	10.10	9.72	1.039	1.041
"	10.13	10.13	"	1.042	
0.5	12.75	12.75	12.15	1.049	1.048
"	12.71	12.71	"	1.046	
0.6	15.43	15.43	14.58	1.058	1.058
"	15.41	15.41	"	1.057	
0.7	18.03	18.05	17.02	1.061	1.060
"	18.02	18.04	"	1.060	
0.8	20.75	20.75	19.45	1.067	1.067
"	20.71	20.76	"	1.067	
0.9	23.71	23.75	21.88	1.085	1.085
"	23.71	23.75	"	1.085	
1.0	26.33	26.35	24.31	1.084	1.087
"	26.39	26.49	"	1.090	
				Mean = 1.059	

SERIES VIII.*

The loss in rotation in Series VI amounted to 0.11 per cent and to 0.10 per cent in Series VII. There was little prospect of further improvement in the manipulation concerned in the closing and opening of the cells, and it was therefore concluded that the continued small dilution of the more concentrated solutions could not be wholly suppressed as long as the rubber stopper was retained as one of the features of the cell. Various devices for closing the cell without it had been studied and more or less tested, but none of them had proved to be entirely practicable except the forerunner of the arrangement seen in Figure 9,

TABLE 33.—*Cane sugar, Series VIII. Temperature; observed osmotic pressures; calculated gas pressures of solute; and ratios of osmotic to gas pressures.*

Concentration.	Temperature.	Observed osmotic pressure.	Calculated gas pressure.	Ratio.	Mean ratio.
	degrees.				
0.1	20.00	2.53	2.39	1.059	1.057
"	"	2.52	"	1.054	
0.2	"	5.03	4.78	1.052	1.050
"	"	5.02	"	1.050	
"	"	5.02	"	1.050	
0.3	"	7.45	7.17	1.039	1.039
"	"	7.45	"	1.039	
0.4	"	9.98	9.56	1.044	1.042
"	"	9.94	"	1.040	
"	"	9.97	"	1.043	
0.5	"	12.49	11.95	1.045	1.045
"	"	12.49	"	1.045	
"	"	12.50	"	1.046	
0.6	"	15.18	14.34	1.059	1.060
"	"	15.22	"	1.061	
0.7	"	17.83	16.73	1.066	1.066
"	"	17.85	"	1.067	
"	"	17.83	"	1.066	
0.8	"	20.57	19.12	1.076	1.077
"	"	20.62	"	1.078	
"	"	20.62	"	1.076	
0.9	"	23.36	21.51	1.086	1.084
"	"	23.31	"	1.084	
"	"	23.27	"	1.082	
1.0	"	26.12	23.90	1.093	1.093
"	"	26.13	"	1.093	
"	"	26.11	"	1.093	
				Mean =	1.061

page 19, which was altered and improved until it became satisfactory. The requirements of such a device were that it should permit of a practically instantaneous closing or opening of the cells, and that it should render an enlargement of cell capacity under pressure impossible. In general, it is difficult to meet the second requirement if any rubber whatever is used in closing the cells, and we should have been glad to dispense with that material altogether. But after securely closing a cell, it is necessary to bring upon the contents an initial pressure which is nearly equal to, or even a little above, the osmotic pressure of the

*Measurements by H. N. Morse and W. W. Holland. Am. Chem. Jour., XLI, 257.

solution. Otherwise, much time is lost in waiting for equilibrium, and some dilution occurs in consequence of the compression of the gas in the manometer. Up to the present time, however, the writer has been unable to devise a successful means for producing this initial pressure which did not involve the use of rubber.

Throughout Series VII and VIII, the temperatures of the bath were constant, and with the introduction into the latter of the new device for closing the cells, the last traces of loss in rotation disappeared. With Series VIII, therefore, the four years' struggle against *thermometer effects* and *dilution* was brought to a successful issue.

The progress of the work from the beginning to the end of the endeavor to eliminate the large sources of error from the direct method of measuring osmotic pressure is summarized, and can be reviewed at a glance in Tables 34, 35, and 36.

TABLE 34.—*Cane sugar, Series I to VIII. Fluctuations in bath temperature.*

Concentration.	Series I.	Series II.	Series III.	Series IV.	Series V.	Series VI.	Series VII.	Series VIII.
	degrees.	*degrees.*	*degrees.*	*degrees.*	*degrees.*	*degrees.*	*degrees.*	*degrees.*
0.1	4.48	0.05	0.18	0.80	0.00	0.00	0.00	0.00
"	1.36	0.05	0.12	0.80	0.00	0.00	0.00	0.00
"	....	....	0.24	....	....	....	....	....
"	....	....	0.24	....	....	....	....	....
0.2	2.11	0.50	0.10	0.60	0.20	0.30	0.00	0.00
"	0.42	0.53	0.04	0.65	0.20	0.10	0.00	0.00
"	....	0.35	....	....	....	....	....	0.00
0.3	1.44	0.15	0.16	0.15	0.00	0.10	0.00	0.00
"	1.60	0.40	0.04	0.15	0.10	0.00	0.00	0.00
0.4	0.40	0.27	0.06	0.90	0.10	0.10	0.00	0.00
"	0.40	0.10	0.10	0.40	0.10	0.10	0.00	0.00
"	....	....	0.08	....	....	....	....	0.00
"	....	....	0.04	....	....	....	....	....
0.5	0.16	0.20	0.24	0.50	0.10	0.00	0.00	0.00
"	0.88	0.00	0.16	0.50	0.00	0.10	0.00	0.00
"	....	....	0.06	....	....	....	....	0.00
"	....	....	0.04	....	....	....	....	....
0.6	0.70	0.10	0.12	0.50	0.00	0.00	0.00	0.00
"	1.10	0.15	0.05	0.70	0.00	0.00	0.00	0.00
"	....	0.00	0.00	....	....	....	....	....
0.7	0.90	0.65	0.12	0.30	0.10	0.00	0.00	0.00
"	1.90	0.20	0.05	0.35	0.10	0.00	0.00	0.00
"	....	....	....	....	....	....	....	0.00
0.8	0.92	0.03	0.10	0.75	0.20	0.00	0.00	0.00
"	1.00	0.05	0.10	0.15	0.00	0.00	0.00	0.00
"	....	....	....	....	....	....	....	0.00
0.9	1.10	0.25	0.03	0.10	0.00	0.00	0.00	0.00
"	....	0.25	0.10	0.50	0.00	0.00	0.00	0.00
"	....	....	....	....	....	....	....	0.00
1.0	1.80	0.07	0.14	0.70	0.30	0.00	0.00	0.00
"	1.10	....	0.10	0.35	0.20	0.00	0.00	0.00
"	1.10	....	....	....	....	....	....	0.00
Totals...	29.14	4.35	2.81	9.85	1.70	0.80	0.00	0.00
Means..	1.22	0.21	0.10	0.49	0.08	0.04	0.00	0.00

Table 34 gives the fluctuations in bath temperature for each of the 175 experiments of Series I to VIII, inclusive. The test and the measure of progress in the improvement of the facilities for the main-

tenance of temperature are, in a general way, the diminution, from series to series, in the fluctuations of bath temperature. It has already been pointed out, however, that certain series can not be fairly judged by such a comparison.

Variations in bath temperature during the individual experiments are only a rough measure of *thermometer effects*. The very complex character of these phenomena and their highly pernicious effects upon the precision of the measurements of osmotic pressure have been discussed in a former chapter, and it is not necessary again to emphasize the necessity of their eliminiation.

When, as in Series VII and VIII, no fluctuations are given, it is not meant thereby that the temperature was absolutely constant throughout, but simply that the variation was less than 0.05°. In the "*final measurements*" to be presented in later chapters, it will mean that the variation was less than 0.02°.

TABLE 35.—*Cane sugar, Series I to VIII. Upward displacements of the manometers (mm.).*

Concentration.	Series I.	Series II.	Series III.	Series IV.	Series V.	Series VI.	Series VII.	Series VIII.
0.1	(*)	0.07	0.07	0.40	0.00	0.00	0.00	0.00
"	(*)	0.54	0.07	0.34	0.00	0.00	0.00	0.00
"	(*)	....	0.09	....	....	....	....	....
"	(*)	....	0.09	....	....	....	....	....
0.2	(*)	2.78	0.05	0.22	0.00	0.00	0.00	0.00
"	(*)	1.44	0.05	0.04	0.00	0.00	0.00	0.00
"	(*)	0.19	....	....	....	....	....	0.00
0.3	(*)	0.12	0.06	0.07	0.00	0.00	0.00	0.00
"	(*)	0.10	0.06	0.07	0.00	0.00	0.00	0.00
0.4	(*)	0.30	0.08	0.03	0.00	0.00	0.00	0.00
"	(*)	1.18	0.07	0.15	0.00	0.00	0.00	0.00
"	(*)	....	0.22	....	....	....	....	0.00
"	(*)	....	0.04	....	....	....	....	....
0.5	(*)	0.16	0.24	0.30	0.00	0.00	0.00	0.00
"	(*)	0.32	0.22	0.17	0.00	0.00	0.00	0.00
"	(*)	....	0.07	....	....	....	....	0.00
"	(*)	....	0.38	....	....	....	....	....
0.6	(*)	3.78	0.48	0.26	0.00	0.00	0.00	0.00
"	(*)	0.83	0.10	0.05	0.00	0.00	0.00	0.00
"	(*)	0.64	....	....	....	....	....	....
0.7	(*)	0.24	0.61	0.23	0.00	0.00	0.00	0.00
"	(*)	0.07	0.45	0.49	0.00	0.00	0.00	0.00
"	(*)	....	....	....	....	....	....	0.00
0.8	(*)	0.32	0.01	0.32	0.00	0.00	0.00	0.00
"	(*)	1.80	0.34	0.19	0.00	0.00	0.00	0.00
"	(*)	....	....	....	....	....	....	0.00
0.9	(*)	1.21	0.44	0.19	0.00	0.00	0.00	0.00
"	(*)	....	0.05	0.40	0.00	0.00	0.00	0.00
"	(*)	....	....	....	....	....	....	0.00
1.0	(*)	0.88	0.23	0.41	0.00	0.00	0.00	0.00
"	(*)	2.97	0.59	0.59	0.00	0.00	0.00	0.00
"	(*)	....	0.91	....	....	....	....	0.00
	Means..	0.94	0.22	0.24				

*Not determined.

Tables 35 and 36 summarize the progress made in suppressing dilution. The first gives the upward displacements of the manometers which attended distortions of the rubber stoppers under pressure. They are to be regarded merely as a symptom of such distortion, and not as a measure of the increase in the capacity of the cells. The more important of the two tables is 36, which gives the losses in rotation, that is, the amounts of dilution from all sources which the solutions suffered while in the cells.

TABLE 36.—*Cane sugar, Series I to VIII. Loss in rotation (degrees).*

Concentration.	Series I.	Series II.	Series III.	Series IV.	Series V.	Series VI.	Series VII.	Series VIII.
0.1	(*)	0.50	0.20	0.10	0.00	0.00	0.00	0.00
"	(*)	0.50	0.10	0.10	0.00	0.00	0.00	0.00
"	(*)	....	0.05	....	....	....	....	....
"	(*)	....	0.10	....	....	....	....	....
0.2	(*)	0.70	0.15	0.30	0.00	0.10	0.00	0.00
"	(*)	0.70	0.15	0.05	0.00	0.00	0.00	0.00
"	(*)	0.50	....	....	....	....	....	0.00
0.3	(*)	0.50	0.50	0.30	0.00	0.00	0.00	0.00
"	(*)	0.60	0.60	0.30	0.00	0.00	0.00	0.00
0.4	(*)	0.80	0.55	0.40	0.00	0.00	0.00	0.00
"	(*)	1.30	0.60	0.90	0.00	0.00	0.00	0.00
"	(*)	....	0.40	....	....	....	....	0.00
"	(*)	....	0.40	....	....	....	....	....
0.5	(*)	1.40	0.90	0.75	0.00	0.00	0.00	0.00
"	(*)	1.20	1.00	0.75	0.10	0.00	0.00	0.00
"	(*)	....	1.05	....	....	....	....	0.00
"	(*)	....	0.75	....	....	....	....	....
0.6	(*)	2.80	1.20	0.50	0.00	0.00	0.00	0.00
"	(*)	1.90	1.30	0.70	0.00	0.00	0.00	0.00
"	(*)	1.80	....	....	....	....	....	....
0.7	(*)	2.60	1.20	1.00	0.10	0.10	0.10	0.00
"	(*)	2.20	1.10	1.40	0.00	0.05	0.10	0.00
"	(*)	....	....	....	....	....	....	0.00
0.8	(*)	3.20	1.55	1.55	0.20	0.20	0.00	0.00
"	(*)	3.90	1.60	1.40	0.10	0.15	0.20	0.00
"	(*)	....	....	....	....	....	....	0.00
0.9	(*)	2.50	1.85	1.60	0.40	0.30	0.15	0.00
"	(*)	2.40	1.95	1.65	0.40	0.15	0.25	0.00
"	(*)	....	....	....	....	....	....	0.00
1.0	(*)	2.40	2.90	1.70	0.60	0.00	0.10	0.00
"	(*)	4.00	3.50	2.10	0.60	0.30	0.40	0.00
"	(*)	....	2.00	....	....	....	....	0.00
Totals.....		38.40	27.65	17.55	2.50	1.35	1.30	0.00
Per cent.....		2.86	1.73	1.41	0.20	0.11	0.10	0.00
Osmotic pressure.		9.37	6.74	4.30	0.64	0.34	0.31	0.00

*Loss in rotation not determined.

The main object in view during the second period of the investigation was the development of the method—specifically, the suppression of *thermometer effects* and *dilution*—and hitherto the data of Series I to VIII have been arranged or discussed principally with reference to the progress made in that direction. The present chapter might properly

be concluded at this point. But, since the results of the measurements foreshadow much that was afterwards established by means of greater precision, it has been thought worth while to arrange them in Tables 37 to 39, with a view to ascertaining what general conclusions they suggest with reference to the osmotic pressure of cane-sugar solutions.

Section A of Table 37 gives all of the observed osmotic pressures of Series I to VIII, except those of the 0.05 and 0.25 concentrations of Series I; these concentrations are omitted, as they were abandoned after the first series. Section B gives the observed osmotic pressures of Section A, corrected for dilution proportional to the observed losses in rotation. Section C gives, for each experiment, the ratio of the corrected osmotic pressure to the calculated gas pressure of the solute.

TABLE 37.—*Cane sugar, Series I to VIII.* SECTION A. OBSERVED OSMOTIC PRESSURES.

Conc.	Series I. 17°–25°.	Series II. 20°–24°.	Series III. 0.12°–0.38°.	Series IV. 4°–5°.	Series V. 10°.	Series VI. 15°.	Series VII. 25°.	Series VIII. 20°.
0.1	2.37	2.58	2.45	2.40	2.43	2.47	2.56	2.53
"	2.44	2.62	2.45	2.40	2.44	2.48	2.56	2.52
"	.....	....	2.37	.....	.....	.....	.....	.....
"	.....	.....	2.39	.....	.....	.....	.....	.....
0.2	4.77	4.75	4.78	4.74	4.81	4.92	5.09	5.03
"	4.83	4.82	4.77	4.76	4.83	4.90	5.10	5.02
"	.....	4.88	.....	.....	.....	.....	.....	5.02
0.3	7.23	7.28	7.09	7.10	7.22	7.31	7.58	7.45
"	7.23	7.31	7.11	7.04	7.15	7.35	7.55	7.45
0.4	9.51	9.76	9.37	9.44	9.53	9.77	10.10	9.98
"	9.72	9.71	9.34	9.41	9.61	9.78	10.13	9.94
"	.....	.....	9.36	.....	.....	.....	.....	9.97
"	.....	.....	9.31	.....	.....	.....	.....	.....
0.5	12.02	12.28	11.66	11.79	11.96	12.29	12.75	12.49
"	12.17	12.41	11.73	11.85	12.02	12.29	12.71	12.49
"	.....	.....	11.89	....	.....	.....	.....	12.50
"	.....	.....	11.79	.....	.....	.....	.....	.....
0.6	14.34	14.82	14.12	14.41	14.53	14.91	15.43	15.18
"	14.57	15.00	14.11	14.45	14.55	14.81	15.41	15.22
"	.....	15.06	.....	.....	.....	.....	....	.....
0.7	16.79	17.38	16.55	16.73	17.10	17.42	18.03	17.83
"	17.02	17.32	16.71	16.85	17.08	17.36	18.02	17.85
"	.....	.....	.....	.....	.....	.....	.....	17.83
0.8	19.39	19.83	19.16	19.27	19.73	20.07	20.75	20.57
"	19.54	19.77	19.13	19.34	19.77	20.11	20.71	20.62
"	.....	.....	.....	.....	.....	.....	.....	20.62
0.9	21.89	22.35	21.92	22.07	22.28	22.97	23.71	23.36
"	.....	22.32	21.86	22.22	22.28	22.91	23.67	23.31
"	.....	.....	.....	.....	.....	.....	.....	23.27
1.0	24.80	24.83	24.53	24.52	25.08	25.39	26.33	26.12
"	24.39	24.78	24.54	24.53	25.03	25.44	26.39	26.13
"	24.50	.....	24.57	.....	.....	.....	.....	26.11

TABLE 37.—SECTION B. OBSERVED OSMOTIC PRESSURES CORRECTED FOR DILUTION.

Conc.	Series I. 17°–25°.	Series II. 20°–24°.	Series III. 0.12°–0.38°.	Series IV. 4°–5°.	Series V. 10°.	Series VI. 15°.	Series VII. 25°.	Series VIII. 20°
0.1	(*)	2.69	2.49	2.42	2.43	2.47	2.56	2.53
"	(*)	2.73	2.47	2.42	2.44	2.48	2.56	2.52
"	(*)	.....	2.38	.....	.....	.....	.....	.....
"	(*)	.....	2.41	.....	.....	.....	.....	.....
0.2	(*)	4.89	4.81	4.80	4.81	4.94	5.09	5.03
"	(*)	4.96	4.80	4.77	4.83	4.90	5.10	5.02
"	(*)	4.98	.....	.....	.....	.....	.....	5.02
0.3	(*)	7.38	7.19	7.16	7.22	7.31	7.58	7.45
"	(*)	7.43	7.13	7.10	7.15	7.35	7.55	7.45
0.4	(*)	9.92	9.48	9.50	9.53	9.77	10.10	9.98
"	(*)	9.98	9.46	9.59	9.61	9.78	10.13	9.94
"	(*)	.....	9.44	.....	.....	.....	.....	9.97
"	(*)	.....	9.39	.....	.....	.....	.....	.....
0.5	(*)	12.58	11.84	11.94	11.96	12.29	12.75	12.49
"	(*)	12.67	11.93	12.00	12.04	12.29	12.71	12.49
"	(*)	.....	12.02	.....	.....	.....	.....	12.50
"	(*)	.....	11.94	.....	.....	.....	.....	.....
0.6	(*)	15.44	14.37	14.51	14.53	14.91	15.43	15.18
"	(*)	15.42	14.38	14.60	14.55	14.81	15.41	15.22
"	(*)	15.46	.....	.....	.....	.....	.....	.....
0.7	(*)	17.96	16.91	16.94	17.13	17.44	18.05	17.83
"	(*)	17.81	16.96	17.15	17.08	17.37	18.04	17.85
"	(*)	.....	.....	.....	.....	.....	.....	17.83
0.8	(*)	20.57	19.50	19.61	19.77	20.11	20.75	20.57
"	(*)	20.68	19.48	19.65	19.80	20.14	20.76	20.62
"	(*)	.....	.....	.....	.....	.....	.....	20.62
0.9	(*)	22.83	22.34	22.44	22.37	23.04	23.75	23.36
"	(*)	22.67	22.29	22.59	22.37	22.98	23.75	23.31
"	(*)	.....	.....	.....	.....	.....	.....	23.27
1.0	(*)	25.43	25.21	24.91	25.23	25.39	26.35	26.12
"	(*)	25.74	25.37	25.02	25.18	25.51	26.49	26.13
"	(*)	.....	24.73	.....	.....	.....	.....	26.11
SECTION C. RATIOS OF CORRECTED OSMOTIC TO GAS PRESSURE OF SOLUTE.								
0.1	(*)	1.114	1.117	1.066	1.052	1.052	1.053	1.059
"	(*)	1.124	1.108	1.066	1.056	1.055	1.053	1.054
"	(*)	.....	1.067	.....	.....	.....	.....	.....
"	(*)	.....	1.081	.....	.....	.....	.....	.....
0.2	(*)	1.021	1.078	1.060	1.041	1.051	1.047	1.052
"	(*)	1.033	1.076	1.046	1.045	1.043	1.049	1.050
"	(*)	1.021	.....	.....	.....	.....	.....	1.050
0.3	(*)	1.031	1.076	1.055	1.043	1.037	1.040	1.039
"	(*)	1.031	1.067	1.046	1.033	1.043	1.036	1.039
0.4	(*)	1.032	1.064	1.049	1.031	1.039	1.039	1.044
"	(*)	1.036	1.061	1.060	1.040	1.040	1.042	1.040
"	(*)	.....	1.058	.....	.....	.....	.....	1.043
"	(*)	.....	1.054	.....	.....	.....	.....	.....
0.5	(*)	1.043	1.063	1.056	1.036	1.046	1.049	1.045
"	(*)	1.047	1.071	1.057	1.043	1.046	1.046	1.045
"	(*)	.....	1.079	.....	.....	.....	.....	1.046
"	(*)	.....	1.072	.....	.....	.....	.....	.....
0.6	(*)	1.060	1.075	1.067	1.050	1.058	1.058	1.059
"	(*)	1.061	1.076	1.069	1.051	1.051	1.057	1.061
"	(*)	1.063	.....	.....	.....	.....	.....	.....
0.7	(*)	1.060	1.084	1.070	1.060	1.061	1.061	1.066
"	(*)	1.052	1.087	1.083	1.057	1.057	1.060	1.067
"	(*)	.....	.....	.....	.....	.....	.....	1.066
0.8	(*)	1.063	1.094	1.084	1.070	1.070	1.067	1.076
"	(*)	1.068	1.093	1.086	1.072	1.072	1.067	1.078
"	(*)	.....	.....	.....	.....	.....	.....	1.076
0.9	(*)	1.044	1.114	1.102	1.077	1.090	1.085	1.086
"	(*)	1.037	1.111	1.106	1.077	1.087	1.085	1.084
"	(*)	.....	.....	.....	.....	.....	.....	1.082
1.0	(*)	1.051	1.132	1.100	1.092	1.081	1.084	1.093
"	(*)	1.060	1.139	1.106	1.090	1.086	1.090	1.093
"	(*)	.....	1.109	.....	.....	.....	.....	1.093

*Not corrected; dilution unknown.

Table 38 is a condensation of Sections A and B of Table 37. Section D gives, for each of the ten concentrations of solution, the mean observed osmotic pressure. Section E gives, for each concentration of solution, the mean of the corrected osmotic pressures.

TABLE 38.—*Cane sugar, Series I to VIII.*

SECTION D. MEAN OBSERVED OSMOTIC PRESSURES.

Conc.	Series I. 17°–25°.	Series II. 20°–24°.	Series III. 0.12°–0.38°.	Series IV. 4°–5°.	Series V. 10°.	Series VI. 15°.	Series VII. .25°.	Series VIII. 20°.
0.1	2.41	2.60	2.42	2.40	2.44	2.48	2.56	2.53
0.2	4.80	4.82	4.78	4.75	4.82	4.91	5.10	5.03
0.3	7.23	7.60	7.10	7.07	7.19	7.33	7.57	7.45
0.4	9.62	9.74	9.35	9.43	9.57	9.78	10.12	9.96
0.5	12.10	12.35	11.77	11.82	11.99	12.29	12.73	12.49
0.6	14.46	14.96	14.12	14.43	14.54	14.86	15.42	15.20
0.7	16.91	17.35	16.68	16.79	17.09	17.39	18.03	17.84
0.8	19.47	19.80	19.15	19.31	19.75	20.09	20.73	20.60
0.9	21.89	22.29	21.89	22.15	22.28	22.94	23.69	23.31
1.0	24.56	24.81	24.45	24.53	25.06	25.42	26.36	26.12
	SECTION E. MEAN CORRECTED OSMOTIC PRESSURES.							
0.1	(*)	2.71	2.44	2.42	2.44	2.48	2.56	2.53
0.2	(*)	4.94	4.81	4.79	4.82	4.92	5.10	5.03
0.3	(*)	7.41	7.16	7.13	7.19	7.33	7.57	7.45
0.4	(*)	9.95	9.44	9.55	9.57	9.78	10.12	9.96
0.5	(*)	12.63	11.93	11.97	12.00	12.29	12.73	12.49
0.6	(*)	15.44	14.38	14.56	14.54	14.86	15.42	15.20
0.7	(*)	17.89	16.94	17.05	17.11	17.41	18.05	17.84
0.8	(*)	20.63	19.49	19.63	19.79	20.13	20.76	20.60
0.9	(*)	22.75	22.32	22.52	22.37	23.01	23.75	23.31
1.0	(*)	25.59	25.10	24.97	25.21	25.45	26.42	26.12

*Not corrected; dilution unknown.

TABLE 39.—*Mean ratio of corrected osmotic to calculated gas pressure.*

Series.	Temperature.	Concentration.									
		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	degrees.										
I	17 to 25			(Series I not corrected. Dilution unknown.)							
II	20 24	1.119	1.025	1.031	1.034	1.045	1.061	1.056	1.066	1.041	1.056
III	0.12 0.38	1.093	1.077	1.071	1.059	1.071	1.076	1.086	1.094	1.113	1.127
IV	4 5	1.066	1.053	1.051	1.055	1.057	1.068	1.077	1.085	1.104	1.103
Means (I–IV) . . .		(1.093)	(1.052)	(1.051)	(1.049)	(1.058)	(1.068)	(1.073)	(1.082)	(1.086)	(1.095)
V	10	1.054	1.043	1.038	1.036	1.040	1.051	1.058	1.071	1.077	1.091
VI	15	1.054	1.047	1.040	1.040	1.046	1.055	1.059	1.071	1.089	1.083
VIII	25	1.057	1.050	1.039	1.042	1.045	1.060	1.066	1.077	1.084	1.093
VII	20	1.053	1.048	1.038	1.041	1.048	1.058	1.060	1.067	1.085	1.087
Means (V–VIII) .		(1.055)	(1.047)	(1.039)	(1.040)	(1.045)	(1.056)	(1.061)	(1.072)	(1.084)	(1.089)

Table 39 gives, for each concentration of solution, the mean of the ratios of the corrected osmotic pressures to calculated gas pressures. It is divided into two groups of four series each; and from the first of these

the data pertaining to Series I are omitted because the extent of the dilution in that series is unknown. Throughout the three remaining series of the first division the means of maintaining temperature were very imperfect, and the dilution of the cell contents, as determined by the loss in rotation, was large. These unsatisfactory conditions are reflected in the large variations in the ratios obtained at different temperatures for the individual concentrations of solution—that is, in the ratios which are placed in the several vertical columns.

Throughout the series of the second group, on the other hand, the temperatures maintained were constant, or very nearly so, and there was very little or no loss in concentration. The better conditions under which V to VIII were carried out are likewise reflected in the closer agreement of the ratios in the several vertical columns—the mean variation for all concentrations being 0.007, and the largest for any single concentration, 0.012. It is clear that any conclusions which may be drawn from the relations found in the table should be based upon the data in the second group only. An inspection of these will show that:

1. The mean ratios of osmotic to gas pressure for every concentration of solution, as well as all the individual ratios, are considerably above unity. This is also true throughout the first group. The observation that between 0° and 25°, the osmotic pressure of cane-sugar solutions is considerably higher than the calculated gas pressure of the solute has been amply confirmed by later measurements. It is not necessary, at the present time, to search for an explanation of this excessive osmotic pressure, but the fact that all ratios have been found to become unity at high temperatures suggests a concentration of the solutions through hydration.

2. The ratios, from concentration to concentration, are irregular, but, in general, they diminish from the 0.1 weight-normal solution, then show a tendency to become constant through the 0.2, 0.3, and 0.4 concentrations, and finally they rise again continuously through the 0.5 and all succeeding concentrations. The general trend is obviously as stated, though it is somewhat confusing in its details. Later investigations have shown that the ratio is relatively high in the 0.1 solution; markedly lower, but constant, through the 0.2, 0.3, and 0.4; higher again in the 0.5, and still higher in each succeeding concentration. This lack of constancy of ratio from concentration to concentration suggests, but does not prove, that the osmotic pressures of cane-sugar solutions do not conform to the law of Boyle.

