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THE OSMOTIC PRESSURE OF SUCROSE SOLUTIONS AT 30°.[1]

BY J. C. W. FRAZER AND R. T. MYRICK.

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Introduction.

The purpose of this work was to modify the method of measuring osmotic pressures developed by Morse and Frazer, so that it would be applicable to a study of concentrated solutions and, possibly, to solutions of electrolytes. This demands two things: first, the semipermeable membrane must have greater strength in order to withstand the greater pressures and, second, it must be able to establish equilibrium between the "escaping tendencies" of the solvent on the two sides of the membrane much more quickly, so that a measurement may be secured before the ions of electrolytes have time to destroy the colloidal nature of the membrane. Greater strength and greater speed of action have both been secured and the efficiency of the method for the measurement of the osmotic pressure of concentrated solutions, tested and proven. Its applicability to electrolytes is an unsettled question, but the prospects are every encouraging. It is planned to make a thorough trial of this in the near future.

The method[2] of measuring osmotic pressure developed in this laboratory is in brief as follows: A semipermeable membrane of copper ferro-

[1] This work has been aided by the Carnegie Institution of Washington, D. C.

[2] *Pub. Carnegie Inst.*, No. 198.

lytically deposited on the inside and in the pores, near of a clay cell. The solution to be measured is placed and a manometer is tightly fastened in its mouth. The rsed in the solvent and the pressure, developed by the through the membrane into the solution, is registered .

n of this method, which it is the purpose of this article ntially a reversal of the above-mentioned process. The sited on, and in the pores near, the outer surface of the fastened inside of a hollow bronze cylinder to which s attached. The solution to be measured is placed nder around the clay cell, the solvent being placed in- This position of the membrane is similar to that used Hartley.[1] However, these investigators applied me- to the solution until equilibrium was established, while tance the solution developed its own pressure as in the eretofore in this laboratory.

Description of the Apparatus.

construction are shown in the accompanying diagram size. M is the clay cell with the membrane of copper deposited on its exterior. This extends only as far e heavy line K, the neck and shoulder of the cell being ight joints. J is the bronze cylinder into which the cell ns of the plug P. The latter has three legs upon which nds and which serve as a means of screwing the plug N is a thick rubber washer and O is a piece of com- Packing," about a millimeter and a half thick. This fect satisfaction, while ordinary rubber will not with- ures. At all other joints, N, G, H, the packing is sur- es so it can not get away, hence in these places the softer swer very well. In fact, it is desirable to have N and mm.) and soft so that initial pressure may be secured ion.

ube held in the mouth of the cell by means of the rub- his is simply to keep the solvent L up in the cell and to the atmosphere. I is the solution to be measured. r attachment and is fastened onto the cylinder by means a thick rubber washer described above. A is a piece tubing to which the manometer is sealed. The square ver end of A is secured by sealing on to a piece of tubing, for A, another piece, having somewhat larger external joint is kept soft and the glass allowed to flow together

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until a considerable enlargement is secured, the internal diameter being kept of original size by careful blowing. After cooling, the larger piece of tubing is cut off close to the enlarged joint. A is then mounted in the lathe and the enlarged end ground to the desired size and shape. The grinding is done with carborundum dental wheels mounted on the lathe carriage and rotated at a high speed by a small electric motor. In this manner the lower end of A is made to fit accurately into the lower end of E, as shown in the diagram. To hold A in position, B is sealed onto A by means of sealing wax (Khotinsky) and after putting D into position, C is screwed onto B. Now it will be seen that by turning D to the left, A is raised and held tightly in position in E against the washer H. By turning D to the right, A is lowered and excess solution is allowed to escape. This method of joining glass and metal is of general application and has proven most satisfactory. Such a joint will hold tight under any pressure which will not actually break the glass.

Several points of advantage over the old type of cell deserve especial mention. In the first place the clay cell will withstand far greater pressure exerted upon its exterior than upon its interior, as would be expected from a consideration of the principles of arch construction. Secondly, the membrane itself is made stronger, for the pressure tends to force it farther into the pores and so compresses it, making it more firm and compact. With the membrane on the inside of the cell the pressure of the inclosed solution tends to expand the membrane out into the pores of the cell thus stretching the particles of the membrane and so making ruptures more likely to occur.