3. The ratios at different temperatures are fairly constant for each concentration. Constancy in this respect is a test of conformity to the law of Gay-Lussac. It will be shown later that, between 0° and 25°, all solutions of cane sugar ranging in concentration from 0.1 to 1.0 weight-normal do obey this law.

CHAPTER VII.

GLUCOSE.

PRELIMINARY DETERMINATIONS OF OSMOTIC PRESSURE.

The three series of measurements of the osmotic pressure of glucose, which are to be reported in the present chapter, were each made concurrently with one or another of the eight preliminary series on cane sugar, which have been described in Chapter VI. Their principal purpose, like that of the earlier work upon cane sugar, was the development of the method.

It was apprehended that greater difficulty would be experienced in securing *solute-proof* membranes for glucose than for cane sugar, and such was found to be the case. It was not possible to decide, however, whether this was due to the easier penetration of the membranes by glucose, or to the fact that the membranes in cells containing glucose were (apparently) much more vigorously attacked by penicillium than those in cells containing cane sugar.

The manipulation and the facilities for the maintenance of temperature were precisely the same for glucose as for the cotemporary work upon cane sugar; and, since these have been fully described in connection with the latter, it will be necessary only to designate the chronological parallelisms of the work upon the two substances.

SERIES I.*

Series I (for glucose) and Series II (for cane sugar) were carried out during the same year and under the same conditions.

The material employed was the so-called "*Traubenzucker Kahlbaum.*" It was pulverized and freely aerated over calcium chloride by means of a current of dried air, in order to hasten the removal of the odor of alcohol. After this treatment, the material did not sensibly lose in weight when heated to a higher temperature in an air-bath. It melted quite sharply at 146°. Two determinations of carbon and hydrogen gave 40.03 and 40.04 instead of 39.98 per cent for the former, and 6.48 and 6.83 instead of 6.71 per cent for the latter.

The penicillium was not under good control at this time and its attacks upon the membranes were persistent and destructive throughout the whole series. Without doubt the results suffered somewhat, in point of accuracy, on that account.

*Measurements by H. N. Morse, J. C. W. Frazer and B. F. Lovelace. Am. Chem. Jour., XXXVII, 324.

The data of Series I are given, in a condensed form, in Table 40, under the following heads: Extreme bath temperature, mean bath temperature, percentage loss in rotation, osmotic pressure corrected for dilution, calculated gas pressure of solute, and ratio of corrected osmotic to calculated gas pressure.

TABLE 40.—*Glucose, Series I.*

Concentration.	Extreme temperature.	Mean temperature.	Loss in rotation.	Corrected osmotic pressure.	Calculated gas pressure.	Ratio.
	degrees.	*degrees.*	*p. ct.*			
0.1	23.90 to 24.40	24.10	3.70	2.39	2.42	0.988
"	25.00 25.20	25.10	0.00	2.42	2.43	0.996
0.2	24.00 24.20	24.10	0.94	4.76	4.85	0.981
"	24.70 25.20	24.93	0.94	4.77	4.86	0.981
0.3	22.20 22.30	22.20	0.00	7.12	7.22	0.986
"	23.30 23.60	23.48	0.64	7.17	7.25	0.989
0.4	26.80 27.00	26.90	0.48	9.70	9.78	0.992
"	26.60 26.70	26.60	0.48	9.65	9.77	0.988
0.5	21.75 21.90	21.86	1.94	12.07	12.03	1.003
"	23.80 24.50	24.17	1.16	12.00	12.12	0.990
0.6	23.30 22.70	22.57	3.76	14.56	14.46	1.007
"	22.35 22.45	22.40	1.96	14.32	14.40	0.994
"	22.30 22.40	22.30	0.32	14.29	14.45	0.997
0.7	22.20 22.32	22.26	2.54	16.82	16.85	0.998
"	25.30 25.60	25.43	2.82	16.96	17.04	0.996
"	22.70 22.70	22.70	1.69	16.75	16.88	0.992
0.8	23.00 23.00	23.00	2.76	19.27	19.31	0.998
"	23.10 23.50	23.28	1.74	19.16	19.33	0.991
"	23.60 23.70	23.64	1.74	19.25	19.35	0.993
0.9	23.70 24.10	23.80	1.45	21.64	21.80	0.993
"	22.50 22.70	22.58	1.00	21.49	21.70	0.990
"	23.00 23.10	23.10	0.66	21.63	21.74	0.995
1.0	22.00 22.30	22.20	0.91	24.12	24.08	1.002
"	22.60 22.70	22.60	0.91	24.00	24.11	0.995
"	22.10 22.10	22.10	1.72	24.03	24.07	0.998
						Mean = 0.994

Table 41 gives the extreme variations in temperature for each experiment.

TABLE 41.—*Glucose, Series I. Fluctuations in bath temperature.*

Concentration.	Variation.	Concentration.	Variation.	Concentration.	Variation.
	degrees.		*degrees.*		*degrees.*
0.1	0.50	0.5	0.15	0.8	0.00
"	0.20	"	0.70	"	0.40
0.2	0.20	0.6	0.40	"	0.10
"	0.50	"	0.10	0.9	0.40
0.3	0.10	"	0.10	"	0.20
"	0.30	0.7	0.12	"	0.10
0.4	0.20	"	0.30	1.0	0.30
"	0.10	"	0.00	"	0.10
				"	0.00
				Sum =	5.57
				Mean =	0.22

The sum of the variations in bath temperature was 5.57° and the mean was 0.22°. The corresponding values for the parallel cane-sugar series (II) were 4.35° and 0.21°, which shows that the success attained in maintaining temperature was about the same in glucose Series I as in cane-sugar Series II.

The sum of the rotations of all the solutions used in glucose Series I was 758.85°. The sum of all the losses was 8.60° or 1.13 per cent. The dilution in the companion cane-sugar series was 2.86 per cent, or 2.53 times as large as in the case of glucose.

The observed osmotic pressures have been corrected for all of the loss in rotation, though, as explained in the preceding chapter, the dilution which occurs when the cells are opened, if known, should be deducted. But, since the total dilution was only 1.13 per cent, and since certainly *less* than half of it occurred when the cells were opened, the results do not greatly suffer by the inclusion of the latter.

The striking features of Table 40 will be found in the last column, in which are given the ratios of osmotic to the calculated gas pressures of the solute. Considering the still undeveloped condition of the method by which they were obtained, these ratios are remarkably *uniform* throughout the whole series. The mean of all of them is 0.994, and the greatest divergences from this mean are +0.013 and −0.013. It will be recalled in this connection that, in the case of cane sugar, the ratios of osmotic to gas pressure varied considerably from concentration to concentration. The second noteworthy feature of these ratios is that they approach *unity*—quite as closely probably as the defects of the method at that time could be expected to permit. If the approximate correctness of the pressures given in Table 40 is established by later investigations, it will mean that, within the range of temperatures 22° to 25°, the osmotic pressure of glucose solutions obeys the laws both of Boyle and Gay-Lussac, since that is the only interpretation of the unit ratios of osmotic to gas pressure. It is not yet known whether this ratio will be confirmed for the temperatures in question, since the work at 25° has not been repeated under conditions insuring precision. It is already known, however, that *at 30°*, *40°*, and *50°* the ratio of osmotic to gas pressure *is* unity for solutions of glucose.

The molecular weight for glucose which is derived from the mean ratio 0.994—under the assumption that osmotic pressure obeys the laws of Boyle and Gay-Lussac—is 179.82 instead of 178.74.

In the case of cane sugar, Series I—*without correction*—gave a molecular weight of 341.41 (O = 16) instead of 342.22; while Series II—*after correction for the loss in rotation as inversion*—gave a molecular weight of 337.59 (H = 1) instead of 339.60. The excellent molecular weight which was *legitimately* derived from the results in glucose Series I was partly responsible for the pertinacity with which, for a time, the mis-

taken views regarding cane-sugar Series I and II were held—the views, namely, (1) that, not having found much invert sugar in Series I by the method of Fehling, the solutions had maintained their concentration; and (2) that, having found considerable loss in rotation in Series II, it was due to *inversion* caused by penicillium. The early errors of interpretation regarding cane-sugar Series I and II have been corrected in the preceding chapter; but, up to the present time, no good reason has appeared for questioning the general correctness of the results of glucose Series I as they are presented in Table 40.

Series II.*

Glucose Series II and cane-sugar Series III were carried out at about the same time and under identical conditions. It was sought in both to maintain a temperature as close as possible to 0°. The means which were employed for this purpose have been described in connection with the account which was given of the work in cane sugar Series III.

The material used was *Traubenzucker Kahlbaum*, but in the beginning it was distinctly less pure than that employed in Series I. After aerating the pulverized substance and allowing it to stand in an exhausted desiccator until it gave no reaction for alcohol, it was found to have a somewhat uncertain melting-point of 143°. Four determinations of carbon and hydrogen gave: for the former, 40.28, 40.26, 40.35, and 40.35 instead of 39.98 per cent; and for the latter, 6.60, 6.66, 6.62, and 6.69 instead of 6.71 per cent. A solution, containing 32.65 grams of the glucose in 100 cubic centimeters at 17.5°, gave a rotation of 101.45 instead of 100 saccharimetric degrees. Before using the material for the determination of osmotic pressure, it was four times recrystallized by precipitation from aqueous solution by alcohol. Thus purified, its melting-point was found to be 145° to 146° instead of 146°, and the standard solution gave a rotation of 100.5 saccharimetric degrees. Two analyses gave: for carbon, 40.09 and 39.96 instead of 39.98 per cent; and for hydrogen, 6.64 and 6.77 instead of 6.71 per cent.

The sum of all the fluctuations in bath temperature was 1.47° and the mean was 0.07°. In the parallel cane-sugar series (III) the sum was 2.81°, and the mean was 0.10°.

The sum of the rotation of all the solutions of glucose Series II was 552.90°. The sum of all the losses in rotation was 5.84°, or 1.06 per cent. In the companion cane-sugar series, the percentage loss in rotation was 1.73 per cent. The dilution in the glucose series was, therefore, less by 0.67 per cent than in that of cane sugar.

Except in the case of the 0.1 normal solution, the ratios of osmotic to gas pressure are quite uniform. In this respect glucose Series II,

*Measurements by H. N. Morse, J. C. W. Frazer, and F. M. Rogers. Am. Chem. Jour., xxxvii, 558.

like glucose Series I, differs strikingly from all of the eight cane-sugar series, in which the ratios differed from concentration to concentration. The mean ratio for the 0.1 normal solution is 1.076, while the mean ratio for the whole series is 1.058. It would be premature to discuss this apparent exception at the present time, but it may be noted in passing that a similar increase in the osmotic pressure of very dilute solutions, *when near their freezing-points*, has been observed in the case of cane sugar.

TABLE 42.—*Glucose, Series II.*

Concentration.	Extreme temperature.	Mean temperature.	Loss in rotation.	Corrected osmotic pressure.	Calculated gas pressure.	Ratio.
	degree.	*degree.*	*p. ct.*			
0.1	0.26 to 0.38	0.28	0.38	2.40	2.23	1.074
"	0.18 0.28	0.24	0.00	2.40	"	1.077
0.2	0.10 0.12	0.12	0.96	4.66	4.45	1.047
"	0.12 0.14	0.13	0.48	4.68	"	1.051
0.3	0.16 0.24	0.19	0.64	7.04	6.68	1.054
"	0.17 0.26	0.26	0.71	7.04	"	1.054
0.4	0.12 0.14	0.13	0.73	9.35	8.91	1.049
"	0.14 0.30	0.21	0.87	9.33	"	1.047
0.5	0.12 0.19	0.17	0.58	11.69	11.14	1.050
"	0.14 0.29	0.24	0.98	11.69	"	1.049
0.6	0.08 0.14	0.12	1.47	14.12	13.36	1.057
"	0.08 0.08	0.08	1.47	14.12	"	1.057
0.7	0.06 0.10	0.08	0.99	16.44	15.59	1.055
"	0.06 0.06	0.06	0.57	16.42	"	1.053
0.8	0.12 0.15	0.13	1.13	18.86	17.82	1.058
"	0.12 0.15	0.13	0.88	18.86	"	1.058
0.9	0.10 0.24	0.16	1.58	21.37	20.05	1.066
"	0.10 0.24	0.15	0.91	21.40	"	1.067
1.0	0.12 0.22	0.17	1.43	23.77	22.28	1.067
"	0.12 0.22	0.17	1.20	23.72	"	1.064
					Mean	= 1.058

The most noteworthy feature of the ratios is their high value as compared with the corresponding ratios of glucose Series I. The mean ratios of the two series are 0.994 and 1.058 respectively. The difference between them is about *6 per cent.* The only essential difference in the conditions under which the two series were carried out was that of *temperature*, Series I having been done at approximately 25° and Series II at approximately 0°. The decrease in ratio with rise in temperature suggests a hydration of the solute at lower temperatures, which diminishes or disappears when the temperature is raised. But this matter can be discussed more advantageously when more facts concerning glucose have been established, and in connection with similar conduct on the part of cane-sugar solutions.

SERIES III.*

Glucose III and cane sugar V were parallel series. Before they were undertaken, the means of maintaining temperature and the manipulation concerned in the closing and opening of the cells had been greatly improved, with corresponding reduction in temperature fluctuations and in dilution of the cell contents.

The material employed in Series III was the same as in glucose Series II.

TABLE 43.—*Glucose, Series III.*

Concentration.	Extreme temperature.	Mean temperature.	Loss in rotation.	Corrected osmotic pressure.	Calculated gas pressure.	Ratio.
	degrees.	*degrees.*	*p. ct.*			
0.1	10.10 to 10.10	10.10	0.96	2.38	2.31	1.036
"	10.20 10.20	10.20	0.00	2.39	"	1.034
0.2	10.40 10.40	10.40	0.00	4.78	4.63	1.032
"	10.20 10.20	10.20	0.00	4.74	4.61	1.028
0.3	10.00 10.00	10.00	0.00	7.11	6.92	1.027
0.4	10.10 10.20	10.15	0.00	9.50	9.24	1.028
"	10.10 10.20	10.15	0.00	9.54	"	1.032
0.5	10.05 10.30	10.18	0.00	11.91	11.55	1.032
"	10.00 10.20	10.10	0.00	11.90	11.54	1.031
0.6	10.00 10.20	10.10	0.00	14.30	13.85	1.032
"	10.00 10.00	10.00	0.00	14.31	13.84	1.034
0.7	10.00 10.10	10.05	0.56	16.70	16.16	1.033
"	10.00 10.10	10.05	0.00	16.69	"	1.033
0.8	10.00 10.15	10.08	0.25	19.04	18.46	1.031
"	10.00 10.00	10.00	0.00	19.05	"	1.032
0.9	10.00 10.20	10.10	0.34	21.39	20.78	1.036
"	10.00 10.00	10.00	0.45	21.38	20.77	1.029
1.0	10.00 10.10	10.05	0.30	23.79	23.08	1.031
"	10.00 10.10	10.05	0.41	23.80	"	1.031
						Mean = 1.031

The sum of all fluctuations in bath temperature was 1.60° and the mean variation was 0.08°. In the companion cane-sugar series, the mean variation was also 0.08°.

The sum of the rotations of all the solutions employed in glucose Series III was 541.70°, and the total loss was 1.05°, or 0.20 per cent. The loss in the corresponding cane-sugar series was also 0.20 per cent. The decline of the dilution from 1.06 per cent in glucose Series II to 0.20 per cent in Series III is a fair measure of the improvement which had been made in the manipulation of the cells. The decline in dilution in the case of the parallel cane-sugar series was from 1.73 to 0.20 per cent.

The ratios of osmotic to gas pressure in Series III are even more uniform throughout the whole range of concentration than are those of Series I and II. This uniformity of ratio, which is characteristic of

*Measurements by H. N. Morse and W. W. Holland. Am. Chem. Jour., XL, 1.

glucose solutions, but not of solutions of cane sugar—except at comparatively high temperatures—appears to signify that the osmotic pressure of glucose obeys the law of Boyle. Perfect uniformity of ratio at a given temperature means, of course, that the osmotic pressures are proportional to the concentration of the solutions, which is the form of Boyle's law as applied to solutions. But any extended discussion of this subject at the present time would be premature.

The essential facts connected with glucose Series I to III are summarized in Tables 44, 45, and 45*a*.

TABLE 44.—*Parallel series of glucose and cane sugar.*

	Glucose I.	Cane sugar II.	Glucose II.	Cane sugar III.	Glucose III.	Cane sugar V.
1. Mean variation in bath temperature.....	*degrees.* 0.22	*degrees.* 0.21	*degrees.* 0.07	*degrees.* 0.10	*degrees.* 0.08	*degrees* 0.08
2. Percentage dilution.....	1.13	2.86	1.06	1.73	0.20	0.20

TABLE 45.—*Glucose, Series I to III.*

Concentration.	Extreme variations in bath temperature.			Loss in rotation.		
	Series I.	Series II.	Series III.	Series I.	Series II.	Series III.
	degrees.	*degrees.*	*degrees.*	*degrees.*	*degrees.*	*degrees.*
0.1	0.50	0.12	0.00	0.20	0.02	0.05
"	0.20	0.10	0.00	0.00	0.00	0.00
0.2	0.20	0.02	0.00	0.10	0.10	0.00
"	0.50	0.02	0.00	0.10	0.05	0.00
0.3	0.10	0.08	0.00	0.00	0.10	0.00
"	0.30	0.09	....	0.10	0.11	....
0.4	0.20	0.02	0.10	0.10	0.15	0.00
"	0.10	0.16	0.10	0.10	0.18	0.00
0.5	0.15	0.07	0.25	0.50	0.15	0.00
"	0.70	0.15	0.20	0.30	0.25	0.00
0.6	0.40	0.06	0.20	0.15	0.55	0.00
"	0.10	0.00	0.00	0.60	0.45	0.00
"	0.10	....	....	0.10	....	....
0.7	0.12	0.04	0.10	0.90	0.35	0.20
"	0.30	0.00	0.10	1.00	0.20	0.00
"	0.00	....	....	0.60	....	....
0.8	0.00	0.03	0.15	1.10	0.45	0.10
"	0.40	0.03	0.00	0.70	0.35	0.00
"	0.10	....	....	0.70	....	....
0.9	0.40	0.14	0.20	0.65	0.70	0.15
"	0.20	0.14	0.00	0.45	0.40	0.20
"	0.10	....	....	0.30	....	....
1.0	0.30	0.10	0.10	0.45	0.70	0.15
"	0.10	0.10	0.10	0.45	0.58	0.20
"	0.00	....	....	0.85	....	....
Means.....	0.22	0.07	0.08	1.13	1.06	0.20

TABLE 45*a*.—*Glucose, Series I to III.*

Concentration.	Mean osmotic pressures.			Mean ratios of osmotic to gas pressure.		
	Series I. 22°–25°	Series II. 0.06°–0.38°	Series III. 10.00°–10.40°	Series I. 22°–25°	Series II. 0.06°–0.38°	Series III. 10.00°–10.40°
0.1	2.40	2.40	2.39	0.992	1.076	1.035
0.2	4.77	4.67	4.76	0.981	1.049	1.030
0.3	7.15	7.04	7.11	0.988	1.054	1.027
0.4	9.68	9.34	9.52	0.990	1.048	1.030
0.5	10.04	11.69	11.91	0.997	1.050	1.032
0.6	14.39	14.12	14.31	0.999	1.057	1.033
0.7	16.84	16.43	16.70	0.995	1.054	1.033
0.8	19.23	18.86	19.05	0.994	1.058	1.032
0.9	21.59	21.39	21.39	0.993	1.067	1.030
1.0	24.05	23.75	23.80	0.998	1.066	1.031
Means..	.....	.....	.....	0.994	1.058	1.031

CHAPTER VIII.

CANE SUGAR.

FINAL DETERMINATIONS OF OSMOTIC PRESSURE.

The determinations of osmotic pressure which were made after the method had been perfected as described in Chapters VI and VII are designated as "*final*," because they are believed to be in a high degree reliable. It is characteristic of them all that there was neither any material variation in bath temperature during any experiment, nor any dilution of the cell contents which could be detected by the polariscope. It is not meant thereby that we were able to maintain absolutely constant temperatures in the large baths which were employed. There were frequent fluctuations which amounted sometimes to 0.02°, but usually to not more than 0.01°. If the variation in bath temperature did not exceed 0.02° during an experiment, it was considered to have remained sufficiently constant. Occasionally accidents happened to the regulating devices, and the baths were temporarily thrown "off temperature" in consequence. If the difficulty was soon discovered and quickly remedied, the resulting fluctuation in bath temperature was small, and the experiment was saved by discarding all readings of pressure until the cell contents had had ample time to recover from any thermometer effects due to the accident. If the trouble occurred during the night and was not, therefore, discovered until the temperature of the bath had risen or fallen a considerable fraction of a degree, the determination was usually discarded. The most frequent cause of difficulty with the regulating devices was a temporary interruption of the main current at its source, i. e., at the power house.

The sugar which was employed for the "*preliminary*" determinations described in Chapters VI and VII was "rock candy," which was not purified by recrystallization. This material is known, however, to contain, as a rule, some mother liquor and to be otherwise impure, notwithstanding its fine appearance. Moreover, it had been observed that the material obtained from rock candy by reprecipitation gave somewhat higher pressures than had been obtained with the unpurified sugar. It was decided, therefore, to subject the sugar which was to be used for the "*final*" measurements to a thorough-going purification. The method employed was essentially that of Cohen and Commelin.* 150 pounds—approximately 70 kilograms—of the best rock candy were procured and subjected to the treatment described below. Kilogram quantities of it were dissolved, each in 500 c.c. of previously boiled distilled water which, when making

*Zeitschrift für physikalische Chemie, LXVI, 1.

the solutions, was warmed, but not to a temperature above 60°. The solution (sometimes thinned with a little alcohol) was filtered, and from the filtrate the sugar was precipitated by alcohol which had been distilled from lime—a few crystals of the purest sugar being used to start the precipitation. The precipitated sugar was collected on a perforated porcelain disk in the bottom of a glass funnel, and freed as perfectly as possible from mother liquor by means of the filter pump. The material was then transferred from the funnel to a porcelain dish and mixed to a thin paste with 85 per cent alcohol. Finally it was again filtered, and then nearly dried by drawing through it filtered air. The original rock candy and the product of the first crystallization will be designated hereafter by the letters *A* and *B*. The yield of *B* was 32 kilograms.

The various portions of *B* were thoroughly mixed and then resubjected to the treatment which has already been described, except that the product of the second precipitation was washed first with diluted ethyl alcohol and afterwards with warm methyl alcohol. The yield of the twice recrystallized sugar, which will be designated by the letter *C*, was about 16 kilograms.

A portion of *C* was again dissolved, reprecipitated, and washed with both ethyl and methyl alcohols. The product of the third precipitation will be designated by the letter *D*.

Combustions were made of all four products, namely *A*, the original rock candy; *B*, which had been precipitated once; *C*, twice; and *D*, three times. The results are given below in percentages of hydrogen and carbon.

TABLE 46.

	A.		B.		C.		D.	
	H	C	H	C	H	C	H	C
1	6.432	42.156	6.436	42.116	6.466	42.151	6.484	42.047
2	6.495	42.081	6.451	42.059	6.420	42.081	6.487	42.031
3	6.477	42.099	6.465	42.151	6.471	42.116	6.485	42.101
Mean	6.468	42.112	6.451	42.109	6.452	42.116	6.485	42.060
Theoretical	6.481	42.083	6.481	42.083	6.481	42.083	6.481	42.083
Differences	−0.013	+0.029	−0.030	+0.026	−0.029	+0.033	−0.004	−0.023

The differences between the percentages of hydrogen and carbon which were found and the theoretical values are all within the unavoidable errors of analysis, and there was, therefore, no reason to be discovered in the figures given above for regarding any one sample of the sugar purer than another. A determination of carbon and hydrogen does not, however, suffice for the detection of glucose or invert sugar in cane sugar; and evidence of the probable presence of reducing sugars could be discovered

in all the specimens by other means. Much time was spent in attempts to establish the limits within which these might be present. Finally, however, the whole question of the purity of the materials was referred to the Bureau of Standards at Washington. The report which was received from the Bureau is given below.

Sample A.—Reducing substances in terms of invert sugar, 0.08 per cent ± 0.005 per cent.

Sample B.—Reducing substances in terms of invert sugar, 0.01 per cent ± 0.005 per cent.

Sample C.—Polarization, 99.93°. Reducing substances in terms of invert sugar, 0.01 per cent ± 0.005 per cent.

Sample D.—Polarization, 99.95°. Reducing substances in terms of invert sugar, 0.005 per cent ± 0.005 per cent.

The material employed for the "final" determinations of osmotic pressure was that designated by the letter *C*, in which the Bureau of Standards had found 0.01 per cent of reducing sugar. The sample *D* which had been three times recrystallized was doubtless somewhat purer, but it was feared that the quantity of *D* in hand would not suffice for all the determinations which were to be made, and uniformity of material was of quite as much importance as absolute purity.

The baths which were devised for the regulation of temperature have been sufficiently described in Chapter III, and it will only be necessary to explain in the present chapter certain points as to their use in the measurement of pressure.

It has been stated elsewhere that the cells, whether in or out of use, are maintained at all times at the temperature at which they are to be employed for the determination of pressure. This statement is correct for all low and moderate temperatures. But when they are to be used at high temperatures, e. g., above 40°, it is necessary to maintain them at a temperature a little higher than that at which the measurements are to be made, in order to compensate the cooling effects of exposure while the cells are being filled and closed.

The same is also true of the solutions. They are made up at the temperature of the room, and then cooled or warmed, as the case may require, in closed flasks, in the baths. The baths which are used for such purposes are maintained at the temperature at which measurements are to be made, if the temperature in question is a low or moderate one; otherwise, at a slightly higher temperature. The amount of the provision which is thus made for the cooling effect of exposure while filling the cells is entirely a matter of judgment and experience. The mercury in the manometers is always at the temperature of the room when the cells are filled, and its subsequent expansion in a bath of higher temperature must be taken into account; for this partially compensates any contraction of the solution

when its temperature falls from a higher level to that of the bath. Hence it is always intended, when working at high temperatures, to have the solution a little too hot when the cell goes into its final bath. It is not possible, however, to regulate the temperature conditions so perfectly that, after filling a cell and introducing it into the bath, the contraction of the solution will exactly balance the expansion of the mercury in the manometer. For that reason the cells are often placed in a so-called "preliminary bath" which is more accessible and less elaborate than that in which the measurements of pressure are made; and they are there observed while coming to temperature. If the observed pressures are considerably above the approximately known osmotic pressures, small portions of the solutions are allowed to escape from the cells. If, on the other hand, they are much below the true osmotic pressures for the given temperature, an additional mechanical pressure is brought upon the contents of the cells. When the temperature of the cells and their contents has finally reached that of the bath, the pressures should be very nearly equal to the true osmotic pressures of the solutions; since, otherwise, the inclosed solutions must suffer some concentration or dilution. The supplementary process of pressure-adjustment, described above, can not be dispensed with in high-temperature work. At moderate and low temperatures, sufficiently close adjustments of pressure can usually be secured at the time of closing the cells; that is, the probable changes in the volumes of the solutions and of the mercury in the manometers can be more accurately estimated. Nevertheless, even at low and moderate temperatures, the cells are carefully watched until it is certain that no further adjustments of pressure will be necessary in order to prevent a sensible change in the concentration of the solutions. The pressures to which the cells are adjusted before placing them in the final bath, or leaving them to come undisturbed to equilibrium, are known as "*initial*" pressures. They are, of course, only temporary values.

It has been proved by a large number of experiments that it is immaterial from which direction the final equilibrium pressure is approached, i. e., whether from a higher or lower initial pressure. It is only necessary that the interval between the initial and final pressures shall not be sufficient to produce —through change in the volume of the cell contents—a sensible concentration or dilution of the inclosed solution. In some series of measurements, it has been customary to so adjust the initial pressures in duplicate determinations that the equilibrium pressure was approached in one instance from above and in the other from below.

The importance of demonstrating that a solution has maintained its original concentration throughout a measurement of pressure can not be over-emphasized; accordingly, whenever a cell has been filled and closed, a part of the solution has been reserved for comparison, with respect to concentration, with the solution which was removed from the cell at the close of the experiment. In all the measurements recorded in the present

chapter—except one which is introduced to illustrate concentration in the cell—the two portions of the solutions were found to have identical rotations. In other words, all experiments in which the solutions were found to have suffered a change in concentration have been discarded. Whenever a gain or loss in concentration has occurred in the course of the work, it has usually been due to a faulty adjustment of the initial pressure, i. e., the interval between it and the final pressure has been left too large. The osmotic pressures of solutions whose concentration has changed in the cells are readily correctible, if one could only *prove* that the cells have not leaked. But the one certain proof that no solute has escaped through the membrane is the fact that the solution taken from the cell at the close of an experiment has the same concentration as the one which was put into it in the beginning. All other demonstrations of the integrity of the membrane have one or more weak points.

It will be seen that the possibility of a sensible dilution or concentration of the solution in the cell depends on the relation of the nitrogen volumes at *initial* and at *equilibrium* pressures. If the difference between these is very small as compared with the volume of the solution, there can be no material change in concentration. It follows that, so far as actual pressures are concerned, the preliminary adjustments of pressure must be much closer in the case of dilute than in that of concentrated solutions; moreover, that the difference between initial and final pressures must be made smaller when manometers of large capacity are used, than when those with only moderate gas volumes are employed. Since the cells all have a capacity of about 20 c.c., it is only necessary, when adjusting the initial pressure, to consider whether the subsequent contraction or expansion of the nitrogen will constitute an appreciable fraction of that volume.

The work included in the present chapter required three years for its completion. The number of measurements reported is 270. The average rate of progress was, therefore, 90 determinations per year, or 10 for each working month. It is to be remembered in this connection, however, that the labor required for the mere measurement of osmotic pressure is insignificant when compared with that which must be bestowed upon the cells, the membranes, and the manometers during the intervals between measurements. If the measurements reported in the present chapter were arranged in a strictly chronological order, it would be observed that a cell, once used, reappears only after a long interval.

It was intended, in the beginning, to carry the measurement of the osmotic pressure of cane sugar from 0° to 100°, or as near to the latter temperature as possible. The temperature-intervals selected were 5° between 0° and 30°, and 10° between 30° and 100°. The work progressed steadily until the temperature of 80° was reached, when it was necessary to discontinue the measurements for the three summer months. The cells were allowed to cool down to the temperature of the air and were then placed in thymol water to soak through the summer. No serious

consequences to the cells were apprehended from this treatment; for in all previous work at moderate and low temperatures it had been found that—provided adequate measures were taken to prevent infection—the membranes were greatly improved by the customary summer soaking in water free from electrolytes. We were, therefore, wholly unprepared for the calamity which resulted (apparently) from too rapid cooling of the membranes from 80° to the temperature of the air. On resuming work in the fall, it was found that none of the membranes would sustain the full osmotic pressures of the solutions either at high or moderate temperatures. More than three months were spent in applying all the known means for the restoration and improvement of membranes, but to no purpose. None of them could be made to measure pressure at any temperature. It was evident that the material of the membranes had undergone some change in structure which robbed them, at least to a great extent, of their semipermeable character. Moreover, it was to be inferred from the impossibility of building up good new membranes in the presence of the old ones, that probably a similar transformation was quickly *induced* in all newly deposited membrane material.

Having found that cells which had formerly been in excellent condition for work at high temperatures could not be restored to a usable condition, they were consigned to a solution of thymol in order to test the effect of prolonged soaking in water. It was then necessary to begin again at the bottom, that is, to make new cells, to build up in them membranes at some moderate temperature, and afterward to perfect these membranes at higher and higher temperature-intervals. The preparation of the clays, and the making, burning, and glazing of the cells require considerable time, but by no means as much as the "training" of the membranes for work at high temperatures. For that purpose it is necessary to deposit the first membranes at a low or moderate temprature, probably not above 30°, and then to develop them at that temperature until they are found to measure osmotic pressure satisfactorily. Though measuring perfectly at 30°, they will be found defective at 40°, and must be again developed at the latter temperature, etc. The cells with which the work reported in this chapter is to be resumed at 70° are now (15 months after beginning their manufacture) measuring satisfactorily at 50°.

In the following statement of the results obtained between 0° and 80°, the few data which accompany each of the 270 records of observed pressures, namely, the cell used, the resistance of the membrane, and the "initial" pressure, are included because they serve to illustrate many of the points which have been made in previous chapters. After these, are given the *mean* daily pressures, beginning with the day on which the pressure was supposed to have reached a close approximation to equilibrium. Several readings were made each day, and it is the mean of all of these which is to be understood by the term "*mean* daily pressure." Between 0° and 25° it was customary to correct the mean of the total pressures of

each day by the mean barometric pressure for the given 24 hours. But between 30° and 80° the mean daily *total* pressures are recorded, and the correction for atmospheric pressure is applied by deducting, from the mean of all the mean daily total pressures, the mean barometric pressure of the whole time the cells were under observation. This change in practice was due to the fact that, as the membranes grow older, the duration of barometer effects, as well as of thermometer effects, increases. No confusion will result from the change in the form of stating results, if it is remembered that "total" pressure means osmotic plus atmospheric pressure, while "osmotic" pressure means total observed minus atmospheric pressure.

TABLE 47.—*Determinations of osmotic pressure at 0°.*

(Measurements by H. N. Morse, J. C. W. Frazer, and E. G. Zies.)

[W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.]

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily osmotic pressure.					Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
						Second day.	Third day.	Fourth day.	Fifth day.	Mean osmotic pressure.		
0.1 W. N. S. at 0°	1	K_3	545,000	13	2.20	2.461	2.456	.....	.....	2.460	2.462	1.106
C. G. P. 2.227...	2	K_3	224,000	6	2.00	2.465	2.460	.....	.....	2.464		
	3	K_3	226,000	6	2.30	2.463	2.460	.....	.....	2.463		
0.2 W. N. S. at 0°	1	Z_3	290,000	5	4.46	4.719	4.719	.....	.....	4.719	4.722	1.061
C. G. P. 4.453...	2	Q_2	220,000	6	4.70	4.731	4.727	.....	.....	4.730		
	3	K_3	193,000	6	4.50	4.715	4.720	.....	.....	4.717		
	4	M_3	278,000	6	4.60	4.726	4.727	.....	.....	4.726		
0.3 W. N. S. at 0°	1	M_3	224,000	11	6.75	7.083	7.074	.....	.....	7.078	7.085	1.061
C. G. P. 6.680...	2	M_3	224,000	11	7.0	7.113	7.106	7.102	.....	7.107		
	3	M_3	185,000	6	7.0	7.068	7.074	.....	.....	7.071		
0.4 W. N. S. at 0°	1	D_3	236,000	13	9.51	9.440	9.460	.....	.....	9.450	9.442	1.060
C. G. P. 8.906...	2	E_3	183,000	6	9.10	9.425	9.434	9.440	.....	9.435		
0.5 W. N. S. at 0°	1	M_3	160,000	11	11.80	11.914	11.912	11.890	.....	11.907	11.895	1.068
C. G. P. 11.133..	2	E_3	140,000	6	11.70	11.866	11.884	11.912	.....	11.882		
0.6 W. N. S. at 0°	1	E_3	151,000	6	14.02	14.364	14.370	.....	.....	14.367	14.381	1.0765
C. G. P. 13.359..	2	Q_3	212,000	11	14.389	14.389	14.402	.....	.....	14.395		
0.7 W. N. S. at 0°	1	M_3	515,000	5	16.82	16.888	16.875	.....	.....	16.881	16.886	1.083
C. G. P 15.586..	2	D_3	280,000	6	16.59	16.902	16.892	16.876	.....	16.891		
0.8 W. N. S. at 0°	1	H_3	366,000	5	19.10	19.485	19.496	19.478	.....	19.486	19.476	1.093
C. G. P. 17.812..	2	D_3	550,000	11	19.01	19.448	19.495	19.470	19.452	19.466		
0.9 W. N. S. at 0°	1	F_3	550,000	11	21.45	22.163	22.135	.....	.....	22.149	22.118	1.104
C. G. P. 20.04...	2	D_3	160,000	5	21.78	22.077	22.106	22.086	.....	22.087		
1.0 W. N. S. at 0°	1	D_3	180,000	20	24.35	24.883	24.878	24.864	.....	24.878	24.825	1.115
C. G. P. 22.265..	2	D_3	555,000	11	24.63	24.762	24.798	24.776	.....	24.774		

It will be seen that the equilibrium pressure was reached in many cases on the second day; in others, on the third day; and in some, only after several days. This apparent inconsistency has been explained in a former chapter as due, principally, to the varying ages of the membranes; it having been observed that, as a membrane grows older, the solvent passes through it more slowly. There are other minor causes of differences in the

activity of membranes, but they need not be discussed in the present connection. In many cases, the record could have been begun earlier than it was, but there is need of caution in the measurement of pressure with "slow" cells, because of the persistence of thermometer effects in them. There is always some danger, when using slow cells, that a thermometer effect may be mistaken for an equilibrium pressure.

TABLE 48.—*Determinations of osmotic pressure at 5°.*

(Measurements by H. N. Morse, W. W. Holland, and E. E. Gill.)

[W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.]

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily osmotic pressure.						Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
						First day.	Second day.	Third day.	Fourth day.	Fifth day.	Mean osmotic pressure.		
0.1 W. N. S. at 5°	1	K_2	366,000	13	2.30	.....	2.455	2.449	.....	.....	2.452	2.452	1.082
C. G. P. 2.267.	2	L_2	550,000	6	2.39	.....	2.453	2.449	.....	.....	2.451		
	3	J_2	228,000	13	2.36	.....	2.454	2.452	.....	.....	2.453		
0.2 W. N. S. at 5°	1	F_2	565,000	6	4.55	.....	.....	4.815	4.810	.....	4.812	4.818	1.063
C. G. S. 4.535...	2	J_3	270,000	9	4.70	.....	4.838	4.822	.....	.....	4.825		
0.3 W. N. S. at 5°.	1	J_3	366,000	6	5.66	.....	7.189	7.186	.....	.....	7.187	7.198	1.058
C. G. P. 6.802..	2	K_2	224,000	9	6.89	.....	.....	7.213	7.198	.....	7.209		
0.4 W. N. S. at 5°	1	F_2	550,000	13	7.27	.....	.....	9.622	9.624	.....	9.623	9.608	1.059
C. G. P. 9.07..	2	E_2	550,000	22	8.79	.....	9.591	9.577	.....	.....	9.584		
	3	K_2	550,000	9	9.28	.....	9.644	9.631	9.517	.....	9.617		
0.5 W. N. S. at 5°	1	H_2	500,000	9	12.00	.....	12.10	12.10	12.09	.....	12.10	12.10	1.067
C. G. P. 11.34..	2	E_2	550,000	13	10.74	.....	12.11	12.09	.....	.....	12.10		
0.6 W. N. S. at 5°	1	J_3	360,000	11	10.28	.....	14.611	14.597	.....	.....	14.604	14.605	1.074
C. G. P. 13.604.	2	L_2	370,000	20	13.59	.....	14.605	14.608	.....	.....	14.606		
0.7 W. N. S. at 5°	1	M_2	275,000	9	15.51	.....	17.228	17.207	.....	.....	17.217	17.206	1.084
C. G. P. 15.872.	2	J_3	270,000	6	16.00	.....	17.191	17.198	.....	.....	17.194		
0.8 W. N. S. at 5°	1	J_3	275,000	20	19.50	.....	19.797	19.795	19.793	19.793	19.795	19.822	1.093
C. G. P. 18.139.	2	B_2	550.000	9	16.61	.....	19.849	19.850	.....	.....	19.849		
0.9 W. N. S. at 5°	1	B_2	500,000	9	17.11	.....	.....	22.46	22.53	22.53	22.51	22.478	1.102
C. G. P. 20.406.	2	Q_2	550,000	20	22.06	.....	.....	22.448	22.439	.....	22.443		
	1	F_2	1,000,000	21	18.56	.....	25.31	25.29	25.30	.....	25.30	25.28	1.115
	2	S_2	550,000	20	20.12	.....	.....	25.29	25.31	.....	25.30		
1.0 W. N. S. at 5°	3	K_2	1,100,000	9	21.83	25.32	25.31	25.26	.....	.....	25.30		
C. G. P. 22.67..	4	J_3	1,000,000	21	20.15	25.23	25.25	25.24	.....	.....	25.24		
	5	G_2	550,000	22	20.91	.....	25.26	25.25	.....	.....	25.26		

The length of the record which the cells were allowed to make, after having reached equilibrium pressure, varies in general from 2 to 15 days. In one case—that of the 0.5 weight-normal solution at 15°—the record was prolonged to 60 days, in order to test the endurance of the membrane. As a rule, however, the length of time a cell was allowed to continue its record depended principally upon the activity of the membrane. If the cell was slow in coming to equilibrium, it was allowed to remain longer in the bath, in order to lessen the errors due to thermometer and barometer effects. Sometimes a cell was allowed to continue its record simply because its manometer was not needed for another cell.

TABLE 49.—*Determinations of osmotic pressure at 10°.*

Measurements by H. N. Morse, W. W. Holland, and W. M. Clark. W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily osmotic pressure.								Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
						First day.	Second day.	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.	Eighth day.	Mean osmotic pressure.	
	1	K_3	160,000	13	2.35	.....	2.495	2.491	.....	.....	.....	.....	.....	2.494	
0.1 W. N. S. at 10°	2	N_3	133,000	11	2.40	2.500	2.495	.....	.....	.....	.....	.....	.....	2.496	
C. G. P. 2.308....	3	O_3	151,000	20	2.43	2.492	2.505	2.508	.....	.....	.....	.....	.....	2.502	2.498 1.082
	4	J_3	176,000	6	2.41	.....	2.501	2.495	.....	.....	.....	.....	.....	2.498	
0.2 W. N. S. at 10°	1	H_3	100,000	13	4.73	.....	4.892	4.889	.....	.....	.....	.....	.....	4.890	
C. G. P. 4.616....	2	I_3	125,000	20	4.13	.....	4.898	4.891	.....	.....	.....	.....	.....	4.896	4.893 1.060
0.3 W. N. S. at 10°	1	F_3	150,000	M	8.00	.....	.....	.....	.....	7.325	7.319	7.347	7.337	7.332	
C. G. P. 6.925....	2	E_5	220,000	9	7.5	.....	.....	.....	.....	7.324	7.353	7.346	7.324	7.337	7.334 1.059
0.4 W. N. S. at 10°	1	D_3	160,000	21	8.76	.....	9.788	9.795	9.792	.....	.....	.....	.....	9.791	
C. G. P. 9.233....	2	O_3	150,000	9	9.38	.....	9.789	9.780	9.793	.....	.....	.....	.....	9.790	9.790 1.060
0.5 W. N. S. at 10°	1	J_3	140,000	24	12.91	.....	12.298	12.298	12.298	.....	.....	.....	.....	12.298	
C. G. P. 11.541...	2	F_3	181,000	15	10.67	.....	.....	12.299	12.292	.....	.....	.....	.....	12.296	12.297 1.066
0.6 W. N. S. at 10°	1	H_3	78,000	15	13.58	.....	14.858	14.854	.....	.....	.....	.....	.....	14.856	
C. G. P. 13.849...	2	J_3	112,000	20	14.63	.....	14.855	14.854	.....	.....	.....	.....	.....	14.854	14.855 1.073
0.7 W. N. S. at 10°	1	F_3	278,000	20	16.73	.....	17.478	17.491	.....	.....	.....	.....	.....	17.488	
C. G. P. 16.157...	2	P_3	191,000	9	17.25	17.530	17.514	.....	.....	.....	.....	.....	.....	17.518	17.503 1.083
0.8 W. N. S at 10°	1	F_3	220,000	20	17.60	.....	20.161	20.143	.....	.....	.....	.....	.....	20.152	
C. G. P. 18.466...	2	L_3	234,000	20	18.72	.....	20.159	20.179	20.159	.....	.....	.....	.....	20.169	20.161 1.092
0.9 W. N. S. at 10°	1	F_3	220,000	9	19.45	.....	22.914	22.909	.....	.....	.....	.....	.....	22.911	
C. G. P. 20.774...	2	B_3	138,000	21	19.02	.....	22.860	22.856	.....	.....	.....	.....	.....	22.857	22.884 1.102
1.0 W. N. S. at 10°	1	F_3	550,000	6	23.83	.....	.....	25.714	25.694	.....	.....	.....	.....	25.704	
C. G. P. 23.082..	2	B_3	220,000	20	22.46	.....	.....	25.686	25.670	.....	.....	.....	.....	25.682	25.693 1.113

TABLE 50.—*Determinations of osmotic pressure at 15°.*

Measurements by H. N. Morse, W. W. Holland, and C. N. Myers. W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily osmotic pressure.										
						First day.	Second day.	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.	Eighth day.	Ninth day.	Tenth day.	Eleventh day.
	1	F_3	225,000	20	2.4	.....	.....	.....	.....	2.551	2.553	2.544	2.540	.....	.....	.....
0.1 W. N. S. at 15°	2	Ni_2	70,000	9	2.466	.....	.....	2.528	2.538	2.538	2.535	.....	.....	.....	.....	.....
C. G. P. 2.349....	3	Ni_5	104,000	M	2.315	.....	2.544	2.547	2.536	2.537	.....	.....	.....	.....	.....	.....
	4	Ni_2	112,000	9	2.5	.....	2.532	2.535	2.548	2.545	2.546	2.538	2.535	2.530	.....	.....
0.2 W. N. S. at 15°	1	I_3	190,000	6	4.6	.....	.....	.....	.....	.....	.....	.....	.....	.....	4.994	4.978
C. G. P. 4.698....	2	R_3	550,000	22	5.03	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.3 W. N. S. at 15°	1	C_5	230,000	6	7.3	.....	.....	.....	7.465	7.463	7.466	.....	.....	.....	.....	.....
C. G. P. 7.047....	2	T_3	110,000	M	7.68	.....	.....	.....	.....	.....	.....	7.481	7.498	7.498	7.465	.....
0.4 W. N. S. at 15°	1	M_3	150,000	24	9.92	.....	.....	.....	9.920	9.952	9.979	9.949	.....	.....	.....	.....
C. G. P. 9.396....	2	N_3	160,000	6	9.86	.....	.....	9.937	9.947	9.971	9.931	.....	.....	.....	.....	.....
0.5 W. N. S. at 15°	1	F_5	160,000	15	12.563	.....	.....	12.563	12.575	12.565	12.558	12.566	.....	.....	.....	.....
C. G. P. 11.745...	2*	C_5	100,000	24	12.50	.....	12.522	.....	.....	.....	.....	.....	.....	.....	12.524	.....
0.6 W. N. S. at 15°	1	A_5	160,000	9	14.17	15.148	15.149	15.126	15.125	15.115	15.130	15.128	15.123	15.117	15.116	.....
C. G. P. 14.094. .	2	A_5	140,000	20	14.569	.....	.....	.....	15.185	15.162	15.149	15.152	.....	.....	.....	.....
0.7 W. N. S. at 15°	1	Z_3	565,000	9	16.50	.....	.....	17.819	17.820	17.824	.....	.....	.....	.....	.....	.....
C. G. P. 16.443. .	2	M_3	220,000	24	17.2	.....	17.811	17.827	17.797	17.797	.....	.....	.....	.....	.....	.....
	1	Z_3	555,000	9	19.5	.....	20.500	20.539	20.554	.....	.....	.....	.....	.....	.....	.....
0.8 W. N. S. at 15°	2	H_5	110,000	22	19.3	.....	.....	.....	20.505	20.531	20.539	.....	.....	.....	.....	.....
C. G. P. 18.792...	3	E_5	150,000	9	19.6	.....	.....	20.550	20.545	20.539	20.557	.....	.....	.....	.....	.....
0.9 W. N. S. at 15°	1	T_3	185,000	9	20.5	.....	23.325	23.321	23.311	23.300	.....	.....	.....	.....	.....	.....
C. G. P. 21.141...	2	R_3	330,000	20	22.711	.....	.....	.....	23.338	23.309	23.268	.....	.....	.....	.....	.....
1.0 W. N. S. at 15°	1	G_3	370,000	9	26.05	.....	26.212	26.194	26.207	.....	.....	.....	.....	.....	.....	.....
C. G. P. 23.49....	2	D_3	355,000	15	26.00	.....	.....	26.182	26.180	26.162	.....	.....	.....	.....	.....	.....

*The daily records of this experiment will be found in Chapter IV, page 93, Table 5.

TABLE 50.—*Determinations of osmotic pressure at 15°*—Continued.

	Observed mean daily osmotic pressure.													Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	Twelfth day.	Thirteenth day.	Fourteenth day.	Fifteenth day.	Sixteenth day.	Seventeenth day.	Eighteenth day.	Twentieth day.	Thirtieth day.	Fortieth day.	Fiftieth day.	Sixtieth day.	Mean osmotic pressure.		
0.1 W. N. S. at 15°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2.547		
C. G. P. 2.349	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2.535	2.540	1.082
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2.541		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2.538		
0.2 W. N. S. at 15°	4.974	4.979	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	4.981	4.985	1.061
C. G. P. 4.698	5.003	4.996	5.000	4.988	4.992	4.974	4.973	.....	.....	.....	.....	.....	4.988		
0.3 W. N. S. at 15°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	7.465	7.476	1.061
C. G. P. 7.047	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	7.486		
0.4 W. N. S. at 15°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	9.950	9.949	1.059
C. G. P. 9.396	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	9.947		
0.5 W. N. S. at 15°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	12.565	12.549	1.068
C. G. P. 11.745	.....	.....	.....	.....	.....	.....	.....	12.527	12.535	12.529	12.552	12.522	12.533		
0.6 W. N. S. at 15°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	15.128	15.144	1.073
C. G. P. 14.094	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	15.160		
0.7 W. N. S. at 15°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	17.821	17.815	1.083
C. G. P. 16.443	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	17.808		
0.8 W. N. S. at 15°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	20.533		
C. G. P. 18.792	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	20.525	20.535	1.093
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	20.548		
0.9 W. N. S. at 15°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	23.314	23.305	1.102
C. G. P. 21.141	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	23.296		
1.0 W. N. S at 15°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	26.206	26.189	1.115
C. G. P. 23.49	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	26.171		

TABLE 51.—*Determinations of osmotic pressure at 20°.*

Measurements by H. N. Morse, W. W. Holland and J. L. Carpenter. W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily osmotic pressure.								
						First day.	Second day	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.	Eighth day.	Ninth day.
0.1 W. N. S. at 20° C. G. P. 2.39..	1	T_3	350,000	9	2.1	.....	.....	2.595	2.583	.....	.....	.....	.....	.....
	2	I_3	150,000	15	2.2	.....	.....	2.590	2.590	.....	.....	.....	.....	.....
0.2 W. N. S. at 20° C. G. P. 4.780..	1	R_3	100,000	20	4.6	.....	.....	5.057	5.052	.....	.....	.....	.....	.....
	2	Q_3	180,000	15	4.8	.....	.....	.....	5.067	5.065	.....	.....	.....	.....
	3	A_5	140,000	9	4.89	.....	.....	.....	.....	.....	.....	.....	.....	5.080
	4	G_3	120,000	24	5.03	.....	.....	.....	5.052	5.080	5.078	5.065	5.060	5.054
	5	E_5	160,000	15	5.05	.....	.....	.....	.....	5.093	5.079	5.081	5.076	5.074
0.3 W. N. S. at 20° C. G. P. 7.170..	1	I_3	214,000	20	7.5	.....	7.570	7.590	7.582	7.600	.....	.....	.....	.....
	2	T_3	535,000	9	7.8	.....	.....	7.626	7.618	7.627	.....	.....	.....	.....
	3	M_3	270,000	24	7.2	.....	.....	.....	.....	7.629	7.589	7.596	7.609	.....
0.4 W. N. S. at 20° C. G. P. 9.560..	1	G_3	110,000	9	10.2	.....	10.138	10.148	10.137	10.121	.....	.....	.....	.....
	2	I_3	285,000	9	10.4	.....	.....	.....	10.148	10.125	10.129	.....	.....	.....
0.5 W. N. S. at 20° C. G. P. 11.950.	1	G_3	367,000	15	11.50	12.741	12.754	12.738	12.735	.....	.....	.....	.....	.....
	2	R_3	162,000	15	12.55	.....	12.753	12.763	12.757	12.742	.....	.....	.....	.....
0.6 W. N. S. at 20° C. G. P. 14.339.	1	Z_3	550,000	6	15.00	.....	15.407	15.404	.....	.....	.....	.....	.....	.....
	2	O_3	350,000	5	14.1	.....	15.365	15.388	15.387	15.339	.....	.....	.....	.....
0.7 W. N. S. at 20° C. G. P. 16.729..	1	M_3	380,000	6	17.00	.....	18.106	18.183	18.142	18.110	.....	.....	.....	.....
	2	D_3	380,000	5	17.10	.....	18.138	18.115	18.085	18.146	.....	.....	.....	.....
0.8 W. N. S. at 20° C. G. P. 19.119.	1	Z_3	570,000	5	19.00	.....	20.942	20.914	.....	.....	.....	.....	.....	.....
	2	Z_3	275,000	24	19.30	.....	20.900	20.879	20.892	20.861	.....	.....	.....	.....
	3	E_3	140,000	9	19.41	.....	.....	20.907	20.857	20.866	20.922	20.922	20.918	.....
	4	D_5	250,000	6	20.50	.....	.....	.....	20.921	20.907	20.891	20.912	20.915	.....
0.9 W. N. S. at 20° C. G. P. 21.509.	1	D_3	550,000	15	20.4	.....	23.721	23.707	23.727	23.701	.....	.....	.....	.....
	2	A_5	250,000	22	20.65	.....	23.703	23.702	23.702	23.733	23.731	23.734	.....	.....
1.0 W. N. S. at 20° C. G. P. 23.899.	1	P	370,000	21	23.00	.....	26.629	26.654	26.663	26.645	.....	.....	.....	.....
	2	H_5	200,000	21	25.19	.....	26.620	26.645	26.644	26.598	.....	.....	.....	.....

TABLE 51.—*Determinations of osmotic pressure at 20°*—Continued.