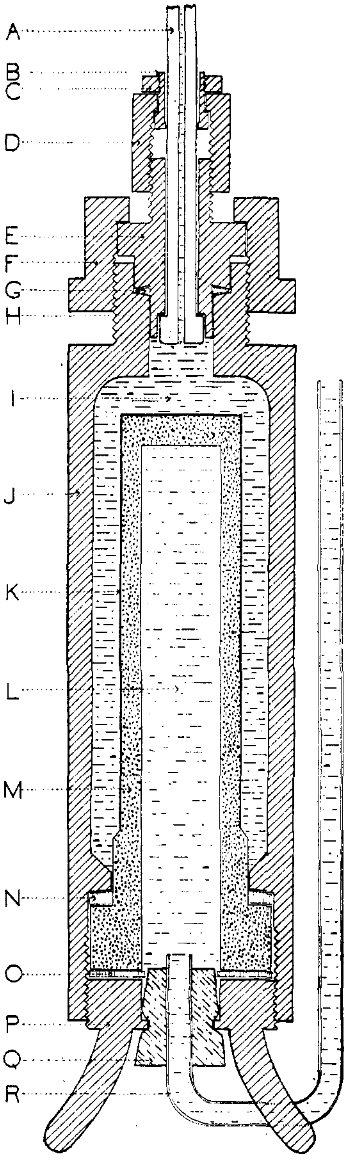

Fig. 1.

The new cells are about the same size as the old, but having the membrane on the outer surface greatly increases its area, hence equilibrium is much more readily established.

A distinct advantage in construction is apparent in the method of attaching the manometer. In the case of the old apparatus the lower end of the manometer terminated in a rubber-covered, cone-shaped attachment which was forced into the tapered neck of the cell. This often resulted in splitting the cell simply by the mechanical pressure used in securing a tight joint between manometer and cell. In the apparatus described above it will be noticed that the manometer is attached, not to the *cell*, but to the bronze cup, hence a tight joint is easily secured without danger of breaking the cell.

This form of apparatus fulfilled all expectations, proving convenient, strong, and of quick action, as the results of Experiments No. 1 to 7, inclusive (see data which follows) show. Equilibrium was reached in from 10 to 12 hours and in even less time when the initial pressure was as much as half the equilibrium pressure. The so-called "Thermometer effects,"[1] which were so troublesome with the old type apparatus, proved negligible in the new form of cell. Solutions whose osmotic pressures are not over 100 atmospheres can be measured with ease and expediency in the apparatus as described. It was impossible, however, to get glass manometers which would withstand greater pressure than this. Experiment No. 5 was the only successful measurement of a higher pressure (124 atmospheres) and this could not be duplicated. In Experiment No. 7 a pressure of 165 atmospheres was recorded for a few hours before the manometer broke. Having strengthened the cell successfully, the problem resolved itself into a matter of securing a suitable means of measuring the higher pressures with a fair degree of accuracy.

The solution of this question was found in the electrical resistance[2] gage, the form adopted being that developed and used by Johnston and Adams in their work on high pressures at the Geophysical Laboratory, Carnegie Institution, Washington. They kindly lent one of their gages for this preliminary test of the method, and gave detailed instructions for the construction, calibration and use of this type of gage. The principle upon which this method of measuring pressure is based, is that the resistance of certain conductors to an electric current increases with pressure, the relation being very nearly linear. Pressures are measured by comparing the resistance of two similar resistance coils when both are subjected to the *same* pressure (that of the atmosphere), and again when one is subjected to the pressure to be determined. The change in resistance which the gage coil undergoes is a measure of the magnitude of the pressure in question.

The coils used in this instance were each made from 1 meter of No.

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[1] *Pub. Carnegie Inst.*, No. 198.

[2] Lisell, Dissertation, Upsala, 1903; Lafay, *Compt. rend.*, 149, 566–569 (1909); Bridgman, *Proc. Am. Acad. Arts & Sci.*, 47, 11, 335 (1911); 49, 11, 640 (1913).

40 "Therlo" wire, double silk covered, wound noninductively upon a mica frame. This frame was made of two plates of mica intersecting each other at right angles. The coils were shellaced, baked, temperature seasoned at 150° for 16 hours, pressure seasoned at 1000 atmospheres for 24 hours, and at 8000 atmospheres for one-half hour. All joints to terminals and leads are silver soldered, to insure constancy of resistance.

"Therlo" is an alloy of copper, manganese and aluminium, and is used on account of its low temperature coefficient (+0.0000056 per degree centigrade) and its negligble thermoelectric effect against copper. Compared with manganin, these factors are considerably smaller and the therlo has the further advantage of being more stable in its electrical and mechanical behavior. Its specific resistance is also higher than that of manganin.