	Observed mean daily osmotic pressure.													
	Tenth day.	Eleventh day.	Twelfth day.	Thirteenth day.	Fourteenth day.	Fifteenth day.	Sixteenth day.	Seventeenth day.	Eighteenth day.	Nineteenth day.	Twentieth day.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
0.1 W. N. S. at 20° C. G. P. 2.39.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2.589	2.590	1.084
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2.590		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	5.056		
0.2 W. N. S. at 20° C. G. P. 4.780.	5.086	5.071	5.060	5.061	5.070	5.062	5.058	5.035	5.033	5.035	5.042	5.066	5.064	1.062
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	5.058		
	5.061	5.064	5.083	5.085	.....	.....	.....	.....	.....	.....	.....	5.065		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	5.074		
0.3 W. N. S. at 20° C. G. P. 7.170.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	7.586	7.605	1.060
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	7.624		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	7.606		
0.4 W. N. S. at 20° C. G. P. 9.560.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	10.136	10.137	1.060
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	10.138		
0.5 W. N. S. at 20° C. G. P. 11.950.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	12.742	12.748	1.067
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	12.754		
0.6 W. N. S. at 20° C. G. P. 14.339.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	15.405	15.388	1.073
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	15.370		
0.7 W. N. S. at 20° C. G. P. 16.729.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	18.135	18.128	1.084
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	18.121		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	20.928		
0.8 W. N. S. at 20° C. G. P. 19.119.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	20.883	20.905	1.093
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	20.899		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	20.909		
0.9 W. N. S. at 20° C. G. P. 21.509.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	23.715	23.717	1.103
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	23.718		
1.0 W. N. S. at 20° C. G. P. 23.899.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	26.648	26.638	1.115
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	26.627		

TABLE 52.—*Determinations of osmotic pressure at 25°.*

Measurements by H. W. Morse, W. W. Holland, and C. N. Myers. W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily osmotic pressure.						
						First day.	Second day.	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.
0.1 W. N. S. at 25° C. G. P. 2.431	1	T_3	367,000	9	2.3	.....	.....	.....	2.633	2.642	.....	.....
	2	Ni_2	65,000	9	2.64	.....	2.629	2.635	.....	.....	.....	.....
0.2 W. N. S. at 25° C. G. P. 4.862	1	A_4	560,000	9	4.5	.....	5.156	5.153	.....	.....	.....	.....
	2	Q_3	180,000	9	4.5	.....	.....	.....	5.143	5.136	.....	.....
	3	M_3	535,000	11	4.7	.....	5.159	5.141	.....	.....	.....	.....
0.3 W. N. S. at 25° C. G. P. 7.292	1	K_3	280,000	20	7.15	.....	7.731	7.740	.....	.....	.....	.....
	2	R_2	92,000	20	6.9	.....	.....	7.731	7.708	.....	.....	.....
	3	5	200,000	6	7.3	.....	7.725	7.723	7.715	.....	.....	.....
	4	D_5	190,000	9	6.5	.....	.....	7.740	7.732	7.732	7.742	.....
0.4 W. N. S. at 25° C. G. P. 9.723	1	Q_4	540,000	9	10.129	.....	10.305	10.305	10.292	.....	.....	.....
	2	T_4	357,000	9	10.91	.....	10.298	10.285	10.312	10.285	.....	.....
0.5 W. N. S. at 25° C. G. P. 12.154	1	W_2	275,000	9	13.00	.....	12.871	12.948	12.937	12.920	12.918	.....
	2	T_2	285,000	9	12.51	.....	12.997	12.955	12.915	12.915	.....	.....
	3	Q_2	220,000	11	12.74	.....	12.912	12.951	.....	.....	.....	.....
	4	T_1	370,000	9	11.32	.....	12.984	12.935	.....	.....	.....	.....
0.6 W. N. S. at 25° C. G. P. 14.585	1	M_2	275,000	11	15.54	.....	15.623	15.619	15.628	15.659	.....	.....
	2	K_2	525,000	9	13.45	.....	.....	.....	15.602	15.627	15.624	15.606
	3	R_1	96,000	9	14.6	.....	.....	.....	15.632	15.619	15.619	15.609
	4	Q_1	110,000	15	14.85	.....	.....	.....	.....	.....	.....	15.654
0.7 W. N. S. at 25° C. G. P. 17.015	1	F_3	367,000	9	16.94	.....	.....	18.383	18.471	18.445	18.445	.....
	2	M_1	560,000	9	18.84	18.419	18.450	18.452	18.446	18.413	18.423	.....
0.8 W. N. S. at 25° C. G. P. 19.446	1	F_2	140,000	9	19.06	.....	21.281	21.253	21.256	21.281	21.280	21.258
	2	W_1	367,000	11	20.77	.....	.....	21.252	21.225	21.257	21.267	.....
0.9 W. N. S. at 25° C. G. P. 21.877	1	D_3	220,000	9	20.28	.....	24.127	24.148	24.120	24.102	24.125	.....
	2	B_5	550,000	9	22.2	.....	24.126	24.114	24.131	24.124	.....	.....
1.0 W. N. S. at 25° C. G. P. 24.308	1	E_2	550,000	15	26.95	.....	27.113	27.081	27.000	26.971	26.976	.....
	2	W_2	366,000	9	26.00	.....	.....	27.024	27.106	27.101	27.074	.....

TABLE 52.—*Determinations of osmotic pressure at 25°*—Continued.

	Observed mean daily osmotic pressure.									Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	Eighth day.	Ninth day.	Tenth day.	Eleventh day.	Twelfth day.	Thirteenth day.	Fourteenth day.	Fifteenth day.	Mean osmotic pressure.		
0.1 W. N. S. at 25° C. G. P. 2.431									2.638	2.634	1.084
									2.632		
0.2 W. N. S. at 25° C. G. P. 4.862									5.154	5.148	1.059
									5.139		
									5.150		
0.3 W. N. S. at 25° C. G. P. 7.292									7.735	7.729	1.060
									7.719		
									7.722		
									7.738		
0.4 W. N. S. at 25° C. G. P. 9.723									10.301	10.298	1.059
									10.295		
									12.919	12.943	1.065
0.5 W. N. S. at 25° C. G. P. 12.154									12.947		
									12.932		
									12.960		
0.6 W. N. S. at 25° C. G. P. 14.585									15.632	15.625	1.071
									15.615		
									15.620		
			15.623	15.628	15.629				15.634		
0.7 W. N. S. at 25° C. G. P. 17.015									18.436	18.435	1.083
									18.434		
0.8 W. N. S. at 25° C. G. P. 19.446	21.238	21.238	21.266	21.257	21.249	21.249	21.246	21.264	21.258	21.254	1.093
									21.250		
0.9 W. N. S. at 25° C. G. P. 21.877									24.126	24.126	1.102
									24.125		
1.0 W. N. S. at 25° C. G. P. 24.308									27.030	27.053	1.113
									27.076		

TABLE 53.—*Determinations of osmotic pressure at 30°.**

Measurements by H. N. Morse, W. W. Holland, and C. N. Myers. W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.												
						Second day.	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.	Eighth day.	Ninth day.	Tenth day.	Eleventh day.	Twelfth day.	Thirteenth day.	Fourteenth day.
	1	Ni_2	500,000	L_1	3.60	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.1 W. N. S. at 30°	2	K_3	250,000	15	3.51	3.482	3.468	3.463	3.465	3.462	3.466	3.462	3.466	3.474	3.475	3.475	.....	.....
C. G. P. 2.427..	3	F_5	209,000	24	3.42	.....	.....	3.468	3.461	3.458	3.461	3.464	3.469	3.472	3.476	3.480	3.483	.....
	4	L_5	159,000	15	3.45	3.461	3.465	3.479	3.484	3.484	3.481	3.485	3.491	3.484	3.489	3.492	3.484	.....
0.2 W. N. S. at 30°	1	C_5	120,000	9	6.152	.....	.....	6.049	6.031	6.039	6.046	6.045	6.045	6.044	6.046	6.046	6.046	.....
C. G. P. 4.943..	2	L_5	150,000	20	8.128	.....	.....	.....	6.056	6.052	6.050	6.046	6.042	6.040	6.038	6.041	6.041	6.039
0.3 W. N. S. at 30°	1	B_5	110,000	11	9.03	.....	.....	.....	.....	.....	.....	.....	8.660	8.654	8.640	8.646	8.646	8.638
C. G. P. 7.415..	2	H_5	110,000	24	8.63	.....	.....	.....	.....	.....	.....	.....	8.685	8.675	8.675	8.668	8.648	8.650
0.4 W. N. S. at 30°	1	L_5	110,000	29	12.08	.....	.....	.....	.....	.....	.....	11.309	11.313	11.305	11.305	11.294	11.313	.....
C. G. P. 9.886..	2	C_5	250,000	24	11.66	.....	.....	11.297	11.278	11.279	11.271	11.286	11.287	11.284	11.284	11.287	11.292	.....
0.5 W. N. S. at 30°	1	I_5	110,000	4	16.62	.....	.....	.....	.....	.....	.....	13.996	13.976	13.966	13.974	13.976	13.972	13.974
C. G. P. 12.358..	2	O_5	100,000	15	13.90	.....	13.962	13.971	13.975	13.979	13.986	13.981	13.982	13.986	13.981	.....	13.981	.....
	1	105	250,000	24	17.96	.....	16.672	16.771	16.712	16.702	16.694	16.693	16.699	.....	.....	.....	.....	.....
0.6 W. N. S. at 30°	2	H_5	200,000	15	19.73	.....	16.733	16.698	.....	16.691	16.693	16.688	16.683	16.684	16.691	16.688	16.688	.....
C. G. P. 14.830..	3	110	150,000	29	17.47	.....	16.734	16.790	16.782	16.772	16.760	16.752	16.751	.....	.....	.....	.....	.....
	4	B_5	200,000	9	18.39	.....	.....	.....	.....	16.704	16.693	16.698	16.665	.....	.....	.....	.....	.....
0.7 W. N. S. at 30°	1	H_5	225,000	24	19.86	.....	.....	.....	19.505	19.490	19.487	19.487	19.497	19.497	19.505	19.483	19.483	19.483
C. G. P. 17.301..	2	B_5	110,000	9	19.56	.....	19.524	19.514	19.507	19.510	19.496	19.490	19.482	19.490	.....	.....	.....	.....
0.8 W. N. S. at 30°	1	C_5	220,000	29	22.45	.....	.....	22.421	22.392	22.392	22.396	22.381	22.387	.....	.....	.....	.....	.....
C. G. P. 19.773..	2	A_5	110,000	9	22.41	.....	22.389	22.361	22.339	22.347	22.342	22.342	22.352	.....	.....	.....	.....	.....
0.9 W. N. S. at 30°	1	Z_3	250,000	15	24.98	.....	.....	.....	25.249	25.198	25.214	25.194	25.193	.....	.....	.....	.....	.....
C. G. P. 22.244..	2	C_0	240,000	24	24.28	.....	25.246	25.227	25.245	25.220	25.245	25.245	.....	.....	.....	.....	.....	.....
	1	R_5	110,000	9	25.60	.....	.....	28.317	28.206	28.186	.....	.....	.....	.....	.....	.....	.....	.....
1.0 W. N. S. at 30°	2	Z_5	300,000	9	24.85	28.219	28.212	28.212	28.227	28.206	28.212	28.227	.....	.....	.....	.....	.....	.....
C. G. P. 24.716..	3	F_5	147,000	9	25.60	28.227	28.234	28.250	28.242	28.242	.....	.....	.....	.....	.....	.....	.....	.....
	4	G_5	140,000	15	25.88	.....	28.205	28.215	28.192	.....	.....	.....	.....	.....	.....	.....	.....	.....

*Beginning with 30°, the correction for atmospheric pressure is not applied each day, but at the end of the experiment, when the mean barometric pressure for the whole period is deducted from the mean of all the mean daily total pressures, giving the mean osmotic pressure for the whole time the cell was under observation.

TABLE 53.—*Determinations of osmotic pressure at 30°.*—Continued.*

	Observed mean daily total pressures.												Mean of all daily pressures.	Mean barometric pressures.	Mean osmotic pressures.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	Fifteenth day.	Sixteenth day.	Seventeenth day.	Eighteenth day.	Nineteenth day.	Twentieth day.	Twenty-first day.	Twenty-second day.	Twenty-third day.	Twenty-fourth day.	Twenty-fifth day.	Twenty-sixth day.					
	.....	.....	3.482	3.465	3.492	3.488	3.477	3.481	3.482	3.484	3.467	3.463	3.478	1.002	2.476		
0.1 W. N. S. at 30°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	3.468	0.996	2.472		
C. G. P. 2.427	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	3.469	1.001	2.468	2.474	1.019
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	3.4816	1.002	2.4796		
0.2 W. N. S. at 30°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.0437	1.004	5.0397		
C. G. P. 4.943	6.053	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.0498	1.002	5.0478	5.0438	1.020
0.3 W. N. S. at 30°	8.637	8.641	8.644	8.643	.....	.....	.....	.....	.....	.....	.....	.....	8.6449	1.004	7.6409		
C. G. P. 7.415	8.652	8.652	8.651	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.6556	1.003	7.6526	7.6468	1.031
0.4 W. N. S. at 30°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	11.307	1.002	10.305		
C. G. P. 9.886	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	11.285	1.000	10.285	10.295	1.040
0.5 W. N. S. at 30°	13.990	13.999	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	13.9804	1.000	12.9804		
C. G. P. 12.358	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	13.9784	1.003	12.9754	12.9779	1.050
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	16.706	1.000	15.706		
0.6 W. N. S. at 30°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	16.6937	1.000	15.6937		
C. G. P. 14.830	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	16.763	1.000	15.763	15.7132	1.0595
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	16.690	1.000	15.690		
0.7 W. N. S. at 30°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	19.4917	0.998	18.4937		
C. G. P. 17.301	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	19.5016	0.997	18.5046	18.4992	1.069
0.8 W. N. S. at 30°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	22.395	0.999	21.396		
C. G. P. 19.773	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	22.353	0.999	21.354	21.375	1.081
0.9 W. N. S. at 30°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	25.2096	0.995	24.2146		
C. G. P. 22.244	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	25.238	1.000	24.238	24.2263	1.089
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	28.236	0.996	27.240		
1.0 W. N. S. at 30°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	28.2164	1.001	27.2154		
C. G. P. 24.716	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	28.239	0.996	27.242	27.2234	1.101
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	28.203	1.007	27.196		

*Beginning with 30°, the correction for atmospheric pressure is not applied each day, but at the end of the experiment, when the mean barometric pressure for the whole period is deducted from the mean of all the mean daily total pressures, giving the mean osmotic pressure for the whole time the cell was under observation.

TABLE 54.—*Determinations of osmotic pressure at 40°.*

Measurements by H. N. Morse, W. W. Holland, and G. Cash. W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.											
						Second day.	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.	Eighth day.	Ninth day.	Tenth day.	Eleventh day.	Twelfth day.	Thirteenth day.
0.1 W. N. S. at 40°	1	E_5	600,000	9	3.51	.....	.....	.....	.....	.....	3.563	3.568	3.567	3.567	3.567	3.564	3.559
C. G. P. 2.553...	2	F_5	95,000	24	4.46	.....	.....	.....	.....	.....	3.563	3.578	3.577	3.581	3.588	3.575	3.571
	3	D_5	120,000	22	4.50	.....	.....	.....	.....	.....	3.663	3.657	3.657	3.661	3.656	3.646	3.646
0.2 W. N. S. at 40°	1	I_5	120,000	11	6.12	.....	6.176	6.159	6.179	6.169	6.150	6.147	6.166	.....	.....	.....	.....
C. G. P. 5.107...	2	P_3	150,000	5	6.601	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	1	D_3	80,000	39	7.45	.....	.....	.....	.....	.....	.....	.....	8.805	8.820	8.834	8.795	8.807
0.3 W. N. S. at 40°	2	D_5	110,000	22	9.05	.....	8.849	8.838	8.821	8.849	8.854	8.856	8.865	8.867	8.865	8.874	8.859
C. G. P. 7.660...	3	E_6	80,000	6	7.72	.....	.....	.....	.....	.....	8.854	8.828	8.844	8.839	8.843	8.820	8.813
	4	F_5	110,000	24	8.35	.....	.....	8.824	8.808	8.827	8.840	8.842	8.853	8.848	8.846	.....	.....
	1	D_3	126,000	15	10.66	.....	.....	.....	.....	.....	.....	.....	11.605	11.596	11.609	11.586	11.566
0.4 W. N. S. at 40°	2	R_3	205,000	38	11.16	.....	11.617	11.603	11.592	11.606	.....	.....	.....	.....	.....	.....	.....
C. G. P. 10.213..	3	N_3	190,000	6	14.15	.....	.....	.....	.....	.....	.....	.....	11.612	11.583	11.620	11.621	11.615
	4	I_5	120,000	5	11.53	11.562	11.621	11.621	11.568	11.596	11.567	11.577	.....	.....	.....	.....	.....
0.5 W. N. S. at 40°	1	A_5	100,000	9	14.48	.....	14.359	14.363	14.338	14.334	.....	.....	.....	.....	.....	.....	.....
C. G. P. 12.767..	2	B_5	80,000	24	14.82	.....	14.346	14.338	14.381	14.378	.....	.....	.....	.....	.....	.....	.....
0.6 W. N. S. at 40°	1	H_5	110,000	6	15.07	.....	17.138	17.153	17.150	17.144	.....	.....	.....	.....	.....	.....	.....
C. G. P. 15.320..	2	E_5	110,000	6	18.32	.....	.....	17.150	17.159	17.161	.....	.....	.....	.....	.....	.....	.....
0.7 W. N. S. at 40°	1	A_5	90,000	6	21.29	.....	.....	.....	19.943	19.999	19.956	19.960	19.947	.....	.....	.....	.....
C. G. P. 17.873..	2	C_5	110,000	24	19.84	19.934	19.895	19.892	19.887	19.900	19.911	.....	.....	.....	.....	.....	.....
	1	I_5	100,000	5	23.26	.....	.....	.....	22.779	22.788	22.780	22.767	.....	.....	.....	.....	.....
0.8 W. N. S. at 40°	2	A_5	225,000	9	19.60	.....	.....	.....	22.831	22.817	22.822	.....	.....	.....	.....	.....	.....
C. G. P. 20.426..	3	B_5	220,000	6	22.86	22.859	22.768	22.842	22.813	22.842	22.836	.....	.....	.....	.....	.....	.....
	4	D_5	333,000	22	22.53	22.788	22.800	22.823	22.845	22.836	22.829	.....	.....	.....	.....	.....	.....
0.9 W. N. S. at 40°	1	Ni_3	80,000	29	24.1	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
C. G. P. 22.980..	2	H_5	80,000	9	23.60	.....	.....	25.738	25.720	25.751	25.707	25.726	25.745	.....	.....	.....	.....
	3	R_5	125,000	22	26.06	.....	.....	.....	.....	25.710	25.763	25.718	25.733	25.741	25.761	.....	.....
1.0 W. N. S. at 40°	1	B_5	150,000	20	30.00	28.697	28.641	28.687	.....	.....	.....	.....	.....	.....	.....	.....	.....
C. G. P. 25.533..	2	R_5	110,000	9	28.63	.....	28.785	28.739	28.732	28.732	28.725	28.732	.....	.....	.....	.....	.....
	3	F_5	112,000	5	27.04	.....	.....	.....	.....	28.695	28.639	28.684	28.721	.....	.....	.....	.....

TABLE 54.—*Determinations of osmotic pressure at 40°*—Continued.

	Observed mean daily total pressures.										Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	Fourteenth day.	Fifteenth day.	Sixteenth day.	Seventeenth day.	Eighteenth day.	Nineteenth day.	Twentieth day.	Twenty-first day.	Twenty-second day.	Twenty-third day.					
0.1 W. N. S. at 40°	3.553	3.552	3.546	.....	.....	.....	.....	.....	.....	.....	3.5606	1.006	2.5546		
C. G. P. 2.553...	3.565	3.552	3.546	.....	.....	.....	.....	.....	.....	.....	3.5696	1.008	2.5616	2.5597	1.003
	3.644	3.637	.....	.....	.....	.....	.....	.....	.....	.....	3.652	1.008	2.644*		
0.2 W. N. S. at 40°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.164	0.996	5.168		
C. G. P. 5.107...	.....	.....	.....	.....	6.162	6.162	6.180	6.176	6.166	6.165	6.1685	1.0105	5.158	5.163	1.011
	8.814	8.817	.....	.....	.....	.....	.....	.....	.....	.....	8.813	0.997	7.817		
0.3 W. N. S. at 40°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.854	1.001	7.853		
C. G. P. 7.660...	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.834	1.003	7.831	7.844	1.024
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.836	1.001	7.835		
	11.599	11.581	11.614	11.575	.....	.....	.....	.....	.....	.....	11.593	0.994	10.599		
0.4 W. N. S. at 40°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	11.6045	1.002	10.6025		
C. G. P. 10.213..	11.607	.....	.....	.....	.....	.....	.....	.....	.....	.....	11.6097	1.003	10.6067	10.5987	1.0377
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	11.5874	1.001	10.5864		
0.5 W. N. S. at 40°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	14.349	1.000	13.349		
C. G. P. 12.767..	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	14.361	1.000	13.361	13.355	1.046
0.6 W. N. S. at 40°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	17.141	1.004	16.137		
C. G. P. 15.320..	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	17.157	1.003	16.152	16.146	1.054
0.7 W. N. S. at 40°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	19.961	0.999	18.962		
C. G. P. 17.873..	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	19.902	1.001	18.901	18.932	1.0592
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	22.779	1.000	21.779		
0.8 W. N. S. at 40°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	22.823	1.010	21.813		
C. G. P. 20.426..	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	22.827	1.008	21.819	21.8055	1.0674
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	22.820	1.009	21.811		
0.9 W. N. S. at 40°	.....	25.701	25.745	25.740	25.737	25.743	25.748	.....	.....	.....	25.738	1.000	24.738		
C. G. P. 22.980..	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	25.731	1.001	24.730	24.735	1.076
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	25.738	1.000	24.738		
1.0 W. N. S. at 40°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	28.675	1.002	27.673		
C. G. P. 25.533..	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	28.741	0.998	27.743	27.701	1.085
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	28.685	0.997	27.688		

*Reduced by correction for concentration in the cell to 2.563.

TABLE 55.—*Determination of osmotic pressure at 50°.*

Measurements by H. N. Morse, W. W. Holland, and L. Van Doren. W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.										
						Second day.	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.	Eighth day.	Ninth day.	Tenth day.	Eleventh day.	Twelfth day.
0.1 W. N. S. at 50°	1	U_5	55,000	1_0	3.92	.....	.....	.....	.....	.....	.....	.....	.....	.....	3.650	3.646
C. G. P. 2.635....	2	E_5	100,000	15	3.75	.....	.....	.....	.....	.....	.....	.....	.....	3.644	3.637	3.642
	3	V_5	110,000	9	4.21	.....	.....	.....	.....	.....	3.632	3.627	3.629	3.629	3.629	3.630
0.2 W. N. S. at 50°	1	Q_5	75,000	29	6.56	.....	.....	.....	.....	.....	6.281	6.263	6.277	6.280	6.284	6.285
C. G. P. 5.270....	2	S_5	65,000	39	6.23	.....	.....	.....	.....	.....	.....	6.266	6.290	6.300	6.299	6.300
	3	R_5	80,000	27	6.70	.....	.....	.....	.....	6.274	6.316	6.284	6.284	6.277	6.279	6.282
0.3 W. N. S. at 50°	1	B_5	75,000	38	10.79	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
C. G. P. 7.905....	2	T_5	60,000	5	11.63	.....	.....	.....	.....	.....	.....	.....	9.005	8.995	8.976	8.980
	3	P_5	75,000	3	8.86	.....	.....	8.970	8.981	8.978	8.992	8.978	9.001	8.959	8.942	8.981
0.4 W. N. S. at 50°	1	S_5	71,000	38	13.46	.....	.....	.....	.....	.....	.....	11.750	11.759	11.750	11.748	11.742
C. G. P. 10.540...	2	H_5	190,000	4	12.31	.....	.....	.....	.....	.....	.....	11.695	11.704	11.718	11.729	11.724
0.5 W. N. S. at 50°	1	I_5	81,000	1_0	13.78	.....	.....	.....	.....	.....	14.534	14.511	14.541	14.541	14.501	14.512
C. G. P. 13.175...	2	F_3	377,000	29	18.77	.....	.....	.....	.....	.....	14.416	14.451	14.487	14.499	14.515	14.513
	3	L_5	94,000	9	17.02	.....	.....	.....	.....	.....	14.435	14.487	14.522	14.504	14.526	14.511
0.6 W. N. S. at 50°	1	C_5	59,000	31	19.49	.....	.....	.....	.....	17.332	17.339	17.332	17.333	17.337	17.318	17.323
C. G. P. 15.810...	2	R_5	118,000	5	18.16	.....	.....	.....	.....	.....	.....	17.302	17.296	17.321	17.313	17.309
0.7 W. N. S. at 50°	1	D_3	110,000	29	25.09	.....	.....	.....	.....	.....	.....	.....	.....	20.272	20.237	20.211
C. G. P. 18.445...	2	Z_3	150,000	4	23.71	.....	.....	.....	.....	.....	.....	.....	20.297	20.103	20.186	20.178
0.8 W. N. S. at 50°	1	C_5	110,000	28	23.10	23.095	23.116	23.180	23.164	23.164	23.146	23.146	23.158	23.165	23.135	23.115
C. G. P. 21.080...	2	J_5	100,000	31	22.60	.....	.....	23.069	23.079	23.068	23.102	23.135	23.149	23.131	23.122	23.107
0.9 W. N. S. at 50°	1	G_5	100,000	1_0	27.62	.....	.....	.....	26.103	26.127	26.133	26.127	26.115	26.139	26.161	26.127
C. G. P. 23.715...	2	F_3	100,000	38	36.45	.....	.....	.....	26.128	26.142	26.127	26.124	26.108	26.082	26.105	26.105
1.0 W. N. S. at 50°	1	R_3	55,000	9	29.68	29.194	29.177	29.186	29.178	29.193	29.230	29.194	.....	.....	.....	.....
C. G. P. 26.350...	2	P_5	110,000	29	29.44	.....	29.230	29.228	29.250	29.236	29.225	29.221	29.240	29.243	29.213	29.209
	3	E_5	62,000	5	37.40	.....	.....	.....	.....	29.130	29.153	29.164	29.150	29.218	29.211	29.218

TABLE 55.—*Determination of osmotic pressure at 50°*—Continued.

	Observed mean daily total pressures.											Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	Thirteenth day.	Fourteenth day.	Fifteenth day.	Sixteenth day.	Seventeenth day.	Eighteenth day.	Nineteenth day.	Twentieth day.	Twenty-first day.	Twenty-second day.	Twenty-third day.					
0.1 W. N. S. at 50°	3.643	3.648	3.649	3.644	3.646	3.650	3.650	3.644	3.643	3.644	.....	3.646	1.003	2.643		
	3.646	3.642	3.637	3.635	3.635	3.635	3.635	.....	.....	.....	.....	3.6388	1.005	2.6383	2.6353	1.000
C. G. P. 2.635.	3.630	3.624	3.629	.....	.....	.....	.....	.....	.....	.....	.....	3.629	1.000	2.629		
	6.283	6.285	6.288	6.287	.....	.....	.....	.....	.....	.....	.....	6.2813	1.008	5.2733		
0.2 W. N. S. at 50°	6.300	6.300	6.301	6.299	6.295	.....	.....	.....	.....	.....	.....	6.295	1.009	5.286	5.2784	1.0016
C. G. P. 5.270.	6.279	6.283	6.279	6.282	.....	.....	.....	.....	.....	.....	.....	6.284	1.007	5.277		
	.....	.....	8.945	8.950	8.962	8.968	8.968	8.967	8.968	8.961	8.964	8.961	1.001	7.960		
0.3 W. N. S. at 50°	8.978	8.994	9.012	9.003	8.995	8.991	.....	.....	.....	.....	.....	8.9929	1.005	7.9879	7.9739	1.009
C. G. P. 7.905.	8.925	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.9707	0.997	7.9737		
0.4 W. N. S. at 50°	11.738	11.732	11.731	11.725	11.726	.....	.....	.....	.....	.....	.....	11.740	1.003	10.737	10.724	1.017
C. G. P. 10.540.	11.711	11.713	11.711	11.702	11.724	.....	.....	.....	.....	.....	.....	11.713	1.003	10.710		
	14.527	14.493	14.496	14.512	.....	.....	.....	.....	.....	.....	.....	14.5168	1.002	13.5148		
0.5 W. N. S. at 50°	14.520	14.524	14.518	14.504	.....	.....	.....	.....	.....	.....	.....	14.495	1.002	13.4927	13.5037	1.025
C. G. P. 13.175.	14.524	14.518	14.522	14.508	.....	.....	.....	.....	.....	.....	.....	14.5057	1.002	13.5037		
0.6 W. N. S. at 50°	17.318	17.320	17.318	17.320	17.324	17.320	.....	.....	.....	.....	.....	17.325	1.003	16.322	16.319	1.032
C. G. P. 15.810.	17.313	17.302	17.301	17.316	17.313	17.312	.....	.....	.....	.....	.....	17.309	1.003	16.306		
0.7 W. N. S. at 50°	20.211	20.194	20.198	.....	.....	.....	.....	.....	.....	.....	.....	20.2205	0.996	19.2245	19.2019	1.041
C. G. P. 18.445.	20.164	20.143	20.164	.....	.....	.....	.....	.....	.....	.....	.....	20.1764	0.997	19.1794		
0.8 W. N. S. at 50°	23.075	23.095	23.115	.....	.....	.....	.....	.....	.....	.....	.....	23.1335	1.005	22.1285	22.116	1.049
C. G. P. 21.080.	23.103	23.118	23.107	.....	.....	.....	.....	.....	.....	.....	.....	23.1075	1.004	22.1035		
0.9 W. N. S. at 50°	26.150	26.139	.....	.....	.....	.....	.....	.....	.....	.....	.....	26.132	1.000	25.132	25.1228	1.0593
C. G. P. 23.715.	26.107	26.108	.....	.....	.....	.....	.....	.....	.....	.....	.....	26.1136	1.000	25.1136		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	29.193	0.994	28.199		
1.0 W. N. S. at 50°	29.213	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	29.228	0.997	28.231	28.213	1.071
C. G. P. 26.250.	29.164	29.224	29.211	29.211	29.224	.....	.....	.....	.....	.....	.....	29.190	0.994	28.196		

TABLE 56.—*Determinations of osmotic pressure at 60°.*

Measurements by H. N. Morse, W. W. Holland, and C. N. Myers. W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.										
						Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.	Eighth day.	Ninth day.	Tenth day.	Eleventh day.	Twelfth day.	Thirteenth day.
0.1 W. N. S. at 60°	1	W_5	37,000	15	3.80	.....	.....	.....	.....	.....	.....	.....	.....	3.724	3.721	3.720
C. G. P. 2.717...	2	B_5	37,000	11	3.53	.....	.....	.....	.....	.....	.....	.....	.....	3.718	3.719	3.716
0.2 W. N. S. at 60°	1	E_5	50,000	1_0	6.57	.....	.....	.....	.....	6.457	6.449	6.441	6.456	6.452	6.445	6.444
C. G. P. 5.433...	2	K_5	61,000	1_0	8.26	.....	.....	.....	.....	.....	.....	6.442	6.420	6.423	6.429	6.430
0.3* W.N.S. at 60°	1	K_5	75,000	15	17.25 (!)	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	9.147
C. G. P. 8.150...	2	F_5	75,000	11	9.73	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	9.133
	1	G_5	28,000	39	16.06	.....	.....	.....	.....	.....	.....	.....	.....	.....	11.892	11.858
0.4 W. N. S. at 60°	2	F_5	57,000	5	11.59	.....	.....	.....	11.889	11.862	11.882	11.858	11.848	11.827	11.850	11.862
C. G. P. 10.867..	3	C_5	16,000	2_0	12.47	.....	11.900	11.858	11.891	11.890	11.863	11.877	11.890	11.886	11.890	11.880
0.5 W. N. S. at 60°	1	V_5	11,600	31	19.00	.....	.....	.....	.....	.....	.....	14.654	14.654	14.645	14.634	14.646
C. G. P. 13.854..	2	C_5	50,000	4	15.27	.....	14.637	14.608	14.620	14.635	14.759	14.773	14.724	14.703	14.707	14.707
0.6 W. N. S. at 60°	1	R_5	29,000	11	22.34	.....	.....	.....	.....	17.487	17.498	17.478	17.499	17.485	17.522	17.517
C. G. P. 16.300..	2	P_5	23,000	5	18.62	.....	.....	.....	.....	.....	17.555	17.616	17.585	17.553	17.523	17.553
0.7 W. N. S. at 60°	1	Z_5	27,000	39	20.65	.....	.....	.....	20.319	20.357	20.362	20.371	20.450	20.444	.....	20.441
C. G. P. 19.017..	2	A_5	58,000	31	24.13	.....	.....	.....	.....	.....	.....	20.428	20.409	20.417	20.416	20.400
0.8 W. N. S. at 60°	1	P_5	25,000	1_0	23.05	23.358	23.339	23.348	23.348	23.345	23.339	23.318	23.357	23.348	23.339	23.325
C. G. P. 21.734..	2	E_5	20,000	15	24.93	.....	.....	23.291	23.329	23.316	23.286	23.312	23.276	23.298	23.257	23.349
0.9 W. N. S. at 60°	1	G_5	38,000	28	32.35 (!)	.....	.....	.....	.....	.....	.....	.....	.....	.....	26.208	26.225
C. G. P. 24.450..	2	U_5	23,000	5	26.96	.....	.....	26.234	26.234	26.234	26.256	26.276	26.287	26.283	26.276	26.281
1.0 W. N. S. at 60°	1	W_5	3,200	11	32.25	.....	29.358	29.298	29.309	29.282	29.339	29.371	29.439	29.371	29.380	29.358
C. G. P. 27.167..	2	L_5	30,000	5	28.97	.....	.....	29.319	29.353	29.331	29.358	29.377	29.405	29.383	29.377	29.399

*Observed mean daily total pressures, corrected for concentration.

TABLE 56.—*Determinations of osmotic pressure at 60°*—Continued.

	Observed mean daily total pressures.									Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	Fourteenth day.	Fifteenth day.	Sixteenth day.	Seventeenth day.	Eighteenth day.	Nineteenth day.	Twentieth day.	Twenty-first day.	Twenty-second day.					
0.1 W. N. S. at 60°	3.714	3.720	3.729	3.731	3.732	3.730	3.731	.....	.....	3.7252	1.005	2.7202	2.7172	1.000
C. G. P. 2.717....	3.708	3.713	3.718	3.722	3.726	3.726	3.726	.....	.....	3.7192	1.005	2.7142		
0.2 W. N. S. at 60°	6.449	6.414	6.417	6.436	.....	.....	.....	.....	.....	6.446	0.996	5.450	5.438	1.001
C. G. P. 5.433....	6.427	6.432	6.411	6.416	.....	.....	.....	.....	.....	6.4256	1.001	5.4246		
0.3* W. N. S. at 60°	9.137	9.155	9.156	9.142	9.151	9.161	9.157	9.160	9.156	9.1522	1.000	8.1522	8.1403	0.999
C. G. P. 8.150....	9.153	9.136	9.109	9.130	9.117	9.114	9.123	9.134	9.134	9.1283	1.000	8.1283		
0.4 W. N. S. at 60°	11.868	11.853	11.877	11.869	11.874	11.886	11.885	11.886	11.887	11.876	1.005	10.871	10.866	1.000
C. G. P. 10.867...	11.858	.....	.....	.....	.....	.....	.....	.....	.....	11.860	1.007	10.853		
0.5 W. N. S. at 60°	14.643	14.688	14.661	14.649	14.654	14.655	.....	.....	.....	11.883	1.010	10.873	13.662	1.0057
C. G. P. 13.854...	.....	.....	.....	.....	.....	.....	.....	.....	.....	14.653	1.008	13.645		
0.6 W. N. S. at 60°	17.546	17.531	.....	.....	.....	.....	.....	.....	.....	14.6873	1.000	13.6873	16.535	1.014
C. G. P. 16.300...	17.527	17.523	17.519	.....	.....	.....	.....	.....	.....	17.518	0.999	16.519		
0.7 W. N. S. at 60°	20.438	20.426	20.410	.....	.....	.....	.....	.....	.....	17.550	0.999	16.551	19.4037	1.020
C. G. P. 19.017...	20.390	20.400	20.395	20.395	20.395	20.395	.....	.....	.....	20.4018	0.999	19.4028		
0.8 W. N. S. at 60°	23.339	.....	.....	.....	.....	.....	.....	.....	.....	20.4036	0.999	19.4046	22.327	1.027
C. G. P. 21.724...	23.345	23.323	.....	.....	.....	.....	.....	.....	.....	23.342	0.998	22.344		
0.9 W. N. S. at 60°	26.237	26.250	26.260	26.262	26.264	26.271	26.269	26.269	26.283	23.308	0.998	22.310	25.2657	1.0334
C. G. P. 24.450...	26.321	26.342	.....	.....	.....	.....	.....	.....	.....	26.2544	0.998	25.2564		
1.0 W. N. S. at 60°	.....	.....	.....	.....	.....	.....	.....	.....	.....	26.274	0.999	25.275	28.3665	1.044
C. G. P. 27.167...	29.399	29.421	.....	.....	.....	.....	.....	.....	.....	29.351	0.994	28.357		
										29.375	0.999	28.376		

*Observed mean daily total pressures, corrected for concentration.

TABLE 57.—*Determinations of osmotic pressure at 70°.*

Measurements by H. N. Morse, W. W. Holland, and J. B Zinn. W. N. S. = Weight normal solution.
C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures. 2d day.	3d day.	4th day.	5th day.	6th day.
0.5 W. N. S. at 70° C. G. P.	1	E_5	13,000	1_0	17.70	.....	.....	15.015	14.986	14.985
13.992	2	L_5	9,600	38	15.84	.....	14.993	14.984	14.981	14.979
0.6 W. N. S. at 70° C. G. P.	1	B_5	10,000	31	17.81	17.812	17.820	17.824	17.816	17.800
16.790	2	W_5	16,000	15	17.69	.....	.....	.....	17.859	17.822
0.7 W. N. S. at 70° C. G. P.	1	J_5	8,000	38	19.93	.....	.....	.....	.....	.....
19.589	2	F_5	10,000	24	21.42	.....	20.559	20.574	20.600	20.592
0.8 W. N. S. at 70° C. G. P.	1	U_5	23,000	31	25.58	.....	.....	.....	.....	.....
22.387	2	R_5	10,000	31	25.52	.....	23.568	23.565	23.556	23.583
	1	F_5	19,000	24	28.71	.....	.....	.....	.....	.....
0.9 W. N. S. at 70° C. G. P.	2	R_5	16,500	28	30.70	.....	.....	.....	26.589	26.589
25.186	3	C_5	7,700	1_0	25.79	.....	.....	26.552	26.534	26.552
	1	G_5	30,000	28	34.73	.....	.....	.....	29.542	29.558
1.0 W. N. S. at 70° C. G. P.	2	L_5	33,000	5	31.12	.....	29.676	29.623	29.720	29.746
27.984	3	E_5	20,000	1_0	32.57	.....	.....	29.572	29.602	29.602
	4	R_5	33,000	15	31.87	.....	.....	29.608	29.628	29.635

	Observed mean daily total pressures. 7th day.	8th day.	9th day.	10th day.	11th day.	12th day.	13th day.	14th day.	15th day.
0.5 W. N. S. at 70° C. G.	14.978	14.974	.....	.....	.....	.....	.....	.....	.....
P. 13.992	14.981	14.985	.....	.....	.....	.....	.....	.....	.....
0.6 W. N. S. at 70° C. G.	17.795	.....	.....	.....	.....	.....	.....	.....	.....
P. 16.790	17.817	17.801	17.817	17.800	.....	.....	.....	.....	.....
0.7 W. N. S. at 70° C. G.	20.557	20.564	20.516	20.516	20.528	20.534	.....	.....	.....
P. 19.589	20.578	20.566	.....	.....	.....	.....	.....	.....	.....
0.8 W. N. S. at 70° C. G.	23.555	23.549	23.547	23.562	23.574	23.568	.....	.....	.....
P. 22.387	23.576	.....	.....	.....	.....	.....	.....	.....	.....
0.9 W. N. S. at 70° C. G.	.....	.....	.....	.....	.....	.....	26.543	26.593	26.556
P. 25.186	26.565	26.559	26.551	.....	.....	.....	.....	.....	.....
	26.564	26.563	26.541	.....	.....	.....	.....	.....	.....
	29.559	29.630	29.591	29.585	29.589	29.607	29.610	.....	.....
1.0 W. N. S. at 70° C. G.	29.720	29.715	29.635	29.618	29.617	29.646	29.629	.....	.....
P. 27.984	29.602	29.617	29.610	29.590	29.587	29.646	29.632	.....	.....
	29.621	29.628	29.600	29.590	29.596	29.647	29.700	.....	.....

	Observed mean daily total pressures. 16th day.	17th day.	18th day.	19th day.	Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
0.5 W. N. S. at 70° C. G.	.....	.....	.....	.....	14.988	0.994	13.994	13.9905	1.000
P. 13.992	.....	.....	.....	.....	14.984	0.994	13.990		
0.6 W. N. S. at 70° C. G.	.....	.....	.....	.....	17.810	0.995	16.815	16.8195	1.0018
P. 16.790	.....	.....	.....	.....	17.819	0.995	16.824		
0.7 W. N. S. at 70° C. G.	.....	.....	.....	.....	20.543	0.990	19.553	19.568	0.999
P. 19.589	.....	.....	.....	.....	20.577	0.994	19.583		
0.8 W. N. S. at 70° C. G.	.....	.....	.....	.....	23.559	0.992	22.567	22.567	1.008
P. 22.387	.....	.....	.....	.....	23.570	1.003	22.567		
0.9 W. N. S. at 70° C. G.	26.562	26.523	26.549	26.574	26.557	0.998	25.559		
P. 25.186	.....	.....	.....	.....	26.571	0.997	25.574	25.562	1.015
	.....	.....	.....	.....	26.551	0.997	25.554		
	.....	.....	.....	.....	29.590	1.000	28.590		
1.0 W. N. S. at 70° C. G.	.....	.....	.....	.....	29.668	0.997	28.671	28.6235	1.0228
P. 27.984	.....	.....	.....	.....	29.606	0.999	28.607		
	.....	.....	.....	.....	29.625	0.999	28.626		

TABLE 58.—*Determinations of osmotic pressure at 80°.*

W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.					
						Second day.	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.
0.8 W. N. S. at 80°											
C. G. P. 23.041 . . .	1	B_5	9,000	24	33.00	.....	.....	.....	24.087	24.073	24.042
0.9 W. N. S. at 80°	1	E_5	10,000	31	26.85	.....	.....	26.905	26.909	26.914	26.919
C. G. P. 25.921 . . .	2	G_5	10,000	5	23.96	.....	.....	26.974	26.933	26.909	26.873
1.0 W. N. S. at 80°	1	H_5	10,500	31	30.20	29.838	29.811	29.801	29.780	.....	.....
C. G. P. 28.801 . . .	2	L_5	10,000	1_0	28.19	.....	.....	.....	29.770	29.863	29.836

	Observed mean daily total pressures.					Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	Eighth day.	Ninth day.	Tenth day.	Eleventh day.	Twelfth day.					
0.8 W. N. S. at 80°										
C. G. P. 23.041 . .	24.036	.....	.....	.....	.....	24.060	0.998	23.062	.....	1.001
0.9 W. N. S. at 80°	.....	.....	.....	.....	.....	26.912	0.997	25.915	25.919	1.000
C. G. P. 25.921 . .	26.909	.....	.....	.....	.....	26.920	0.998	25.922		
1.0 W. N. S. at 80°	.....	.....	.....	.....	.....	29.808	0.992	28.816	28.8178	1.000
C. G. P. 28.801 . .	29.799	29.785	29.829	29.859	29.799	29.8175	0.998	28.8195		

The results of the foregoing determinations of osmotic pressure have been brought together in tables 59 to 63. Table 59 gives, for each concentration of solution and each temperature, the observed osmotic pressure. Table 60 gives the means of the observed osmotic pressures for each concentration and temperature. Table 61 contains the calculated gas pressure of the solute for all concentrations of solution which were employed, and for all the temperatures at which measurements of osmotic pressure were made—*the volume of the gas being that of the solvent in the pure state, and not that of the solution.* Table 62 gives the ratios of the observed osmotic pressures of the solutions to the calculated gas pressures of the solute, i. e., the results which are obtained by dividing the values in Table 60 by the corresponding values in Table 61. In order to facilitate an interpretation of the results, Tables 60 and 62 have been divided into three sections by means of heavy lines. Attention is called more especially to Table 62, in which are given the ratios of osmotic to gas pressure. If the values on the various horizontal lines, to the left of the vertical heavy line, are compared, it will be seen that the ratio of osmotic to gas pressure, between 0° and 25°, *is very nearly constant for each concentration of solution.* Omitting the ratio for the 0.1 weight-normal solutionat 0°, the means of the ratios for the various concentrations are given in Table 63.

TABLE 59.—*Cane sugar. Osmotic pressures between 0° and 80°.*

Concentration.	0°.	5°.	10°.	15°.	20°.	25°.	30°.	40°.	50°.	60°.	70°.	80°.
0.1	2.460	2.452	2.494	2.547	2.589	2.635	2.476	2.555	2.643	2.720	.....	.....
"	2.464	2.451	2.496	2.535	2.590	2.632	2.472	2.562	2.638	2.714	.....	.....
"	2.463	2.453	2.502	2.541	.....	.....	2.468	2.563	2.629	.....	.....	.....
"	.....	.....	2.498	2.538	.....	.....	2.480	.....	.....	.....	.....	.....
0.2	4.719	4.812	4.890	4.981	5.058	5.154	5.040	5.168	5.273	5.450	.....	.....
"	4.717	4.825	4.896	4.988	5.056	5.139	5.048	5.158	5.286	5.425	.....	.....
"	4.730	.....	.....	.....	5.066	5.150	.....	.....	5.277	.....	.....	.....
"	4.726	.....	.....	.....	5.065	.....	.....	.....	.....	.....	.....	.....
"	.....	.....	.....	.....	5.074	.....	.....	.....	.....	.....	.....	.....
0.3	7.078	7.187	7.332	7.465	7.586	7.735	7.641	7.817	7.960	8.152	.....	.....
"	7.107	7.209	7.337	7.486	7.624	7.719	7.653	7.853	7.988	8.128	.....	.....
"	7.071	.....	.....	.....	7.606	7.722	.....	7.831	7.974	.....	.....	.....
"	.....	.....	.....	.....	.....	7.738	.....	7.835	.....	.....	.....	.....
0.4	9.450	9.623	9.791	9.950	10.136	10.301	10.305	10.599	10.737	10.871	.....	.....
"	9.435	9.584	9.790	9.947	10.138	10.295	10.285	10.603	10.710	10.853	.....	.....
"	.....	9.617	.....	.....	.....	.....	.....	10.607	.....	10.873	.....	.....
"	.....	.....	.....	.....	.....	.....	.....	10.586	.....	.....	.....	.....
0.5	11.907	12.100	12.296	12.565	12.742	12.932	12.980	13.349	13.515	13.645	13.994	.....
"	11.882	12.100	12.298	12.533	12.754	12.972	12.975	13.361	13.493	13.687	13.990	.....
"	.....	.....	.....	.....	.....	12.919	.....	.....	13.504	.....	.....	.....
"	.....	.....	.....	.....	.....	12.947	.....	.....	.....	.....	.....	.....
0.6	14.367	14.604	14.856	15.128	15.405	15.632	15.706	16.137	16.322	16.519	16.815	.....
"	14.395	14.606	14.854	15.160	15.370	15.615	15.694	16.152	16.306	16.551	16.824	.....
"	.....	.....	.....	.....	.....	15.620	15.763	.....	.....	.....	.....	.....
"	.....	.....	.....	.....	.....	15.634	15.690	.....	.....	.....	.....	.....
0.7	16.881	17.217	17.488	17.821	18.135	18.436	18.494	18.962	19.225	19.403	19.553	.....
"	16.891	17.194	17.518	17.808	18.121	18.434	18.505	18.901	19.179	19.405	19.583	.....
0.8	19.486	19.795	20.152	20.533	20.928	21.250	21.396	21.779	22.129	22.344	22.567	23.062
"	19.466	19.849	20.169	20.525	20.883	21.258	21.354	21.813	22.104	22.310	22.567	.....
"	.....	.....	.....	20.548	20.899	.....	.....	21.819	.....	.....	.....	.....
"	.....	.....	.....	.....	20.909	.....	.....	21.811	.....	.....	.....	.....
0.9	22.149	22.443	22.911	23.314	23.715	24.126	24.215	24.738	25.132	25.256	25.559	25.915
"	22.087	22.510	22.857	23.296	23.718	24.125	24.238	24.730	25.114	25.275	25.574	25.922
"	.....	.....	.....	.....	.....	.....	.....	24.738	.....	.....	25.554	.....
1.0	24.878	25.300	25.704	26.206	26.648	27.030	27.240	27.673	28.199	28.357	28.590	28.816
"	24.774	25.300	25.682	26.171	26.627	27.076	27.215	27.743	28.231	28.376	28.671	28.820
"	.....	25.300	.....	.....	.....	.....	27.242	27.688	28.196	.....	28.607	.....
"	.....	25.240	.....	.....	.....	.....	27.196	.....	.....	.....	28.626	.....
"	.....	25.260	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

TABLE 60.—*Cane sugar. Mean osmotic pressures between 0° and 80°.*

Concentration.	0°.	5°.	10°.	15°.	20°.	25°.	30°.	40°.	50°.	60°.	70°.	80°.
0.1	(2.462)	2.452	2.498	2.540	2.590	2.634	2.474	2.560	2.637	2.717	.....	.....
0.2	4.723	4.819	4.893	4.985	5.064	5.148	5.044	5.163	5.279	5.438	.....	.....
0.3	7.085	7.198	7.335	7.476	7.605	7.729	7.647	7.834	7.974	8.140	.....	.....
0.4	9.443	9.608	9.790	9.949	10.137	10.296	10.295	10.599	10.724	10.866	.....	.....
0.5	11.895	12.100	12.297	12.549	12.748	12.943	12.978	13.355	13.504	13.666	13.991	.....
0.6	14.381	14.605	14.855	15.144	15.388	15.625	15.713	16.146	16.314	16.535	16.820	.....
0.7	16.886	17.206	17.503	17.815	18.128	18.435	18.499	18.932	19.202	19.404	19.568	.....
0.8	19.476	19.822	20.161	20.535	20.905	21.254	21.375	21.806	22.116	22.327	22.567	23.062
0.9	22.118	22.477	22.884	23.305	23.717	24.126	24.226	24.735	25.123	25.266	25.562	25.919
1.0	24.826	25.280	25.693	26.189	26.638	27.053	27.223	27.701	28.209	28.367	28.624	28.818

The average deviation from these mean ratios is 0.15 per cent, while the largest single deviation—that of the 0.6 normal solution at 25°—is 0.3 per cent. It is obvious from the relations pointed out above, that between 0° and 25° the osmotic pressure of cane-sugar solutions—ranging in concentration from 0.1 to 1.0 weight-normal—obeys the law of Gay-Lussac for gases. In other words, within the limits designated, the temperature coefficients of gas and osmotic pressures are identical. So much must be conceded on the basis of the experimentally demonstrated facts—whatever may hereafter be found to be true of solutions of cane sugar which are more or less concentrated, or of other substances.

TABLE 61.—*Cane sugar. Calculated gas pressures of solute between 0° and 80°.*

Conc.	0°.	5°.	10°.	15°.	20°.	25°.	30°.	40°.	50°.	60°.	70°.	80°.
0.1	2.227	2.267	2.308	2.349	2.390	2.431	2.472	2.553	2.635	2.717	2.798	2.880
0.2	4.453	4.535	4.616	4.698	4.780	4.862	4.943	5.107	5.270	5.433	5.597	5.760
0.3	6.680	6.802	6.925	7.047	7.170	7.292	7.415	7.660	7.905	8.150	8.395	8.640
0.4	8.906	9.069	9.233	9.396	9.560	9.723	9.886	10.213	10.540	10.867	11.194	11.520
0.5	11.133	11.337	11.541	11.745	11.950	12.154	12.358	12.767	13.175	13.584	13.992	14.401
0.6	13.359	13.604	13.849	14.094	14.339	14.585	14.830	15.320	15.810	16.300	16.790	17.281
0.7	15.585	15.871	16.157	16.443	16.729	17.015	17.301	17.873	18.445	19.017	19.589	20.161
0.8	17.812	18.139	18.466	18.792	19.119	19.446	19.773	20.426	21.080	21.734	22.387	23.041
0.9	20.038	20.406	20.774	21.141	21.509	21.877	22.244	22.980	23.715	24.450	25.186	25.921
1.0	22.265	22.674	23.082	23.490	23.899	24.308	24.716	25.533	26.350	27.167	27.984	28.801

The 0.1 normal solution at 0° appears to present an exception to the rule that the ratio of osmotic to gas pressure for that concentration is about 1.083 at temperatures under 25°. The pressure found was 2.462, which gives a ratio to calculated gas pressure of 1.106; whereas, in order to conform to the rule which holds for the 0.1 normal solution at 5°, 10°, 15°, 20°, and 25°, the pressure should be about 2.227×1.083 equals 2.413. The difference, 2.462 minus 2.413 equals 0.049 atmosphere, is probably too large to be accounted for as due to experimental error—especially in a solution so dilute that unavoidable errors of meniscus and capillary depression are of little moment. Moreover, thermometer effects which are a source of sensible error at other temperatures are insignificant in a properly constructed bath at 0°. It is to be remembered in this connection, as possibly explaining the apparent anomaly, that at 0° the 0.1 normal solution is within less than 0.2° of its freezing temperature. It is desirable to investigate more concentrated solutions at temperatures equally near their freezing-points, but such investigations will obviously be attended by great, if not insurmountable, experimental difficulties. The problem of maintaining constant temperatures below 0° is in itself a difficult one. Moreover, at temperatures below the freezing-point of the solvent, the osmotic pressures of solutions can be measured only by differential methods; that is, the cells must be surrounded by solu-

TABLE 63.

Concentration.	Mean ratio.
0.1	1.083
0.2	1.061
0.3	1.060
0.4	1.060
9.5	1.067
0.6	1.074
0.7	1.083
0.8	1.093
0.9	1.103
1.0	1.114

tions only a little less dilute than those whose osmotic pressure is to be determined.

The ratios of osmotic to gas pressure between 0° and 25°, though constant for each concentration, are all greater than unity. The excess varies from 6 per cent in the 0.2, 0.3, and 0.4 normal solutions, on the one side, to 8.3 per cent in the 0.1 normal solution; and on the other, to 11.4 per cent in the normal solution. The increase in ratio from the 0.4 through the succeeding concentrations exhibits a certain amount of regularity. The increment between the 0.4 and 0.5, and also between the 0.5 and 0.6, is about 0.7 per cent. All the succeeding increments, i. e., those between the 0.6 and 0.7, the 0.7 and 0.8, the 0.8 and 0.9, and the 0.9 and 1.0 concentrations, are approximately 1.0 per cent. A noticeable feature of the 0.2, 0.3, and 0.4 weight-normal solutions is the fact that their osmotic pressures are all about equally (6 per cent) in excess of the calculated gas pressure of the solute.

TABLE 62.—*Cane sugar. Ratio of osmotic to gas pressure.*

Conc.	0°.	5°.	10°.	15°.	20°.	25°.	30°.	40°.	50°.	60°.	70°.	80°.
0.1	(1.106)	1.082	1.082	1.082	1.084	1.084	1.000	1.003	1.000	1.000	.....	.....
0.2	1.061	1.063	1.060	1.061	1.062	1.059	1.020	1.011	1.002	1.001	.....	.....
0.3	1.061	1.058	1.059	1.061	1.060	1.060	1.031	1.024	1.009	0.999	.....	.....
0.4	1.060	1.059	1.060	1.059	1.060	1.059	1.040	1.038	1.017	1.000	.....	.....
0.5	1.068	1.067	1.066	1.068	1.067	1.065	1.050	1.046	1.025	1.006	1.000	.....
0.6	1.0765	1.074	1.073	1.073	1.073	1.071	1.060	1.054	1.032	1.014	1.002	.....
0.7	1.083	1.084	1.083	1.083	1.084	1.083	1.069	1.059	1.041	1.020	0.999	.....
0.8	1.093	1.093	1.092	1.093	1.093	1.093	1.081	1.067	1.049	1.027	1.008	1.001
0.9	1.104	1.102	1.102	1.102	1.103	1.102	1.089	1.076	1.059	1.033	1.015	1.000
1.0	1.115	1.115	1.113	1.115	1.115	1.113	1.101	1.085	1.071	1.044	1.023	1.000

Having found that the law of Gay-Lussac *does* hold for the osmotic pressures of cane-sugar solutions between 0° and 25°, one is inclined to believe that they should also conform to the law of Boyle, and to seek for some rational explanation of the facts: 1st, that the ratios in question are excessive, i. e., above unity; and 2d, that they are not proportional to the supposed concentration of the solutions. The most obvious general explanation (if one attempts to reconcile the pressures between 0° and 25° to the view that the law of Boyle, as well as that of Gay-Lussac, does hold) is *hydration of the solute,* which may be presumed to have the effect of concentrating the solutions. But if one attempts to work out the precise degrees of hydration which would account for the variations of ratio from concentration to concentration, he is quickly entangled in certain hazardous assumptions respecting the relations of solvent to solute and the effect of these upon the osmotic pressure. In the writer's opinion, judgment as to the applicability of Boyle's law to the osmotic pressure of cane-sugar solutions at temperatures below 25° should be suspended until much more is known about the osmotic pressures of the aqueous solutions of other substances.

The half of Table 62 which lies to the right of the heavy vertical line is divided into two areas by a heavy zig-zag line, which begins at the top between 25° and 30°, and ends at the bottom between 70° and 80°. All the ratios between the vertical and the zig-zag lines are greater than unity, but *decrease* continuously with rising temperature. The ratios to the right and above the zig-zag line are *unity* within necessary experimental errors.