The pressure coefficient of resistance for therlo is slightly more than two parts per million per atmosphere, the exact value depending upon the previous history.

The coils as made above have a resistance of about 100 ohms. Hence, in order to measure pressures accurately to $^1/_{10}$ of an atmosphere it is necessary to have a means of measuring changes in resistance of one part in five million. This requirement is met in the Leeds and Northrup Carey Foster Bridge used with their new high sensitivity galvanometer. This outfit, when used with the 100 ohms coil above, has a sensitivity of 0.00001 ohm over a range of 0.01 ohm change in resistance, corresponding to a pressure range of 50 atmospheres; and a sensitivity of 0.0001 ohm over a range of 0.1 ohm change in resistance, corresponding to a pressure range of 500 atmospheres. The latter combination is the one used in this work,—however a plan is in mind for securing the greater sensitivity over the greater range and will be tried when such refinement seems justified.

The courtesy of the Geophysical Laboratory was extended to the authors who took advantage of the opportunity to calibrate this secondary gage against an absolute gage, in terms of resistance as measured by the Carey Foster Bridge. The calibration data follow in Table I.

TABLE I.

Pressure on absolute gage (atmos.).	Change in resistance sf gage coil (ohms × 10^4).			Change in resistance per atmos. (ohms × 10^4).	Deviation from a change in resistance 2×10^{-4} ohms per atmos. (ohms × 10^4).
	No. 1.	No. 2.	Mean.		
17.9	37.0	36.95	37	2.0670	—1.2
83.3	172.0	172.0	172.00	2.0648	—5.4
148.5	308.9	308.1	308.50	2.0774	—11.5
213.8	445.8	446.1	445.95	2.0858	—18.35
279.1	582.7	583.1	582.90	2.0885	—24.7
344.4	721.3	719.8	720.55	2.0922	—31.7
409.8	860.3	856.1	858.40	2.0949	—38.8
Additional value on last point		858.8			

For a working calibration curve the deviations given in the last column were plotted against the mean changes in resistance.

The details of construction of the gage as adapted for use in this work are shown in Fig. 2. Z is the coil described above, the terminals of which are hard soldered to the copper lead wires U and U′. V is a plug through which the lead wires pass to the exterior. and which screws into A′ against the copper washer X. W and Y are packing to prevent leaks around the lead wires. W is composed of three layers of soapstone (alberine) carefully cut and drilled to fit the opening in V and the wires U and U′.

These soapstone plugs were forced into place by application of sufficient mechanical pressure to crush the stone and compress it securely in V tight around the wires. A knot was made in the wires between two of the layers of stone to prevent subsequent flowing of the copper under pressure. The exposed layer of stone was coated with marine glue and after drying a layer of molten Khotinsky wax (Y) was poured on. The function of the latter is chiefly to prevent movement of the lead wires, which causes a loosening of the soapstone around them. Some trouble with leakage on this account was experienced at first, but with the present arrangement there is none. The lead wires at the exterior end are hard-soldered to heavy copper terminals S and S′, which were amalgamated and dip into the mercury cups of the Carey Foster Bridge coil holder.

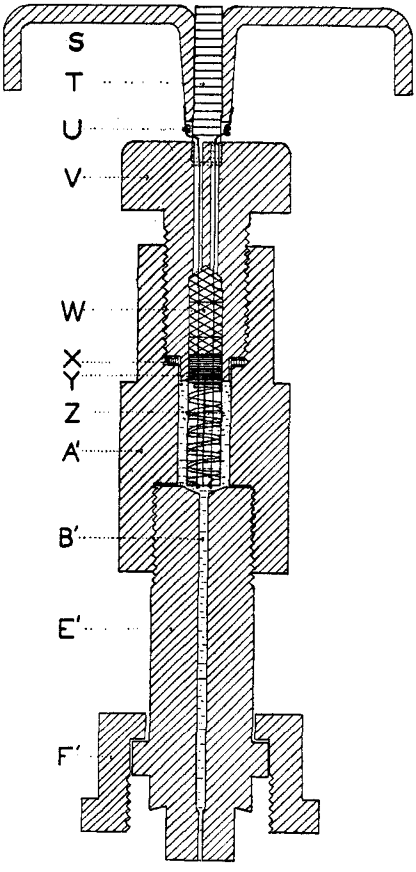

Fig. 2.