The situation disclosed in Table 62 may be summed up as follows: Between 0° and 25°, the ratios of osmotic to gas pressure are all greater than unity, but constant for each concentration. At some temperature between 25° and 30°, these ratios begin to decline, but relatively more rapidly in the dilute than in the concentrated solutions. At some temperature (30° for 0.1; 50° for 0.2; 60° for 0.3 and 0.4; 70° for 0.5, 0.6, and 0.7; and 80° for 0.8, 0.9, and 1.0) the ratio becomes *unity* for every concentration.

The decrease in the ratios of osmotic to gas pressure at temperatures above 25° suggests an increasing dilution of the solutions through the dissociation of unstable hydrates; and it serves to strengthen the impression that the excessive but constant ratios below 25° are due to the presence of stable hydrates.

However the excessive-constant and the excessive-declining ratios may be explained, it is clear that at 30°, 40°, 50°, and 60° the osmotic pressure of the 0.1 weight-normal solution obeys both of the gas laws. The same may safely be affirmed of the 0.2 normal at 50° and 60°; of the 0.3 and 0.4 at 60°; of the 0.5, 0.6, and 0.7 at 70°; and of the 0.8, 0.9, and 1.0 at 80°. It is now important to ascertain whether the ratios, having once declined to unity, maintain that value at all higher temperatures; hence the work of measuring the osmotic pressure of cane sugar at 70° and 80°, and at still higher temperatures, will be resumed as soon as the new cells, previously referred to, have been sufficiently developed for use at those temperatures. The development of membranes from a satisfactory condition at 30° to an efficient state at 70° or 80° will probably require about one year.

Special attention is again called to experiment 2 with the 0.5 weight-normal solution at 15°, where the full osmotic pressure was maintained by the cell for 60 days without any evidence, at the end of that time, of a weakening of the membrane. The experiment is important, not only because it proves the membrane to have great endurance, but also because of the light which it throws upon the question of the *deterioration* of the membranes while in contact with a solute. The cell (C_5) which was used in the experiment in question was brought again into a usable condition within the time ordinarily required for that purpose, and was subsequently employed for eight more determinations which are recorded in the present chapter. A membrane which had been a long time in contact with a 0.4 weight-normal solution of lithium chloride required for its restoration more than 20 months of soaking in water.

CHAPTER IX.

GLUCOSE.

FINAL DETERMINATIONS OF OSMOTIC PRESSURE.

The conditions under which the determinations recorded in this chapter were made were the same as for the "final" measurements of the osmotic pressure of cane sugar. There was no sensible change in the rotation of the solutions while in the cells; and there was, therefore, no gain or loss in their concentration. The temperature maintained in the baths was constant to within 0.02°, except when some unforeseen accident happened to the regulating system. It has already been stated that the usual cause of such accidents is a temporary failure of the current at the power house. If this is promptly discovered, serious results may be avoided by switching the regulating devices to the storage battery. The normal effect of a break in the current is, of course, a drop in the temperature of the baths. Occasionally, the temperature of the baths is forced up above that for which the thermostats are set, but this is always due to a failure to make the "cooling margin" sufficiently ample to cover all possible fluctuations in external temperature conditions. In practice it rarely happens, except when measuring osmotic pressure near the temperature of the outside air. Whenever a deviation in bath temperature has been sufficient to produce a really serious thermometer effect, the fact has been made apparent in this report by omitting from the record the readings of the day or days through which the thermometer effect persisted.

The material employed for the determinations was the same as that used for the measurements reported in Chapter VII.

It was intended originally to begin the "final" measurements of the osmotic pressure of glucose solutions at 0°, and then, as in the case of cane sugar, to repeat the work at each higher interval of 5° or 10° in regular order. But the disaster to the cells explained previously made a change in plan advisable. It was desired to resume and complete the work on cane sugar at high temperatures with the least possible loss of time; and to this end the deposition and development of the membranes in the new cells were begun at the highest practicable temperature, namely, 30°. But as the new cells, after serving at high temperatures, might also be lost on returning to ordinary or low temperatures, it was decided to measure the osmotic pressure of glucose at each temperature-interval for which the membranes must be developed before resuming the work upon cane sugar. In other words, it was decided, after

having developed the membranes at 30°, to measure the pressures of glucose at that temperature before proceeding to develop them at 40°; and, having perfected them at 40°, to measure again the pressures of glucose before proceeding to 50°, etc. On reaching 70° and 80°, at which the measurement of the pressures of cane sugar was discontinued, it is intended to determine the osmotic pressure of both substances concurrently, for those and for all higher temperatures. It has been suggested in a former chapter that perhaps membranes which have served at high temperatures may be saved for work at lower temperatures by reversing the process by which they were developed, that is, by perfecting them at short temperature-intervals in the descending order. This will be attempted after finishing the work upon glucose and cane sugar at high temperatures. The prospect for success is not regarded as very good; since, hitherto, it has been found quite impracticable to rebuild effective membranes out of old ones which have largely lost their semi-permeable character. It appears to make little difference whether the damage to the membranes has resulted from a great and too rapid fall in temperature, or from the action of electrolytes upon them. The only remedy for loss of osmotic activity which has thus far been discovered is a persistent soaking of the membranes in water. They often recover under this treatment.

TABLE 64.—*Determinations of osmotic pressure at 30°.*

Measurements by H. N. Morse, W. W. Holland, and A. S. Musselman. W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.									
						Second day.	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.	Eighth day.	Ninth day.	Tenth day.	Eleventh day.
0.1 W. N. S. at 30°	1	J_8	250,000	5_0	2.52	.....	.....	3.472	3.464	3.464	3.466	3.471	3.474	.....	3.472
C. G. P. 2.472.....	2	H_5	200,000	15	3.23	.....	.....	.....	.....	.....	.....	.....	.....	.....	3.485
0.2 W. N. S. at 30°	1	U_5	300,000	5_0	6.48	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
C. G. P. 4.943.....	2	A_8	200,000	5_0	5.46	.....	.....	.....	.....	.....	5.951	5.949	5.950	5.956	5.954
0.3 W. N. S. at 30°	1	A_8	400,000	5	7.701	.....	.....	.....	8.430	8.422	8.425	8.426	8.418	8.413	8.405
C. G. P. 7.415.....	2	C_8	300,000	31	7.67	.....	.....	8.428	8.397	8.422	8.432	8.422	8.412	8.412	8.397
0.4 W. N. S. at 30°	1	Ni_7	300,000	22	8.68	.....	.....	.....	.....	10.916	10.880	10.871	10.865	10.867	10.869
	2	A_8	200,000	5	10.12	.....	.....	10.868	10.875	10.877	10.887	10.887	10.887	10.889	10.897
C. G. P. 9.886.....	3	J_8	150,000	5	10.11	.....	10.889	10.885	10.877	10.907	10.897	.....	.....	.....	.....
0.5 W. N. S. at 30°	1	A_8	65,000	5	12.58	.....	.....	.....	.....	.....	13.381	13.348	13.361	13.330	.....
	2	G_5	100,000	38	14.47	.....	.....	.....	.....	13.354	13.342	13.352	13.362	13.362	13.360
C. G. P. 12.358....	3	U_5	200,000	38	12.67	.....	13.344	13.313	13.338	13.333	13.337	13.339	13.340	13.342	13.345
0.6 W. N. S. at 30°	1	Q_8	65,000	28	17.79	.....	15.800	15.818	15.833	15.861	15.862	15.861	.....	.....	.....
C. G. P. 14.830....	2	R_8	200,000	1_0	13.67	.....	15.792	15.862	15.862	15.858	15.881	.....	.....	.....	.....
0.7 W. N. S. at 30°	1	3	30,000	5	17.79	18.375	18.325	18.320	18.320	18.320	.....	.....	.....	.....	.....
	2	Q_3	50,000	31	17.08	.....	18.312	18.327	18.332	18.332	18.325	.....	.....	.....	.....
C. G. P. 17.301....	3	E_8	65,000	22	10.71	.....	.....	.....	.....	.....	.....	.....	.....	18.325	18.368
0.8 W. N. S. at 30°	1	G_8	200,000	38	23.14	.....	.....	.....	.....	.....	.....	20.778	20.773	20.774	.....
C. G. P. 19.773....	2	J_8	280,000	28	22.01	.....	.....	.....	.....	.....	20.772	20.789	20.789	(*)	.....
	1	X_8	35,000	5	22.18	.....	.....	.....	.....	23.265	23.235	23.244	23.289	23.280	.....
0.9 W. N. S. at 30°...	2	O_8	1,100,000	27	22.45	23.321	23.295	23.321	23.308	23.276	.....	.....	.....	.....	.....
C. G. P. 22.244....	3	S_8	1,100,000	24	20.60	.....	23.252	23.304	23.335	23.267	.....	.....	.....	.....	.....
1.0 W. N. S. at 30°	1	Ni_7	160,000	5	21.57	.....	25.713	25.713	25.734	(*)	25.755	25.755	.....	.....	.....
	2	U_8.	25,000	29	23.12	.....	.....	.....	.....	25.668	25.693	25.699	25.729	.....	.....
C. G. P. 24.716....	3	R_8	280,000	15	24.71	25.717	25.760	25.762	25.808	25.783	.....	.....	.....	.....	.....

*Therm. effects.

TABLE 64.—*Determinations of osmotic pressure at 30°*—Continued.

	Observed mean daily total pressures.									Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	Twelfth day.	Thirteenth day.	Fourteenth day.	Fifteenth day.	Sixteenth day.	Seventeenth day.	Eighteenth day.	Nineteenth day.	Twentieth day.					
0.1 W. N. S. at 30° C. G.	3.488	3.446	3.463	3.441	3.462	.....	.....	.....	.....	3.468	0.995	2.473	2.475	1.001
P. 2.472	3.484	3.481	3.478	3.482	3.462	.....	3.489	3.485	3.482	3.481	1.004	2.477		
0.2 W. N. S. at 30° C. G.	.....	5.944	5.949	5.942	5.955	5.957	.....	.....	.....	5.949	1.007	4.942	4.9495	1.001
P. 4.943	.....	.....	.....	.....	.....	.....	.....	.....	.....	5.952	0.995	4.957		
0.3 W. N. S. at 30° C. G.	8.399	8.397	8.406	.....	.....	.....	.....	.....	.....	8.414	0.997	7.417	7.417	1.000
P. 7.415	8.409	8.412	.....	.....	.....	.....	.....	.....	.....	8.413	0.997	7.416		
0.4 W. N. S. at 30° C. G.	10.876	10.835	10.878	10.894	.....	.....	.....	.....	.....	10.875	1.000	9.875	9.885	1.000
P. 9.886	10.899	10.897	.....	.....	.....	.....	.....	.....	.....	10.886	1.001	9.885		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	10.891	0.997	9.894		
0.5 W. N. S. at 30° C. G.	.....	.....	.....	.....	.....	.....	.....	.....	.....	13.355	0.994	12.361	12.352	1.000
P. 12.358	13.358	13.360	13.351	13.358	.....	.....	.....	.....	.....	13.356	1.001	12.355		
0.6 W. N. S. at 30° C. G.	.....	.....	.....	.....	.....	.....	.....	.....	.....	13.337	0.998	12.339	14.8365	1.000
P. 14.830	.....	.....	.....	.....	.....	.....	.....	.....	.....	15.839	1.008	14.831		
0.7 W. N. S. at 30° C. G.	.....	.....	.....	.....	.....	.....	.....	.....	.....	15.850	1.008	14.842	17.327	1.002
P. 17.301	.....	.....	.....	.....	.....	.....	.....	.....	.....	18.332	1.006	17.326		
	18.322	(*)	(*)	(*)	18.326	.....	.....	.....	.....	18.325	1.001	17.342		
0.8 W. N. S. at 30° C. G.	.....	.....	(*)	20.777	.....	.....	.....	.....	.....	18.335	1.004	17.331	19.770	0.999
P. 19.773	20.781	20.752	.....	.....	.....	.....	.....	.....	.....	20.775	1.006	19.769		
0.9 W. N. S. at 30° C. G.	.....	.....	.....	.....	.....	.....	.....	.....	.....	20.776	1.005	19.771	22.282	1.002
P. 22.244	.....	.....	.....	.....	.....	.....	.....	.....	.....	23.263	1.004	22.259		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	23.304	1.004	22.300		
1.0 W. N. S. at 30° C. G.	.....	.....	.....	.....	.....	.....	.....	.....	.....	23.290	1.004	22.286	24.727	1.000
P. 24.716	.....	.....	.....	.....	.....	.....	.....	.....	.....	25.732	1.005	24.727		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	25.697	1.004	24.693		
	.....	.....	.....	.....	.....	.....	.....	.....	.....	25.766	1.002	24.764		

*Therm. effects.

TABLE 65.—*Determinations of osmotic pressure at 40°.*

W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.							
						Second day.	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.	Eighth day.	Ninth day.
0.1 W. N. S. at 40° C. G. P. 2.553	1	O_8	25,000	4_0	3.59	.....	.....	.....	.....	.....	.....	.....	.....
	2	X_8	24,000	27	3.04	.....	.....	.....	.....	.....	.....	.....	.....
0.2 W. N. S. at 40° C. G. P. 5.107	1	Ni_7	110,000	5	5.45	.....	.....	6.121	6.116	6.116	6.120	6.119	.....
	2	Q_8	25,000	15	5.64	.....	.....	.....	.....	6.132	6.123	6.109	6.099
0.3 W. N. S. at 40° C. G. P. 7.660	1	R_8	20,000	5	6.28	.....	.....	.....	.....	8.690	8.668	8.665	8.654
	2	A_8	50,000	15	8.71	.....	.....	8.663	8.653	8.647	8.648	8.669	8.666
0.4 W. N. S. at 40° C. G. P. 10.213	1	P_8	70,000	22	7.22	.....	.....	.....	11.159	11.178	11.189	11.183	11.211
	2	V_8	50,000	1_0	12.185	.....	.....	.....	11.269	11.251	11.252	11.221	11.192
0.5 W. N. S. at 40° C. G. P. 12.757	1	A_5	550,000	27	13.40	.....	.....	13.822	13.699	13.734	13.746	13.744	13.748
	2	U_8	35,000	28	13.04	.....	.....	.....	13.750	13.764	13.768	13.766	13.770
0.6 W. N. S. at 40° C. G. P. 15.320	1	Y_8	35,000	5	18.95	.....	.....	16.324	16.298	16.309	16.314	16.330	.....
	2	V_8	25,000	28	15.41	.....	16.358	16.306	16.316	16.327	16.329	.....	.....
0.7 W. N. S. at 40° C. G. P. 17.873	1	V_8	65,000	24	17.99	18.903	18.890	18.896	18.870	18.910	.....	.....	.....
	2	G_8	140,000	15	16.15	.....	.....	.....	.....	.....	18.848	18.866	18.883
	3	U_5	100,000	20	22.57	.....	.....	.....	.....	18.886	18.874	18.851	18.872
0.8 W. N. S. at 40° C. G. P. 20.426	1	U_8	50,000	29	21.04	21.458	21.429	21.429	21.442	21.417	.....	.....	.....
	2	T_5	280,000	31	28.05	.....	.....	.....	21.354	21.375	21.375	21.410	21.429
0.9 W. N. S. at 40° C. G. P. 22.980	1	R_8	20,000	25	24.53	.....	.....	.....	24.057	24.056	24.044	24.030	24.027
	2	A_8	280,000	38	22.09	.....	.....	.....	23.950	23.952	23.961	23.966	23.978
	3	J_8	100,000	28	23.41	23.962	23.969	24.009	24.020	24.065	.....	.....	.....
1.0 W. N. S. at 40° C. G. P. 25.533	1	U_8	24,000	38	25.84	.....	26.582	26.579	26.576	26.573	26.576	.....	.....
	2	P_8	44,000	29	23.87	.....	.....	.....	.....	26.482	26.501	26.514	26.545
	3	Q_8	65,000	5_0	24.20	.....	.....	.....	.....	.....	26.543	26.514	26.558

TABLE 65.—*Determinations of osmotic pressure at 40°*—Continued.

	Observed mean daily total pressures.							Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	Tenth day.	Eleventh day.	Twelfth day.	Thirteenth day.	Fourteenth day.	Fifteenth day.	Sixteenth day.					
0.1 W. N. S. at 40° C. G. P. 2.553	.....	3.563	3.526	3.530	3.533	3.542	.....	3.539	0.998	2.541	2.553	1.000
	.....	.....	3.544	3.568	3.566	3.572	3.564	3.563	0.998	2.565		
0.2 W. N. S. at 40° C. G. P. 5.107	.....	.....	.....	.....	.....	.....	.....	6.118	1.009	5.109	5.112	1.001
	6.104	6.136	.....	.....	.....	.....	.....	6.117	1.002	5.115		
0.3 W. N. S. at 40° C. G. P. 7.660	8.649	.....	.....	.....	.....	.....	.....	8.665	1.000	7.665	7.664	1.001
	.....	.....	.....	.....	.....	.....	.....	8.658	0.995	7.663		
0.4 W. N. S. at 40° C. G. P. 10.213	.....	.....	.....	.....	.....	.....	.....	11.184	1.000	10.184	10.205	0.999
	11.182	11.219	11.201	.....	.....	.....	.....	11.223	0.998	10.225		
0.5 W. N. S. at 40° C. G. P. 12.757	.....	.....	.....	.....	.....	.....	.....	13.749	1.000	12.749	12.756	1.000
	.....	.....	.....	.....	.....	.....	.....	13.763	1.000	12.763		
0.6 W. N. S. at 40° C. G. P. 15.320	.....	.....	.....	.....	.....	.....	.....	16.315	0.998	15.317	15.325	1.000
	.....	.....	.....	.....	.....	.....	.....	16.327	0.994	15.333		
0.7 W. N. S. at 40° C. G. P. 17.873	.....	.....	.....	.....	.....	.....	.....	18.894	1.008	17.886	17.870	1.000
	18.841	18.859	18.848	.....	.....	.....	.....	18.857	1.001	17.856		
	18.856	.....	.....	.....	.....	.....	.....	18.868	0.999	17.869		
0.8 W. N. S. at 40° C. G. P. 20.426	.....	.....	.....	.....	.....	.....	.....	21.435	0.999	20.436	20.411	0.999
	.....	.....	.....	.....	.....	.....	.....	21.388	1.003	20.385		
0.9 W. N. S. at 40° C. G. P. 22.980	.....	.....	.....	.....	.....	.....	.....	24.043	0.994	23.049	23.00	1.000
	.....	.....	.....	.....	.....	.....	.....	23.962	0.993	22.969		
	.....	.....	.....	.....	.....	.....	.....	24.005	1.010	22.995		
1.0 W. N. S. at 40° C. G. P. 25.533	.....	.....	.....	.....	.....	.....	.....	26.577	1.007	25.570	25.533	1.000
	26.558	.....	.....	.....	.....	.....	.....	26.520	1.012	25.508		
	26.558	26.499	.....	.....	.....	.....	.....	26.534	1.011	25.523		

TABLE 66.—*Determinations of osmotic pressure at 50°.*

W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Experiment No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.									
						Second day.	Third day.	Fourth day.	Fifth day.	Sixth day.	Seventh day.	Eighth day.	Ninth day.	Tenth day.	Eleventh day.
0.1 W. N. S. at 50° C.															
G. P. 2.365	1	Q_8	100,000	15	3.51	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.2 W. N. S. at 50° C.	1	A_8	100,000	1_0	7.06	.....	.....	.....	.....	.....	.....	6.281	6.276	6.268	6.285
G. P. 5.270	2	R_8	16,000	24	7.19	.....	6.262	6.270	6.267	6.264	6.266	.....	.....	.....	.....
0.3 W. N. S. at 50° C.	1	X_8	30,000	29	13.13	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
G. P. 7.905	2	P_8	55,000	5	10.66	.....	.....	.....	.....	.....	.....	8.916	8.915	8.924	8.918
0.4 W. N. S. at 50° C.	1	Y_8	44,000	39	19.757	.....	.....	.....	11.567	11.542	11.486	11.492	11.502	11.509	11.512
G. P. 10.540	2	Ni_7	85,000	56	16.89	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.5 W. N. S. at 50° C.	1	V_8	33,000	1_0	11.79	.....	.....	.....	.....	.....	.....	.....	.....	14.185	14.203
G. P. 13.175	2	P_8	30,000	1_0	14.88	.....	.....	.....	14.236	14.207	14.173	14.217	14.204	.....	.....
0.6 W. N. S. at 50° C.	1	W_8	34,000	31	22.134	.....	.....	.....	.....	16.762	16.832	16.802	16.786	16.832	.....
G. P. 15.810	2	O_8	23,000	1_0	15.93	16.820	16.819	16.826	16.785	.....	.....	16.795	16.780	16.795	16.788
0.7 W. N. S. at 50° C.	1	U_8	35,000	1_0	20.22	.....	.....	.....	19.478	19.430	19.471	19.464	19.402	.....	.....
G. P. 18.445	2	R_8	31,000	4_0	20.92	.....	19.412	19.416	19.457	19.489	19.461	.....	.....	.....	.....
0.8 W. N. S. at 50° C.	1	Q_8	73,000	38	22.00	.....	.....	.....	.....	22.124	22.140	22.073	22.056	22.004	.....
G. P. 21.08	2	Q_8	12,000	38	21.7	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.9 W. N. S. at 50° C.	1	U_8	41,000	25	23.92	.....	.....	.....	.....	.....	.....	24.704	.....	24.656	24.650
G. P. 23.715	2	Q_8	40,000	25	28.55	.....	.....	24.712	24.653	24.659	24.659	24.659	.....	.....	.....
1.0 W. N. S. at 50° C.	1	Y_8	35,000	38	28.45	.....	.....	.....	.....	.....	27.308	27.316	27.283	27.280	27.269
G. P. 26.35	2	G_8	370,000	29	21.65	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

TABLE 66.—*Determinations of osmotic pressure at 50°*—Continued.

	Observed mean daily total pressures.										Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	Twelfth day.	Thirteenth day.	Fourteenth day.	Fifteenth day.	Sixteenth day.	Seventeenth day.	Eighteenth day.	Nineteenth day.	Twentieth day.	Twenty-first day.					
0.1 W. N. S. at 50°															
C. G. P. 2.365	.....	.....	.....	.....	.....	.....	3.614	3.637	3.641	3.641	3.633	1.000	2.633	.....	0.999
0.2 W. N. S. at 50°	6.282	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.278	0.995	5.283	5.275	1.001
C. G. P. 5.270	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.266	0.999	5.267		
0.3 W. N. S. at 50°	.....	.....	8.895	8.897	8.900	8.907	8.910	.....	.....	.....	8.902	1.001	7.901	7.909	1.001
C. G. P. 7.905	8.924	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.919	1.002	7.917		
0.4 W. N. S. at 50°	11.516	11.514	11.515	11.515	.....	.....	.....	.....	.....	.....	11.515	0.991	10.524	10.531	0.999
C. G. P. 10.540	11.545	11.529	11.524	11.546	11.526	.....	.....	.....	.....	.....	11.538	1.000	10.538		
0.5 W. N. S. at 50°	14.138	14.184	14.254	.....	.....	.....	.....	.....	.....	.....	14.193	0.996	13.197	13.198	1.002
C. G. P. 13.175	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	14.207	1.009	13.198		
0.6 W. N. S. at 50°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	16.803	0.997	15.806	15.808	1.000
C. G. P. 15.810	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	16.801	0.991	15.810		
0.7 W. N. S. at 50°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	19.449	0.996	18.453	18.446	1.000
C. G. P. 18.445	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	19.447	1.008	18.439		
0.8 W. N. S. at 50°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	22.079	0.997	21.082	21.045	0.998
C. G. P. 21.08	.....	.....	21.971	22.001	22.023	22.008	22.038	.....	.....	.....	22.008	1.001	21.007		
0.9 W. N. S. at 50°	24.644	24.572	24.588	.....	.....	.....	.....	.....	.....	.....	24.636	1.003	23.633	23.649	0.997
C. G. P. 23.715	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	24.667	1.002	23.665		
1.0 W. N. S. at 50°	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	27.291	1.010	26.281	26.324	0.999
C. G. P. 26.35	.....	.....	.....	27.336	27.350	27.375	27.414	27.373	.....	.....	27.369	1.003	26.366		

TABLE 67.—*Osmotic pressure of glucose at 30°, 40°, and 50°.*

Osmotic pressures.	Concentration.									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
At 30°.	2.473	4.942	7.417	9.875	12.361	14.831	17.326	19.769	22.259	24.727
Observed pressures.	2.477	4.957	7.416	9.885	12.355	14.842	17.324	19.771	22.300	24.693
	.....	.....	.....	9.894	12.339	.....	17.331	.....	22.286	24.767
Mean pressures....	2.475	4.950	7.417	9.885	12.352	14.837	17.327	19.770	22.282	24.727
Ratio of osmotic to gas pressure.....	1.001	1.001	1.000	1.000	1.000	1.000	1.002	0.999	1.002	1.000
At 40°.	2.541	5.109	7.655	10.184	12.749	15.317	17.886	20.436	23.049	25.570
Observed pressures.	2.565	5.115	7.663	10.225	12.763	15.333	17.856	20.385	22.969	25.508
	.....	.....	.....	.....	.....	.....	17.869	.....	22.995	.....
Mean pressures....	2.553	5.112	7.664	10.205	12.756	15.325	17.870	20.411	23.000	25.533
Ratio of osmotic to gas pressure.....	1.000	1.001	1.001	0.999	1.000	1.000	1.000	0.999	1.000	1.000
At 50°.	2.633	5.283	7.901	10.524	13.197	15.806	18.453	21.082	23.633	26.281
Observed pressures.	.....	5.267	7.917	10.538	13.198	15.810	18.439	21.007	23.665	26.366
Mean pressures....	2.633	5.275	7.909	10.531	13.198	15.808	18.446	21.045	23.649	26.342
Ratio of osmotic to gas pressure.....	0.999	1.001	1.001	0.999	1.002	1.000	1.000	0.998	0.997	0.999

The foregoing measurements of the osmotic pressure of glucose indicate that, between 30° and 50°, the aqueous solutions of this substance obey the gas laws, since—if we employ the *weight* or *solvent* normal system in making the solutions, and refer the theoretical gas pressure of the solute to the volume of the pure solvent—the ratio of observed osmotic to calculated gas pressure is, in all cases, approximately unity. Stated in another way, the equation of van't Hoff for very *dilute solutions*, $PV = KT$, applies to *concentrated* solutions of glucose between 30° and 50°, provided we allow the V to signify the volume of the pure solvent, instead of the volume of the solution.

The osmotic pressure of glucose, and also of cane sugar, will be measured at 60°, 70°, 80°, and, if possible, at still higher temperatures.

CHAPTER X.

MANNITE.

DETERMINATIONS OF OSMOTIC PRESSURE.

According to the very careful determinations of Loomis,* the molecular depression of the freezing points of the 0.1 to 0.5 weight-normal solutions of mannite is normal, *i. e.*, 1.85°. For this reason the determination of the osmotic pressure of the substance is of especial interest.

It was found, as shown in Chapter V, that the osmotic pressure of cane-sugar solutions, up to and including 25°, can be calculated from the observed *abnormal* depressions of the freezing points, but not for higher temperatures. At and below 25°, the ratio of osmotic to the estimated gas pressure of the solute was the same for each concentration of solution as the ratio of the observed to the theoretical depression of the freezing point. At temperatures above 25° the ratios of osmotic to gas pressure—previously constant but abnormally high—began to decline, and the osmotic pressures of the solutions could, of course, no longer be correctly calculated from the depressions of the freezing points. Stated in another way, the osmotic pressures of cane sugar solutions between 0° and 25° are abnormal to the same degree as the depressions of the freezing points, but not at any higher temperatures. At some temperature above 25°, the ratio of osmotic to gas pressure became unity and *constant.* The osmotic pressures of the solutions could then, of course, be correctly derived, not from the *observed,* but from the *theoretical,* depressions of the freezing points, *i. e.*, from a molecular depression of about 1.85°.

In view of the relations between freezing points and osmotic pressure, which were found to hold in the case of cane sugar, it was to be presumed that the ratio of osmotic to gas pressure in the case of mannite solutions would be found to be unity at all temperatures.

Unfortunately the solubility of mannite in water is limited, the 0.5 weight-normal being the most concentrated solution whose pressures can be measured at low temperatures. Otherwise, it is an excellent substance with which to answer the question whether those compounds which exhibit normal freezing-point depressions may also be expected to exhibit normal osmotic pressures, *i. e.*, pressures which conform to the gas laws. It is readily obtained in sufficient quantity for an extended investigation, and in sufficiently pure condition.