E′ is the attachment by which the gage is connected to the osmotic pressure apparatus. The parts E′ and F′ in Fig. 2 correspond to parts E and F in Fig. 1 and serve as a means of connecting the resistance gage and the glass manometers respectively to the bronze cylinder J (Fig. 1). The coil Z is immersed in oil which fills the compartments in A′ and E′ as indicated by B′. The solution I (Fig. 1) is in contact with the oil at the lower end of the capillary opening in E′ (Fig. 2). The compression of the oil allows some of the solution to be forced up into this capillary. This necessitates frequent renewal of the oil A mercury trap at the lower end of E′ would obviate this difficulty. The comparison coil is immersed in oil in a brass cup and connected by means of mercury contacts to the other arm of the Carey Foster Bridge coil holder.

This gage presents many very decided advantages over the manometric method of measuring pressures. The strength is well nigh unlimited. The old type manometers, depending as they do upon the compression of a gas, involve a considerable change in volume. The only change in volume suffered in the resistance gage is that due to the compression of the oil. Hence dilution of the solution being measured is reduced to a minimum, and as a result, equilibrium is much more rapidly established. Furthermore the deviations of gases from Boyle's law make the manometric method less accurate at high pressures. The percentage error involved in reading the levels of the mercury meniscuses also increases with the compression of the gas to a small volume. So the higher the pressure the less sensitive the manometer becomes. On the other hand, the sensitivity of the resistance gage does not decrease with the pressure.

The results obtained with the modified osmotic pressure cell equipped with the resistance gage are most gratifying. Equilibrium is reached in from an hour and a half to six hours, depending upon the concentration of the solution and the initial pressure developed by compression of the rubber washers. This makes it possible to secure a satisfactory measurement within 24 hours. In this connection especial attention is called to Experiments Nos. 12, 18, 19, 20 and 22.

The objection raised by certain critics of the Morse and Frazer method, on the grounds that the solution is not stirred, may be legitimate in the case of these more concentrated solutions when measurements are completed in such a short time. The solutions *are* very viscous but the amount of water transferred into the solution is small and the area of the membrane is large. Hence it is but a thin film of water over the surface of the cell which must diffuse through the solution. As to whether or not stirring is essential can only be proven by trial. It is planned to introduce a stirring device into this form of apparatus in the near future and settle the question. Such an arrangement may at least hasten the establishment of equilibrium, although the speed with which equilibrium is apparently reached in the present apparatus leaves but little to be desired.

Experimental.

Preparation and Analysis of Solutions.—This work was all done at 30° the apparatus, including the Carey Foster Bridge, being kept in a carefully regulated thermostat.

Aqueous solutions of cane sugar were studied over the complete range of solubility. The sucrose used was carefully purified from rock candy. To facilitate ready comparison with previous work done in this laboratory, the solutions were all made up on the weight molar basis using atomic weights on the H = 1 scale. The concentrations are expressed also in terms of O = 16. The sugar in each instance was dissolved in conductivity water made 0.01 ion normal with potassium ferrocyanide. The solvent against which the osmotic pressures were measured was 0.01 ion normal copper sulfate. The presence of the "membrane formers" repairs ruptures in the membrane made by the pressure. The specific gravity was determined for each solution, so that concentrations might also be expressed in terms of the volume molar system. This was for the purpose of comparison with measurements made by Berkley and Hartley and others who expressed the concentrations in terms of the volume molar system.

The extent to which the solutions were diluted during measurement was ascertained by the saccharimeter in the following manner:

From the optical rotation, the concentration was determined by reference to a curve made by plotting the values of the ratios of the concentrations of the original solutions to their optical rotations against *their* optical rotations, *i. e.*, letting C represent the concentration, and r the optical rotation, the values of C/r were plotted against the values of r. By multiplying the optical rotation of a given solution by the corresponding value of C/r as determined from the curve, the concentration of the solution in grams of sugar per 1000 g. of water was obtained.

In the work on dilute solutions carried on in this laboratory, corrections for changes in concentrations are made by changing the observed pressure the same per cent. that the optical rotation of the solution changes during the measurement. This involves two errors, for it assumes that the change in optical rotation is linearly proportional to the change in concentration and that the osmotic pressure is a linear function of the concentration. The magnitude of the error may be negligible in the case of dilute solutions but in the case of concentrated ones the error would be enormous. Hence in this work the final concentrations are determined from the curve described above and the observed osmotic pressures are recorded as the pressures of solutions of these concentrations.

The contents of the solvent compartment (L, Fig. 1) were examined after each experiment to determine to what extent the sugar had leaked through the membrane.