*Zeitschrift für physikalische Chemie, 32, 599.

The determinations of the osmotic pressures of cane sugar and glucose presented in Chapters VIII and IX were designated as "*final*" in order to express the confidence of the author in the general correctness of the results. The measurements contained in the present chapter are not so designated, because one essential test of their reliability has not been applied to them: It was not *proved* that the solutions of mannite maintained perfectly their concentration while in the cells. It was easy to do this in the case of cane sugar and glucose, because slight changes in the concentration of solutions could be detected and measured by the polariscope; but in that of mannite, there was at the time no convenient analytical method available. The "*interferometer*" made by Zeiss has since been introduced for use with optically inactive substances, and will be employed when the "*final*" determinations of the osmotic pressure of mannite are undertaken. The author's reasons for insisting on a perfect maintenance of concentration while the solutions are in the cells, as an indispensable part of the evidence of credibility, have already been given, and they still seem to him perfectly valid, and worthy of the strongest emphasis. Nevertheless, he does not wish to be understood as intimating that any great amount of suspicion attaches to the present determinations of the osmotic pressure of mannite, because of the absence of this proof. On the contrary, he believes the results to be quite trustworthy.

A large proportion of the cells which were used with mannite had previously been employed in measuring the osmotic pressure of lithium chloride. The effect of exposure to an electrolyte is to render the membranes sluggish. Evidence of that result is probably to be seen (1) in the long time consumed by the cells in coming to equilibrium, and (2) in the considerable thermometer effects, *i. e.*, in the rather large fluctuations in pressure from day to day. As usual when membranes of diminished activity are employed, the cells were generally allowed to make long records for the purpose of minimizing thermometer effects. It is, however, not certain, in this instance, that the remarkable tardiness of the cells in coming to equilibrium was due wholly to the effect of the electrolyte upon the membranes; for it was observed that certain cells, whose membranes had not been in contact with an electrolyte, were likewise very slow in establishing their final pressures. It has not yet been determined whether this was due to the hard burning of the cells—in effect to the limited area of the membranes—or to some peculiarity of the mannite which distinguishes it from cane sugar and glucose, or other non-electrolytes. Hitherto, we have had no reason to suspect, *in the case of non-electrolytes*, that the activity of the membrane varies with the solute. The question is an important one, and it will be carefully investigated.

TABLE 68.—*Determinations of osmotic pressure at 10°.*

Measurements by H. N. Morse, J. C. W. Frazer, and E. L. Frederick. W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Exp. No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.								
						14th day.	15th day.	16th day.	17th day.	18th day.	19th day.	20th day.	21st day.	22d day.
0.1 W. N. S. at 10° C. G. P.	1	Z_7	1,100,000	61	3.135	.....	.....	.....	.....	.....	.....	.....	.....	.....
2.308	2	F_7	1,100,000	60	3.393	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.2 W. N. S. at 10° C. G. P. 4.616	1	R_6	1,100,000	44	5.685	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.3 W. N. S. at 10° C. G. P.	1	J_6	1,100,000	34	8.063	.....	.....	.....	.....	.....	.....	.....	.....	.....
6.925	2	P_6	367,000	32	8.768	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.4 W. N. S. at 10° C. G. P.	1	A_6	550,000	32	9.76	.....	.....	.....	.....	.....	.....	.....	.....	.....
9.233	2	U_6	550,000	37	10.025	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.5 W. N. S. at 10° C. G. P. 11.541	1	5	1,100,000	35	12.426	12.622	12.615	12.600	12.587	12.600	12.626	12.635	12.627	12.612

	Observed mean daily total pressures.												
	23d day.	29th day.	30th day.	31st day.	32d day.	33d day.	34th day.	35th day.	36th day.	37th day.	38th day.	39th day.	40th day.
0.1 W. N. S. at 10° C. G. P.	.....	3.315	3.308	3.310	3.315	3.311	3.313	3.311	3.309	3.309	3.311	.....	.....
2.308	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.2 W. N. S. at 10° C. G. P. 4.616	.....	5.621	5.596	5.582	5.591	5.598	5.596	5.613	5.590	5.594	5.598	.....	.....
0.3 W. N. S. at 10° C. G. P.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
6.925	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.4 W. N. S. at 10° C. G. P.	.....	.....	10.297	10.229	10.160	10.156	10.198	10.155	10.175	10.186	10.173	10.179	10.206
9.233	.....	10.318	10.336	10.207	10.148	10.159	10.195	10.188	10.188	10.202	10.169	10.173	10.209
0.5 W. N. S. at 10° C. G. P. 11.541	12.622	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

TABLE 68.—*Determinations of osmotic pressure at 10°*—Continued.

	Exp. No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures. 46th day.	47th day.	48th day.	49th day.	50th day.	54th day.	55th day.	56th day.	57th day.
0.1 W. N. S. at 10° C. G. P.	1	Z_7	1,100,000	61	3.135	.....	.....	.....	.....	.....	.....	.....	.....	.....
2.308	2	F_7	1,100,000	60	3.393	.....	.....	.....	.....	.....	3.300	3.310	3.317	3.307
0.2 W. N. S. at 10° C. G. P. 4.616	1	R_6	1,100,000	44	5.685	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.3 W. N. S. at 10° C. G. P.	1	J_6	1,100,000	34	8.063	.....	.....	.....	.....	.....	.....	7.958	7.958	7.962
6.925	2	P_6	367,000	32	8.768	7.916	7.932	7.944	7.927	7.946	.....	.....	.....	.....
0.4 W. N. S. at 10° C. G. P.	1	A_6	550,000	32	9.76	.....	.....	.....	.....	.....	.....	.....	.....	.....
9.233	2	U_6	550,000	37	10.025	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.5 W. N. S. at 10° C. G. P. 11.541	1	5	1,100,000	35	12.426	.....	.....	.....	.....	.....	.....	.....	.....	.....

	Observed mean daily total pressures. 58th day.	59th day.	60th day.	61st day.	62d day.	63d day.	64th day.	65th day.	Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
0.1 W. N. S. at 10° C. G. P.	.....	.....	.....	.....	.....	.....	.....	.....	3.311	0.989	2.322	2.314	1.002
2.308	3.317	.....	.....	.....	.....	.....	.....	.....	3.310	1.003	2.307		
0.2 W. N. S. at 10° C. G. P. 4.616	.....	.....	.....	.....	.....	.....	.....	.....	5.598	0.989	4.609	.....	0.998
0.3 W. N. S. at 10° C. G. P.	7.960	7.956	7.942	7.958	9.957	7.938	7.926	7.928	7.949	0.999	6.950	6.940	1.002
6.925	.....	.....	.....	.....	.....	.....	.....	.....	7.933	1.003	6.930		
0.4 W. N. S. at 10° C. G. P.	.....	.....	.....	.....	.....	.....	.....	.....	10.192	0.991	9.201	9.209	0.997
9.233	.....	.....	.....	.....	.....	.....	.....	.....	10.208	0.992	9.216		
0.5 W. N. S. at 10° C. G. P. 11.541	.....	.....	.....	.....	.....	.....	.....	.....	12.615	1.002	11.613	.....	1.006

TABLE 69.—*Determinations of osmotic pressure at 20°.*

W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Exp. No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.								
						2d day.	3d day.	4th day.	5th day.	6th day.	7th day.	8th day.	9th day.	10th day.
0.1 W. N. S. at 20° C. G. P. 2.390	1	U_6	366,700	61	3.44	.....	.....	.....	.....	.....	.....	.....	.....	.....
	2	I_6	157,142	61	3.386	3.386	3.367	3.446	3.416	3.395	3.373	3.358	3.399	3.386
0.2 W. N. S. at 20° C. G. P. 4.78	1	M_6	550,000	34	5.87	.....	.....	.....	.....	.....	.....	.....	.....	.....
	2	P_6	366,666	34	5.91	.....	5.812	5.801	5.792	5.781	5.766	5.757	5.782	5.786
0.3 W. N. S. at 20° C. G. P. 7.17	1	O_6	366,000	32	8.584	.....	.....	.....	.....	.....	.....	.....	.....	.....
	2	G_6	275,000	35	7.74	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.4 W. N. S. at 20° C. G. P. 9.56	1	G_6	550,000	34	11.378	.....	.....	.....	.....	.....	.....	.....	.....	.....
	2	Q_6	550,000	41	9.17	.....	.....	10.571	10.541	10.545	10.551	10.550	10.546	10.578
	3	H_6	367,000	40	8.46	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.5 W. N. S. at 20° C. G. P. 11.95	1	O_6	1,100,000	35	11.65	.....	.....	.....	.....	.....	.....	.....	.....	12.944
	2	S_6	550,000	36	14.67	.....	.....	.....	.....	.....	.....	.....	.....	.....

	Observed mean daily total pressures.												
	11th day.	12th day.	13th day.	14th day.	15th day.	16th day.	17th day.	18th day.	19th day.	20th day.	21st day.	22d day.	23d day.
0.1 W. N. S. at 20° C. G. P. 2.390	.....	.....	.....	.....	.....	.....	.....	.....	3.406	3.400	3.396	3.377	3.376
0.2 W. N. S. at 20° C. G. P. 4.78	5.774	5.764	5.822 5.765	5.806	5.797	5.780	5.769	5.759	5.756	5.743	5.746	5.764	5.754
0.3 W. N. S. at 20° C. G. P. 7.17	.....	.....	.....	.....	.....	.....	8.235	8.195	8.132	8.222	8.168	8.144	8.209
0.4 W. N. S. at 20° C. G. P. 9.56	10.634 10.598	10.661 10.616	10.638 10.634	10.624	10.597	10.578	10.575	10.594	10.594	10.630	10.639	10.647	.....
0.5 W. N. S. at 20° C. G. P. 11.95	12.945	12.916	12.921	12.910	12.956	12.897	12.892 13.017	12.873 12.989	12.911 13.002	12.946 12.993	12.963 12.990	12.971 12.995	..... 13.007

TABLE 69.—*Determinations of osmotic pressure at 20°*—Continued.

	Exp. No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressure.								
						24th day.	25th day.	26th day.	27th day.	28th day.	29th day.	30th day.	31st day.	32d day.
0.1 W. N. S. at 20° C. G. P.	1	U_7	366,700	61	3.44	3.376	3.380	3.380	3.388	3.389	3.384	.....	.....	.....
2.390	2	I_7	157,142	61	3.386	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.2 W. N. S. at 20° C. G. P.	1	M_6	550,000	34	5.87	.....	.....	.....	.....	.....	.....	.....	.....	.....
4.78	2	P_6	366,666	34	5.91	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.3 W. N. S. at 20° C. G. P.	1	O_6	366,000	32	8.584	.....	.....	.....	.....	.....	.....	8.288	8.170	8.175
7.17	2	G_6	275,000	35	7.74	8.212	8.221	8.184	.....	.....	.....	.....	.....	.....
0.4 W. N. S. at 20° C. G. P.	1	G_5	550,000	34	11.378	.....	.....	.....	.....	.....	.....	.....	.....	.....
9.56	2	Q_6	550,000	41	9.17	.....	.....	.....	.....	.....	.....	.....	.....	.....
	3	H_6	367,000	40	8.46	.....	.....	.....	10.451	10.483	10.509	10.513	10.539	10.537
0.5 W. N. S. at 20° C. G. P.	1	O_5	1,100,000	35	11.65	.....	.....	.....	.....	.....	.....	.....	.....	.....
11.95	2	S_6	550,000	36	14.67	12.980	12.965	12.983	.....	.....	.....	.....	.....	.....

	Observed mean daily total pressures.							Mean of all daily pressures.	Mean barometric pressures.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	33d day.	34th day.	35th day.	36th day.	37th day.	38th day.	39th day.					
0.1 W. N. S. at 20° C. G. P.	.....	.....	.....	.....	.....	.....	.....	3.387	0.996	2.391	2.395	1.002
2.390	.....	.....	.....	.....	.....	.....	.....	3.392	0.994	2.398		
0.2 W. N. S. at 20° C. G. P.	.....	.....	.....	.....	.....	.....	.....	5.772	0.994	4.778	4.781	1.000
4.78	.....	.....	.....	.....	.....	.....	.....	5.780	0.997	4.783		
0.3 W. N. S. at 20° C. G. P.	8.167	8.156	8.152	8.150	8.147	8.140	8.128	8.167	0.998	7.169	7.181	1.001
7.17	.....	.....	.....	.....	.....	.....	.....	8.192	1.000	7.192		
0.4 W. N. S. at 20° C. G. P.	.....	.....	.....	.....	.....	.....	.....	10.614	1.001	9.613	9.570	1.001
9.56	10.544	10.542	10.546	10.549	.....	.....	.....	10.573	1.001	9.572		
	.....	.....	.....	.....	.....	.....	.....	10.521	0.997	9.524		
0.5 W. N. S. at 20° C. G. P.	.....	.....	.....	.....	.....	.....	.....	12.927	0.998	11.929	11.960	1.001
11.95	.....	.....	.....	.....	.....	.....	.....	12.992	1.001	11.991		

TABLE 70.—*Determinations of osmotic pressure at 30°.*

W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Exp. No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures. 6th day.	7th day.	8th day.	9th day.	10th day.	11th day.	12th day.	13th day.	14th day.	15th day.
0.1 W. N. S. at 30° C. G. P.	1	Q_6	367,000	9	3.79	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
2.472	2	O_6	550,000	11	3.74	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.2 W. N. S. at 30° C. G. P.	1	O_6	110,000	32	7.41	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
4.943	2	K_6	122,000	32	6.94	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.3 W. N. S. at 30° C. G. P.	1	G_6	367,000	37	9.17	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
7.415	2	H_6	550,000	44	12.66	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.4 W. N. S. at 30° C. G. P.	1	B_6	1,100,000	21	12.69	.....	.....	.....	10.857	10.904	10.907	10.859	10.868	10.842	10.844
9.886	2	Q_6	275,000	19	11.55	10.990	10.970	10.958	10.979	10.958	10.973	10.961	10.956	10.951	10.953
	3	S_6	550,000	36	12.62	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.5 W. N. S. at 30° C. G. P.	1	G_6	550,000	34	11.19	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
12.358	2	C_6	275,000	37	14.60	.....	.....	.....	.....	.....	.....	.....	.....	.....	13.406

	Observed mean daily total pressures. 16th day.	17th day.	18th day.	19th day.	20th day.	21st day.	22d day.	23d day.	24th day.	25th day.	26th day.	27th day.	28th day.
0.1 W. N. S. at 30° C. G. P.	.....	.....	.....	3.415	3.422	th. eff.	3.414	3.481	3.431	3.512	3.467	3.438	3.507
2.472	3.530	3.519	3.531	3.499	3.476	3.470	3.468	3.465	3.461	3.455	3.450	.....	.....
0.2 W. N. S. at 30° C. G. P.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	5.966
4.943	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	5.996	5.947
0.3 W. N. S. at 30° C. G. P.	.....	.....	.....	.....	8.449	8.444	8.438	8.429	8.424	8.419	8.411	8.416	8.435
7.415	.....	.....	.....	.....	.....	8.445	8.436	8.429	8.440	8.446	8.442	8.449	8.456
0.4 W. N. S. at 30° C. G. P.	10.703	10.805	10.753	10.782	10.773	10.743	10.695	10.749	10.753	10.738	10.732	.....	.....
9.886	10.923	10.944	10.949	10.923	10.900	10.928	10.919	10.923	10.919	.....	.....	.....	.....
0.5 W. N. S. at 30° C. G. P.	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
12.358	13.321	13.251	13.311	13.272	13.361	13.437	13.423	13.400	13.530	13.385	13.367	13.279	.....

TABLE 70.—*Determinations of osmotic pressure at 30°*—Continued.

	Exp. No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures. 29th day.	30th day.	31st day.	32d day.	33d day.	34th day.	35th day.	36th day.	37th day.	38th day.
0.1 W. N. S. at 30° C. G. P.	1	Q_6	367,000	9	3.79	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
2.472	2	O_6	550,000	11	3.74	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.2 W. N. S. at 30° C. G. P.	1	O_6	110,000	32	7.41	5.922	5.916	5.950	5.945	5.967	5.939	5.952	5.915	5.907	.....
4.943	2	K_6	122,000	32	6.94	5.952	5.951	5.946	5.958	5.944	5.942	5.936	5.956	5.955	5.941
0.3 W. N. S. at 30° C. G. P.	1	G_6	367,000	37	9.17	8.413	.....	.....	.....	.....	.....	.....	.....	.....	.....
7.415	2	H_6	550,000	44	12.66	8.474	8.334	8.381	8.426	8.426	8.444	8.447	8.440	8.437	8.434
0.4 W. N. S. at 30° C. G. P.	1	B_6	1,100,000	21	12.69	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
9.886	2	Q_6	275,000	19	11.55	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	3	S_6	550,000	36	12.62	.....	.....	.....	.....	.....	.....	.....	.....	10.927	10.895
0.5 W. N. S. at 30° C. G. P.	1	G_6	550,000	34	11.19	.....	13.383	13.346	13.376	13.392	(13.544)	(13.255)	(13.220)	(13.209)	(13.336)
12.358	2	C_6	275,000	37	14.60	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

	Observed mean daily total pressures. 39th day.	40th day.	41st day.	42d day.	43d day.	44th day.	45th day.	Mean of all daily pressures.	Barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
0.1 W. N. S. at 30° C. G. P.	.....	.....	.....	.....	.....	.....	.....	3.454	0.996	2.458	2.4685	0.999
2.472	.....	.....	.....	.....	.....	.....	.....	3.484	1.005	2.479		
0.2 W. N. S. at 30° C. G. P.	.....	.....	.....	.....	.....	.....	.....	5.938	0.998	4.940	4.943	1.000
4.943	.....	.....	.....	.....	.....	.....	.....	5.952	1.006	4.946		
0.3 W. N. S. at 30° C. G. P.	.....	.....	.....	.....	.....	.....	.....	8.428	1.002	7.426	7.430	1.002
7.415	.....	.....	.....	.....	.....	.....	.....	8.432	0.998	7.434		
0.4 W. N. S. at 30° C. G. P.	.....	.....	.....	.....	.....	.....	.....	10.800	0.997	9.803	9.881	0.999
9.886	.....	.....	.....	.....	.....	.....	.....	10.946	0.997	9.949		
	10.964	10.985	10.817	10.810	10.825	10.823	10.822	10.8844	0.993	9.891		
0.5 W. N. S. at 30° C. G. P.	(13.275)	(13.270)	(13.307)	(13.319)	.....	.....	.....	13.326	1.000	12.326	12.345	0.998
12.358	.....	.....	.....	.....	.....	.....	.....	13.365	1.002	12.363		

The pressures which are inclosed in parentheses are regarded with some suspicion. That on the thirty-fourth day has the appearance of a *thermometer effect*, while those which follow appear to be the pressures of a somewhat diluted solution.

TABLE 71.—*Determinations of osmotic pressure at 40°.*

W. N. S. = Weight normal solution. C. G. P. = Calculated gas pressure.

	Exp. No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.										
						11th day.	12th day.	13th day.	14th day.	15th day.	16th day.	17th day.	18th day.	19th day.	20th day.	21st day.
0.1 W. N. S. at 40° C. G. P. 2.553	1	S_6	275,000	61	3.16	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.2 W. N. S. at 40° C. G. P. 5.107	1	O_6	367,000	37	6.33	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.157
	2	Q_6	157,000	40	5.992	6.155	6.148	6.134	6.132	6.101	6.091	6.078	6.110	6.105	6.122	6.111
0.3 W. N. S. at 40° C. G. P. 7.660	1	C_6	110,000	44	8.211	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.4 W. N. S. at 40° C. G. P. 10.213	1	C_6	110,000	41	18.856	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	2	F_6	55,000	37	11.909	.....	.....	.....	11.249	11.227	11.169	11.291	11.163	11.123	11.158	11.168
0.5 W. N. S. at 40° C. G. P. 12.767	1	K_6	58,000	41	13.351	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	2	F_6	55,000	30	15.00	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.6 W. N. S. at 40° C. G. P. 15.32	1	B_6	92,000	42	15.062	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

	Observed mean daily total pressures.														
	22d day.	23d day	24th day.	25th day.	26th day.	27th day.	28th day.	29th day.	30th day.	31st day.	32d day.	33d day.	34th day.	35th day.	36th day.
0.1 W. N. S. at 40° C. G P. 2.553	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	3.563	3.560	3.550
0.2 W. N. S. at 40° C. G. P. 5.107	6.143	6.116	6.093	6.094	6.095	6.078	6.070	6.082	6.077	.....	.....	.....	.....	.....	.....
	6.091	6.051	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.3 W. N. S. at 40° C. G. P. 7.660	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.4 W. N. S. at 40° C. G. P. 10.213	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	11.136	11.256	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.5 W. N. S. at 40° C. G. P. 12.767	.....	.....	.....	13.669	13.601	13.668	13.887	13.858	13.866	13.853	13.773	13.874	13.852	.....	.....
	.....	.....	.....	.....	.....	13.755	13.775	13.762	13.812	13.830	13.844	13.830	13.853	13.832	13.842
0.6 W. N. S. at 40° C. G. P. 15.32	.....	.....	.....	16.457	16.290	16.290	16.285	16.236	16.270	16.456	16.364	16.331	16.253	16.328	.....

TABLE 71.—*Determinations of osmotic pressure at 40°*—Continued.

	Exp. No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.										
						37th day.	38th day	39th day.	40th day.	41st day.	42d day.	43d day.	44th day.	45th day.	46th day.	47th day.
0.1 W. N. S. at 40° C. G. P. 2.553	1	S_6	275,000	61	3.16	3.544	3.551	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.2 W. N. S. at 40° C. G. P. 5.107	1	O_6	367,000	37	6.33	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	2	Q_6	157,000	40	5.992	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.3 W. N. S. at 40° C. G. P. 7.660	1	C_6	110,000	44	8.211	.....	.....	8.606	8.600	8.680	8.677	8.671	8.652	8.644	8.715	8.719
0.4 W. N. S. at 40° C. G. P. 10.213	1	C_6	110,000	41	18.856	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	2	F_6	55,000	37	11.909	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.5 W. N. S. at 40° C. G. P. 12.767	1	K_6	58,000	41	13.351	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	2	F_6	55,000	30	.....	13.816	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.6 W. N. S. at 40° C. G. P. 15.32	1	B_6	92,000	42	15.062	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

	Observed mean daily total pressures.										Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
	48th day.	52d day.	53d day.	54th day.	55th day.	56th day.	57th day.	58th day.	59th day.	60th day.					
0.1 W. N. S. at 40° C. G. P. 2.553	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	3.554	0.997	2.557	.....	0.998
0.2 W. N. S. at 40° C. G. P. 5.107	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.101	0.998	5.103	5.107	1.000
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.110	0.999	5.111		
0.3 W. N. S. at 40° C. G. P. 7.660	8.688	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.663	0.999	7.664	.....	1.001
0.4 W. N. S. at 40° C. G. P. 10.213	.....	11.287	11.279	11.241	11.238	11.237	11.221	11.215	11.188	11.150	11.228	0.998	10.230	10.216	1.000
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	11.194	0.993	10.201		
0.5 W. N. S. at 40° C. G. P. 12.767	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	13.790	0.998	12.792	12.804	1.003
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	13.814	0.998	12.816		
0.6 W. N. S. at 40° C. G. P. 15.32	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	16.324	1.005	15.319	.....	1.000

Measurements of the osmotic pressure of mannite have been made at 10°, 20°, 30°, and 40°. At the three lower temperatures, the 0.1, 0.2, 0.3, 0.4, and 0.5 weight-normal solutions were investigated. At 40°, the increased solubility of mannite in water made it practicable also to measure the osmotic pressure of the 0.6 normal solution.

TABLE 72.—*Osmotic pressures of mannite at 10°, 20°, 30°, 40°.*

Osmotic pressures.	Concentration.					
	0.1	0.2	0.3	0.4	0.5	0.6
At 10°.						
Observed pressures	2.322	4.609	6.950	9.201	11.613	.....
	2.310	.....	6.930	9.216	.....	.....
Mean pressures	2.314	4.609	6.940	9.209	11.613	.....
Ratios of osmotic to gas pressures	1.002	0.998	1.002	0.997	1.006	.....
At 20°.						
Observed pressures	2.391	4.778	7.169	9.613	11.929	.....
	2.398	4.783	7.192	9.572	11.991	.....
	.....	.....	.....	9.524	.....	.....
Mean pressures	2.395	4.781	7.181	9.570	11.960	.....
Ratios of osmotic to gas pressures	1.002	1.000	1.001	1.001	1.001	.....
At 30°.						
Observed pressures	2.458	4.940	7.426	9.803	12.326	.....
	2.479	4.946	7.434	9.949	12.363	.....
	.....	.....	.....	9.891	.....	.....
Mean pressures	2.467	4.943	7.430	9.881	12.345	.....
Ratios of osmotic to gas pressures	0.999	1.000	1.002	0.999	0.998	.....
At 40°.						
Observed pressures	2.557	5.103	7.664	10.230	12.792	15.319
	.....	5.111	.....	10.201	12.816	.....
Mean pressures	2.557	5.107	7.664	10.216	12.804	15.319
Ratios of osmotic to gas pressures	0.998	1.000	1.001	1.000	1.003	1.000

The results are summed up in Table 73, in which are given the mean osmotic pressures of mannite solutions, between 10° and 40°, and the ratios of these pressures to the calculated gas pressures of the solute. It will be seen that all the ratios approach unity, showing that, within the limits thus far investigated, the aqueous solutions of mannite obey the laws of Gay-Lussac and Boyle.

TABLE 73.

Concentration.	10°		20°		30°		40°	
	Osmotic pressures.	Ratio.	Osmotic pressures.	Ratio.	Osmotic pressures.	Ratio.	Osmotic pressures.	Ratio.
0.1	2.314	1.002	2.395	1.002	2.467	0.999	2.557	0.998
0.2	4.609	0.998	4.781	1.000	4.943	1.000	5.107	1.000
0.3	6.940	1.002	7.181	1.001	7.430	1.002	7.664	1.001
0.4	9.209	0.997	9.570	1.001	9.881	0.999	10.216	1.000
0.5	11.613	1.006	11.960	1.001	12.345	0.998	12.804	1.003
0.6	.....	.....	.....	.....	.....	.....	15.315	1.000

CHAPTER XI.

ELECTROLYTES.

It has already been intimated that much of the conduct of osmotic membranes, which might otherwise appear mysterious and capricious, becomes explicable, if one regards the membranes as having a purely *colloidal* structure. This provisional view of their character has been of great utility as a working hypothesis throughout the present investigation, inasmuch as it was only by proceeding in accordance with its suggestions that we have been able to obtain, and to maintain in efficient condition, membranes which were truly semi-permeable and therefore adequate for the measurement of osmotic pressure. Much that is to be said in this connection has been stated, and in some instances strongly emphasized, in previous chapters, particularly in Chapter IV. But the question of the structure of the membrane is of such fundamental importance to the measurement of osmotic pressure that the author makes no apology for recalling here those peculiarities of its behavior which suggest that its structure is *colloidal*. They are:

1. The destructive effect of an accumulation of alkaline hydroxides in the cell during the deposition of the membrane by electrolysis.—This is not, in itself, convincing evidence of the colloidal nature of the membrane, but it acquires some weight in that direction when it is observed that the deterioration of the membrane, under the circumstances, can not be fully accounted for by the solvent action of the alkali upon it, but is probably due, in a great measure, to an accumulation of the cations in the membrane material. As bearing upon this phase of the subject, we will mention the beneficial results which are obtained (1) by greatly diluting the solution of potassium ferrocyanide; (2) by substituting for the potassium salt, lithium ferrocyanide whose cation is much less harmful to colloidal structure; and (3) by employing ferrocyanic acid, rather than any of its salts.

2. The impossibility of forcing the resistance of any membrane above a given value by continued electrolysis.—That progress is stopped in this case by an accumulation of potassium in the membrane is made extremely probable by the fact that, after soaking the membrane in water free from electrolytes and then resuming the electrolysis, a much higher resistance is obtained.

3. The decline in resistance, and the ultimate ruin of the membrane, which result from a too long continued electrolysis.—This also points to an accumulation of potassium in the membrane, which diminishes and finally destroys its semipermeable character.

4. The remedial effect of soaking in pure water membranes which, from any cause whatsoever, have partially lost their semi-permeable character.—The improvement of the membranes under such treatment has not yet

been observed to reach a maximum. It has been stated in general terms that "the longer the soaking is continued, the greater is found to be the improvement of the membranes"; also, that those membranes which have remained submerged in pure water through the three summer months are usually in excellent condition for the resumption of work in the fall. But the most notable demonstration of the value of water as a restorative was observed in connection with certain cells which, after having been used for some time at high temperatures, were allowed to cool quickly down to ordinary temperatures. The subsequent history of these cells has been partly told in earlier chapters, but not all of it. More than three months were spent in trying to restore them to usable state, *i. e.*, to reproduce the semi-permeable condition of the membranes, but without success. They have since remained in water continuously up to the present time. Occasionally, they have been tested as to the state of the membranes by setting them up with solutions of cane sugar or glucose. At the end of twelve months, one of the cells began, to our surprise, to develop and to maintain the full osmotic pressures of the solutions. During the following five months, two others were found to be in suitable condition for the measurement of pressure; and during the eighteenth month, several more were brought into use. The most obvious explanation of the effect of pure water on the semi-permeable state of the membranes is that it preserves and improves their colloidal condition.

5. The auto-degeneration of the membranes.—By "auto-degeneration" is meant the loss of semi-permeability which is observed in such membranes as the ferrocyanide of zinc and the ferrocyanide of manganese. These are moderately active in the beginning, but soon become less so, and within a short time they lose every vestige of the semi-permeable character. To the term "*auto-degeneration,*" there should, perhaps, be added that of *induced-degeneration* to cover a phenomenon which is also observed in the case of zinc ferrocyanide, the fact, namely, that when the membrane has once lost its semipermeability, all later deposits of membrane material immediately lose their osmotic activity. In such cases there is a change in the condition of the material, which appears to consist in a passage from the colloidal to a granular or crystalline state. In the presence of water, and in the absence of electrolytes, membranes consisting of the ferrocyanide of copper, nickel, or cobalt do not appear to be subject to what is here styled "auto-degeneration."

Persuaded as we were (by the large amount of seemingly pertinent evidence, which had been gathered while we were measuring the pressures of non-electrolytes) that the semipermeability of the membranes depends on their colloidal condition, and that the possibility of measuring osmotic pressure depends upon the maintenance of that state—the attempt to measure the pressures of electrolytes was begun with great misgivings. It was, nevertheless, determined to test the copper ferrocyanide membrane with various salts; and in case of failure to institute

a search for other membranes less susceptible to electrolytes. It is proposed to give in the present chapter a brief account of our experience with electrolytes during the early, or preliminary, stages of that investigation.

EXPERIMENT 1.

The first trial was with a 0.5 weight-normal solution of potassium chloride. The cell selected was an unusually *mature* one. It had been in use about four years, and had never failed, when properly treated, to give a reliable measurement of the osmotic pressure of a non-electrolyte. Through long use and frequent reinforcement, the membrane had acquired a very high resistance, and the cell required a long time for the establishment of equilibrium pressures. Nevertheless, because of its proved reliability, it was still highly prized for the measurement of the pressures of concentrated solutions, in which large thermometer and barometer effects are of less relative importance than in dilute solutions. The resistance of the cell at the time of setting it up with the solution of potassium chloride was 1,170,000 ohms, and the temperature of the bath was 30°. The initial pressure was adjusted to about 22.5 atmospheres. There followed some fluctuations of bath temperature and the mercury meniscus did not come to rest until the fourteenth day. The indicated osmotic pressure of the solution at that time was 20.644 atmospheres. Twenty days later, it was 20.679 atmospheres. The intermediate variations in pressure were small, and could be reasonably ascribed to thermometer and barometer effects. On the thirty-fourth day—while still at full equilibrium pressure, and exhibiting no signs of weakness—the cell was opened. The water in which the cell had stood during the experiment was examined for chlorine. The amount found was equivalent to 1.7 milligrams per 100 cubic centimeters. But, since the cell is always somewhat soiled by the solution at the time of filling it, the presence of this small quantity of chlorine was not believed to signify leakage on the part of the membrane. On the whole, this determination of the osmotic pressure of the 0.5 weight-normal solution of potassium chloride was, and still is, regarded as probably very nearly correct. The mean of the osmotic pressures of the first and last days of equilibrium is 20.662, while the mean of all the 20 days of equilibrium is 20.610. The theoretical pressure, calculated—as best it may be—from Kohlrausch's values for the dissociation of potassium chloride, and presuming no hydration of the solute to exist which modifies the osmotic pressure, is 22.110 atmospheres.

It was now to be determined, by means of a series of repetitions of the experiment, whether the membrane had suffered, or does suffer, any deterioration in consequence of contact with the electrolyte. Accordingly the cell was soaked in water for six days, and then set up again with another 0.5 weight-normal solution at the same temperature. The resistance of the membrane on the second occasion was 400,000, whereas it had been 1,170,000 ohms on the first trial. The cell re-

mained in the bath 17 days, and the highest osmotic pressure exhibited by the solution during this time was 18.579 atmospheres. In general, the pressure showed a tendency to decline, and on the seventeenth day it had fallen to 17.407 atmospheres.

In the third trial the cell was soaked in water 8 days and then set up, as on previous occasions, with a 0.5 weight-normal solution of potassium chloride. It remained in the bath 15 days. The highest osmotic pressure observed was 12.515. On the fifteenth day, the pressure had declined to 10.386 atmospheres.

The membrane had no doubt suffered severely in contact with the potassium chloride. The nature of the injury is, of course, indeterminable; but the conduct of the copper ferrocyanide membrane in the presence of this electrolyte resembles that of the zinc ferrocyanide membrane in contact with either water or a solution of a non-electrolyte.

EXPERIMENT 2.

Another cell, which had also made a long and uniformly good record with non-electrolytes, was set up at 30° with a 0.5 weight-normal solution of potassium chloride and allowed to remain in the bath 36 days. The osmotic pressure which it should have developed, according to the record of the cell used in experiment 1, was about 20.6 atmospheres; the highest observed pressure was 18.567 atmospheres. On the thirty-sixth day, the osmotic pressure had fallen to 17.628 atmospheres.

The same cell *was soaked in water for 20 days* and set up again under the same conditions as before. It remained in the bath 24 days. The highest osmotic pressure exhibited by the solution was 16.695 atmospheres. The pressure on the twenty-fourth day was 16.299 atmospheres.

The pressure on the first trial was greater in experiment 1 than in experiment 2, showing that the membrane in the former case was originally the better of the two; but the deterioration at the end of the second trial was relatively less in experiment 2 than in experiment 1. This was probably due to the much longer soaking in water between trials which was given to the membrane in the second cell.

Eight other experiments, in most respects similar to experiments 1 and 2, were carried out with cells whose excellence for the measurement of the osmotic pressure of non-electrolytes had been fully demonstrated, but as no further light was obtained through them, as to the action of electrolytes on the membrane, they are omitted. The results were all confirmatory of the observations made in experiments 1 and 2, and to the effect that the copper ferrocyanide membrane suffers severely in the presence of potassium chloride. The question, whether the ten membranes which have been injured by this electrolyte can be restored to usefulness by long-continued soaking in water, is still to be answered.

Two experiments were made with 0.5 weight-normal solutions of barium chloride, but the results were as unsatisfactory as had been those with potassium chloride.

The supposed "protective" action of such colloids as albumen and gelatin was also tested with the chlorides of potassium and barium, but without discoverable advantage to the membranes.

One experiment was carried through with potassium ferrocyanide, but the membrane gave the same unmistakable evidence of deterioration under the influence of this electrolyte that it had exhibited when tested with potassium chloride.

A few experiments were made with potassium chloride in cells having membranes of nickel ferrocyanide. Membranes of this material are probably somewhat superior to those of copper ferrocyanide for the measurement of the pressures of non-electrolytes. They were found, however, to have no advantage over the latter for use with electrolytes.

Some evidence was gathered to the effect that it will be possible to measure the osmotic pressure of quite dilute solutions of potassium salts, even with the copper ferrocyanide membrane. This is of interest in connection with the fact, as will be shown later, that the practicability of measuring the osmotic pressure of lithium salts is altogether a question of concentration.

When cells of demonstrated excellence were set up with half normal solutions of potassium chloride, there was always obtained on the first trial a high pressure. On one occasion, it was probably the maximum osmotic pressure of the solution. In all succeeding trials, however, smaller and smaller pressures were obtained, until, in some instances, the pressure observed on the third trial had fallen to about one-half of its first value. Such conduct on the part of the cells can only be explained by supposing that the membranes had degenerated to the point of becoming quite permeable to the solute, and one would expect, perhaps, to find considerable chlorine in the water in which the cells had stood. As a matter of fact, however, the amount of it which made its way into the water surrounding the cells was very small, and in no instance sufficient to account for more than a minute fraction of the deficit in pressure. This observation is cited here in order to emphasize again the fact—already more than once stated—that it is useless to attempt to measure osmotic pressure in leaky cells; because the escaped solute always concentrates heavily in the pores of the cell wall, giving a solution of wholly unknown concentration in contact with the exterior surface of the membrane. Such concentration may be due in part to lack of time for diffusion, but it is probably due in much greater measure to adsorption.

In general, high resistance is regarded as a good sign in a membrane; but it is certainly no proof of its ability to measure osmotic pressure, if the membrane has once suffered injury from contact with electrolytes. In some later experiments with potassium chloride, where the cells were unable to develop even half the normal pressures of the solutions, the membranes had still a resistance of more than a half million ohms.

DETERMINATIONS OF THE OSMOTIC PRESSURE OF LITHIUM CHLORIDE AT 30°.*

It has been observed that the lithium salts appear to be much less harmful to the membranes than those of potassium. Abundant evidence of this will appear in the following record of the determinations of the osmotic pressure of lithium chloride solutions, ranging in concentration from 0.1 to 0.6 weight-normal. The superior resistance of the membranes to salts of lithium is possibly due to the large atmosphere of water with which the cation is supposed to be surrounded.

The determinations of the osmotic pressure of lithium chloride here recorded are not regarded as "final," because it was not demonstrated that the solutions maintained perfectly their concentration while in the cells. They will, therefore, be repeated at a later date when an "interferometer" is available for the purpose of detecting and measuring slight differences in concentration. They are believed, however, to be very nearly correct. All the water in which the cells had stood during the experiments was examined for the presence of chlorine. In every case a slight milky appearance was produced by silver nitrate, but the quantity of chlorine thus precipitated did not in any instance exceed 2 milligrams per 100 cubic centimeters of the solution, and that amount could be accounted for as due to a slight unavoidable soiling of the cell while filling it with the solution. The reasonableness of this explanation was confirmed by the fact that the quantities of chlorine found bore no definite relation to the duration of the experiments. After leakage, the most frequent cause of a change in the concentration of the cell contents is, as previously stated, an improper adjustment of the initial pressure. But such adjustments give very little trouble, except at high temperatures, and they are not believed to have affected the concentration of the solutions of lithium chloride at 30°. A third, but at present infrequent, cause of dilution or concentration of the cell contents has not been previously mentioned. It depends on the use of rubber in closing the cells. The employment of this material is, unfortunately, essential to the proper adjustment of initial pressure, but its use carries with it the danger that, through its movements under pressure, the capacity of the cell, and therefore the concentration of the solution, may be altered. The movement of the rubber may be inward, and result in concentration; or outward, and result in dilution. Every effort is made to confine the rubber in such a manner as to reduce its possible movements to the limits essential to the proper adjustment of initial pressure, but the means of effecting this has always been one of the more perplexing mechanical problems of the present investigation. If the solutions of lithium chloride failed to maintain perfectly their concentration, it was probably due to some imperfect confinement of the rubber which was employed in closing the cells.

*Measurements by H. N. Morse, J. C. W. Frazer, and E. L. Frederick.

TABLE 74.—*Determinations of the osmotic pressure of lithium chloride at 30°.*

Measurements by H. N. Morse, J. C. W. Frazer, and E. L. Frederick. W. N. S.=Weight normal solution. C. G. P.=Calculated gas pressure.

	Exp. No.	Cell.	Resistance membrane.	Manometer.	Initial pressure.	Observed mean daily total pressures.							
						9th day.	10th day.	11th day.	12th day.	13th day.	14th day.	15th day.	16th day.
0.1 W. N. S. at 30° C. G. P. (?)	1	N_6	366,666	43	5.87	.....	.....	.....	.....	.....	.....	5.306	5.308
	2	N_6	275,000	40	5.13	.....	.....	.....	.....	.....	.....	.....	.....
0.2 W. N. S. at 30° C. G. P. (?)	1	Y_6	550,000	37	11.50	.....	.....	.....	.....	.....	9.942	9.893	9.901
	2	K_6	183,000	32	10.43	.....	.....	.....	9.941	9.966	10.002	10.007	10.003
0.3 W. N. S. at 30° C. G. P. (?)	1	K_6	110,000	32	15.19	.....	.....	.....	.....	.....	.....	14.717	14.725
	2	T_6	220,000	34	15.63	.....	.....	.....	.....	.....	.....	.....	.....
*0.4 W. N. S. at 30° C. G. P. (?)	1	Q_6	220,000	30	20.39	.....	.....	.....	.....	.....	.....	.....	.....
	2	F_6	1,100,000	55	15.00	.....	.....	.....	.....	.....	.....	.....	.....
0.5 W. N. S. at 30° C. G. P. (?)	1	Y_6	220,000	45	28.95	25.221	25.145	25.068	25.117	25.153	25.121	25.075	25.168
0.6 W. N. S. at 30° C. G. P. (?)	1	T_6	183,000	45	25.78	.....	.....	.....	.....	.....	.....	.....	30.601

	Observed mean daily total pressures.											
	17th day.	18th day.	19th day.	20th day.	21st day.	22d day.	23d day.	24th day.	25th day.	26th day.	27th day.	28th day.
0.1 W. N. S. at 30° C. G. P. (?)	5.312	5.300	5.324	5.325	5.328	5.333	5.344	5.327	.....	.....	.....	.....
	.....	.....	.....	.....	.....	.....	5.296	5.296	5.305	5.309	5.307	5.316
0.2 W. N. S. at 30° C. G. P. (?)	9.923	9.971	9.967	9.932	9.949	9.946	9.957	9.941	.....	.....	.....	.....
	10.020	10.020	10.038	10.022	10.011	10.009	10.028	9.975	.....	.....	.....	.....
0.3 W. N. S. at 30° C. G. P. (?)	14.721	14.739	14.815	14.844	14.784	14.804	14.788	14.838	14.833	14.860	.....	.....
	.....	.....	.....	.....	.....	.....	.....	14.641	14.569	14.582	14.621	14.655
*0.4 W. N. S. at 30° C. G. P. (?)	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.5 W. N. S. at 30° C. G. P. (?)	25.212	25.225	25.248	.....	.....	.....	.....	.....	.....	.....	.....	.....
0.6 W. N. S. at 30° C. G. P. (?)	30.692	30.429	30.601	30.528	30.483	30.588	30.313	30.623	30.427	30.545	30.618	.....

*For experiment 2 of the 0.4 wt. normal solution see table 76, page 219.

TABLE 74.—*Determinations of osmotic pressure of lithium chloride at 30°*—Continued.

	Exp. No.	Cell.	Resistance membrane	Manometer.	Initial pressure.	Observed mean daily total pressures. 29th day.	30th day.	31st day.	32d day.	33d day.	34th day.	35th day.	36th day.
0.1 W. N. S. at 30° C. G. P. (?)	1	N_6	366,666	43	5.87								
	2	N_6	275,000	40	5.13	5.300	5.323	5.314	5.321				
0.2 W. N. S. at 30° C. G. P. (?)	1	Y_6	550,000	37	11.50								
	2	K_6	183,000	32	10.43								
0.3 W. N. S. at 30° C. G. P. (?)	1	K_6	110,000	32	15.19								
	2	T_6	220,000	34	15.63	14.623	14.631	14.650					
*0.4 W. N. S. at 30° C. G. P. (?)	1	Q_6	220,000	30	20.39				19.829	19.763	19.745	19.763	19.838
	2	F_6	1,000,000	55	15.00								
0.5 W. N. S. at 30° C. G. P. (?)	1	Y_6	220,000	45	28.95								
0.6 W. N. S. at 30° C. G. P. (?)	1	T_6	183,000	45	25.78								

	Observed mean daily total pressures. 37th day.	39th day.	40th day.	41st day.	42d day.	43d day.	Mean of all daily pressures.	Mean barometric pressure.	Mean osmotic pressure.	Mean osmotic pressure for experiments.	Ratio of osmotic to gas pressure.
0.1 W. N. S. at 30° C. G. P. (?)							5.321	0.998	4.323	4.317	1.746
							5.302	0.991	4.311		
0.2 W. N. S. at 30° C. G. P. (?)							9.947	1.001	8.946	8.976	1.816
							10.003	0.998	9.005		
0.3 W. N. S. at 30° C. G. P. (?)							14.802	0.993	13.809	13.768	1.857
							14.622	0.996	13.626		
*0.4 W. N. S. at 30° C. G. P. (?)	19.758	19.665	19.792	19.748	19.696	19.686	19.753	0.998	18.755	18.772	1.899
0.5 W. N. S. at 30° C. G. P. (?)							25.159	0.997	24.162		1.955
0.6 W. N. S. at 30° C. G. P. (?)							30.537	1.002	29.535		1.992

*The duration for Experiment No. 2 was 135 days. Observed osmotic pressures by periods of 25 days each. For these figures, refer to Table No. 76.

The pressures which were obtained are very large as compared with the calculated gas pressure of molecular lithium chloride, the ratios being (see table 75) 1.746, 1.816, 1.857, 1.899, 1.955, and 1.992, respectively, for the 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 weight-normal solutions. Such excessive pressures were, of course, to be expected from the known considerable electrolytic dissociation of the salt; but the ratios cited above do not *diminish* with increasing concentration, as would be expected, if the differences between the observed osmotic and the calculated gas pressures were due solely to electrolytic dissociation. On the contrary, the ratios in question *increase* in value with increasing concentration. A similar increase in ratio of osmotic to calculated gas pressure was observed in the case of cane-sugar solutions, and it was tentatively ascribed to a hydration of the solute. It was presumed, in other words, that any withdrawal of solvent molecules for the purpose

TABLE 75.—*Osmotic pressure of lithium chloride at 30°.*

	Concentration.					
	0.1	0.2	0.3	0.4	0.5	0.6
Observed pressures	4.325	8.946	13.809	18.755	24.162	29.535
	4.311	9.005	13.626	18.789	.....	.....
Mean pressures	4.317	8.976	13.768	18.772	24.162	29.535
Calculated gas pressures*	2.472	4.943	7.415	9.886	12.358	14.830
Ratio of osmotic to gas pressure	1.746	1.816	1.857	1.899	1.955	1.992

* For undissociated salt.

of hydrating those of the solute would have the effect of concentrating a solution, and that the result of such concentration would be an apparently abnormally high osmotic pressure. Concentration through hydration of the solute should manifest itself in the form of an increasing ratio of osmotic to gas pressure, such as was observed in the case of lithium chloride at 30° and in that of cane sugar at the lower temperatures.

The electrolytic dissociation of the solutions of lithium chloride, whose osmotic pressures were measured, have not yet been determined, and the data available are insufficient for a safe estimation of the same. It is, therefore, impossible to say at present what proportion of the observed difference between osmotic and gas pressure is to be ascribed, on the one hand, to dissociation; and, on the other, to a conjectured concentration of the solution through hydration of the solute. If the *whole* difference is ascribed to dissociation, the percentages of ionized salt which must be presumed to exist in the 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 weight-normal solutions of lithium chloride are 74.6, 81.6, 85.7, 89.9, 95.5, and 99.2 respectively. Such relations of dissociation to concentration are, of course, quite impossible.

The effect which was produced upon the membranes by the lithium chloride was very pronounced. They became at once *exceedingly slug-*

gish. Hitherto, diminished activity on the part of membranes has usually been the result of age and frequent use. But the membranes which were employed for the measurement of the osmotic pressure of the lithium salt were *new ones*, and they had not been used for any other purpose. With either cane-sugar or glucose solutions, they should have given equilibrium pressures within one or two days. With solutions of lithium chloride, the shortest time required for that purpose was 9 days, while the average time consumed in developing the final pressures was 17 days. The membranes were not wholly ruined by their contact with the electrolyte, as others had been by potassium chloride; for they were afterwards successfully employed for the measurement of the osmotic pressure of mannite solutions. But the state of inertness which they had acquired in the presence of the lithium salt persisted without diminution throughout their later history. Eventually, the cells were withdrawn from use, because of their slowness, and consigned to a solution of thymol, in order to ascertain whether the membranes might not recover their normal activity under the influence of water. This is the course which is now taken with all slow cells whenever their long-continued monopolization of bath space and manometers becomes intolerable. Many membranes do recover a fair degree of activity under such treatment, though the time required for restoration is usually very long—sometimes more than two years.

Particular attention is called to *experiment 2* with the 0.4 weight-normal solution. This was an *endurance* test of the membrane of an unusually thorough character. The cell (F_6), at the time of setting it up, had a resistance of 1,100,000 ohms, and it remained in the bath 145 days. Starting with an initial pressure of 15 atmospheres, it reached an approximate equilibrium in 10 days. The osmotic pressure which the cell sustained during the following 125 days is given in 5 columns, each of 25 daily records. The mean osmotic pressure for the first period was 18.827; for the second, 18.894; for the third, 18.799; for the fourth, 18.636; and for the fifth, 18.405. It is believed that a mean of the records for the first 100 days fairly represents the osmotic pressure of the solution. But during the fifth period, *i. e.*, from the 101st to the 125th day of the record, there was a decline in pressure from 18.609 to 18.140 atmospheres, which can only signify that the membrane had at last begun to weaken. The cell was allowed to remain 10 days longer in the bath, but it gave no evidence of recovering any portion of the loss sustained during the fifth period; in fact, the rate of decline in pressure increased quite perceptibly. The membrane of cell F_6 had evidently suffered severely from its long contact with lithium chloride; for it was found unfit for further measurements of pressure. This does not mean, of course, that it can never be restored to usefulness.

The very considerable resistance of the membrane to the electrolyte, which was exhibited in the case of the endurance experiment with the

0.4 weight-normal solution of lithium chloride, encouraged the hope that it would be found practicable to measure the osmotic pressure of much more concentrated solutions of that salt. But when we proceeded to the investigation of the higher concentrations, it was found that the injury to the membranes by the electrolyte increased rapidly with increasing concentration of solution. The pressure of the 0.5 and 0.6 weight-normal solutions were successfully measured, but only by the sacrifice of two of the best cells in our possession. It was not possible to duplicate these determinations with any other cells which were available at that time. The effect of lithium chloride upon the copper ferrocyanide membrane appears to be milder than that of potassium chloride, but not different in kind.

TABLE 76.

I.	II.	III.	IV.	V.
18.731	18.979	18.925	18.655	18.609
18.671	18.883	18.912	18.646	18.582
18.677	18.880	18.912	18.521	18.552
18.720	18.862	18.939	18.669	18.509
18.768	18.880	18.789	18.672	18.486
18.769	18.918	18.820	18.692	18.470
18.751	18.937	18.812	18.708	18.497
18.793	18.959	18.708	18.710	18.515
18.768	18.935	18.818	18.717	18.559
18.827	18.907	18.792	18.698	18.563
18.840	18.882	18.743	18.681	18.552
18.843	18.885	18.933	18.675	18.521
18.711	18.888	18.829	18.676	18.417
18.889	18.880	18.785	18.587	18.401
18.897	18.881	18.773	18.621	18.391
18.863	18.859	18.750	18.621	18.380
18.857	18.907	18.736	18.609	18.345
18.898	18.853	18.735	18.561	18.240
18.892	18.863	18.739	18.568	18.291
18.910	18.913	18.739	18.611	18.295
18.992	18.869	18.731	18.610	18.225
18.898	18.880	18.759	18.593	18.247
18.917	18.869	18.770	18.585	18.235
18.890	18.799	18.778	18.602	18.113
18.896	18.993	18.745	18.609	18.140
18.827	18.894	18.799	18.636	18.405

Mean osmotic pressure for 100 days, 18.789.

The conclusions to be drawn from the experiences thus far reported are: (1) that it is practicable to measure the osmotic pressure of lithium chloride in all aqueous solutions not *more* concentrated than the 0.6 weight-normal; (2) that it will probably be found possible to measure the osmotic pressure of potassium chloride in aqueous solutions *less* concentrated than the 0.5 weight-normal.

It is hoped that other semi-permeable membranes may be found which are less susceptible to the deleterious influence of electrolytes than are the ferrocyanides of copper and nickel.

CHAPTER XII.

CONCLUSION.

The work reported upon in the preceding chapters is only a fraction of the task which the author hopes to accomplish, or to see accomplished by others. The investigation—already 15 years old—was undertaken, in the first instance, with a view to developing a practicable and fairly precise method for the direct measurement of the osmotic pressure of aqueous solutions. The need of such a method for the investigation of solutions seemed to the author very great and very urgent. The freezing- and boiling-point methods were of great value, but of limited applicability, in that they could give no certain information as to the conditions within a solution, except at two widely separated and rather exceptional temperatures. There appeared to be a need of more comprehensive methods—of methods which could be effectively applied to the investigation of solutions at all temperatures between the freezing and boiling points. Two such methods naturally suggested themselves. One of these was a method for the direct determination of the osmotic pressure, and the other was a method for the measurement of the depression of the vapor tension of solutions. Neither had been perfected to a point where it could be made to yield convincing results. The method selected by the author for development was that for the measurement of osmotic pressure. Nearly eight years were devoted to one or another phase of this part of the enterprise. The difficulties which were encountered during the evolution of the method were great, and often they were baffling and for long periods seemingly insurmountable. Fortunately for the undertaking, it was adopted by the Carnegie Institution of Washington as soon as it became apparent that the problems involved would require many years and large means for their effective solution. It was also fortunate for the enterprise that the author has had associated with him during the greater part of the time two such able and tireless coadjutors as Dr. J. C. W. Frazer and Dr. W. W. Holland, whose resourcefulness has contributed much to whatever success has been attained. The development of the method, which is described in the earlier chapters of this report, is now regarded as reasonably complete—inasmuch as, in the hands of experienced persons, it can be made to yield results which compare favorably with those of other and simpler quantitative operations.

Having perfected the method, it was to be applied to the measurement of osmotic pressure in accordance with a systematic plan. It was determined to measure with all possible care the pressures of four substances over a wide range of concentration and temperature. The

compounds selected for the purpose were cane sugar, glucose, levulose, and mannite. Some of the reasons for this choice of materials are given below:

(1) All four of the compounds named separate from solution *without* water of crystallization, which simplifies the situation by making it possible, for a time, to evade the question whether such water, when a substance is dissolved, belongs to the solute or to the solvent.

(2) The list includes substances which are both *normal* and also, in different ways, *abnormal* in respect to their freezing-point depressions. These compounds therefore afford an excellent opportunity for comparing experimentally determined osmotic pressures with a variety of freezing-point depressions.

(3) Three of the compounds are optically active, and alterations in the concentration of their solutions can be readily detected and measured by the polariscope. Mannite, the fourth substance, was selected, notwithstanding its optical inactivity, because the depression of the freezing points of its solutions are all normal; and, since the introduction of the interferometer, the lack of optical activity is no longer an objection to it.

It was proposed to measure the pressures of the enumerated substances from 0° to the highest temperature at which it is practicable to work—possibly to 100°. It was thought that, by extending the investigation over a wide range of temperature, much light might be obtained on the problem of hydration and its relation to the freezing-point depressions and osmotic pressures of solutions. The work is now in its second stage—in that stage, namely, in which the osmotic pressure of cane sugar, glucose, levulose, and mannite is under investigation. About three years more will be required to complete the proposed study of these substances.

Having finished the investigation of the anhydrous compounds mentioned above, it is proposed to study, in a similar manner, several of the carbohydrates which separate from solution with water of crystallization. It is also proposed to continue the investigation of the osmotic pressure of electrolytes.

Lists of those osmotic pressures which the author regards as established with a reasonable degree of certainty are to be found:

(1) For cane sugar, in Tables 59, 60, and 62, pages 184 and 186.

(2) For glucose, in Table 67, page 196.

(3) For mannite, in Tables 72 and 73, page 207.

The conclusions which were drawn from them have been sufficiently discussed from time to time in the course of this report.