The amount of sugar in the "solvent" could not be detected by the saccharimeter in the case of experiments measuring pressures of solutions up to 5M concentration. In the experiments with the more concentrated solutions (5M and above), the solvent showed an optical rotation of 0.5°, which corresponds to an error in the measurement of the pressure of not more than 0.1 atmosphere and this is within the limits of accuracy of the method at these pressures (150 to 250 atm.). In Experiments No. 16, No. 18 and No. 23, the leakage was somewhat more, due no doubt to the unseasoned conditions of the cells, as mentioned below. The results of these experiments are not considered of value.

Results.

Table II gives a somewhat detailed account of representative experiments. From this can be seen the speed with which measurements can be obtained. Experiment No. 3 was made with a glass manometer, the others with the resistance gage.

In this table R is the resistance in ohms of the membrane. C is the original concentration of the solution expressed in weight molar terms ($H = 1$). o is the optical rotation of the solution after the experiment and c is its final concentration, expressed in grams of sugar per 1000 g. of water. t is the time that the reading was made, expressed in hours after the time at which the cell was set up. dr is the change in resistance of the gage coil expressed in ten thousandths of an ohm (ohms × 10^4). P is the observed osmotic pressure.

Table II.

Experiment No. 3.
Cell No. 6; R 13,400.
$C = 3\text{M}$; $o = 227.4^\circ$; $c = 957.354$.

Time (hours). t.	Pressure (atmos.). P.
19	87.28
26	88.05
45	88.21
66	88.21
90	88.56
114	88.21
128	88.06
152	87.82
176	87.68
Equilibrium pressure	88.10

Experiment No. 12.
Cell No. 5; R 31,000.
$C = 4\text{M}$; $o = 273.6^\circ$; $c = 1300.97$.

Time (hours). t.	Pressure (atmos.). P.
0.1	80.0
1.0	129.3
3.0	131.1
4.0	131.3
5.25	131.4
5.75	131.5
Equilibrium pressure	131.5

Experiment No. 20.
Cell No. 4: R 25,000.
$C = 3\text{M}$; $o = 234.8^\circ$; $c = 1007.21$.

Time (hours). t.	Pressure (atmos.). P.
0.5	79.0
1.5	93.9
2.5	94.7
4.5	93.7
6.0	93.9
7.5	94.2
17.00	94.5
19.00	94.3
20.00	94.1
Equilibrium pressure	94.2

Experiment No. 22.
Cell No. 5: R 44,000.
$C = 5\text{M}$; $o = 306.0^\circ$; $c = 1618.74$.

Time (hours). t.	Pressure (atmos.). P.
0.1	85.6
1.0	165.7
3.0	175.8
4.0	175.7
5.0	175.8
10.0	176.1
21.0	175.3
22.0	176.1
24.0	175.7
Equilibrium pressure	175.8

TABLE III.

Expt. No.	Grams sugar 1000 g. water.	Grams sugar 100 g. sol.	Grams sugar 1000 cc. sol.	Final conc. gms. sugar 1000 gms. water.	Time at which equilibrium was reached.	Osmotic press. in atmospheres. P.	Ratio P/c.
[1]	....	....	....	33.96	3–15 days	2.474	0.0728
[1]	339.6	25.351	280.1700	339.60	3–15 days	27.22	0.08015
1	679.2	40.448	475.3007	676.96	29 hours	57.70	0.08524
2	679.2	40.448	475.3007	668.86	1 hour	57.47	0.08593
6	679.2	40.448	475.3007	664.98	18 hours	57.16	0.08595
3	1018.8	50.464	619.5412	957.35	19 hours	88.10	0.0920
4	1018.8	50.464	619.5412	997.24	20 hours	90.04	0.0903
19	1018.8	50.464	619.5412	1018.80	5 hours	94.75	0.0930
20	1018.8	50.464	619.5412	1007.29	1½ hours	94.20	0.0935
(5)	1358.4	57.598	730.2576	1276.76	6 hours	124.20	0.0980
8	1358.4	57.598	730.2576	1302.34	37 hours	130.80	0.1005
9	1358.4	57.598	730.2576	1289.30	6 hours	130.20	0.10098
10	1358.4	57.598	730.2576	1326.70	3½ hours	134.00	0.1010
11	1358.4	57.598	730.2576	1327.68	6½ hours	133.90	0.1008
12	1358.4	57.598	730.2576	1300.97	3 hours	131.50	0.1010
(7)	1698.0	62.932	817.7248	?	19 hours	165.00	?
(13)	1698.0	62.932	817.7248	1623.90	7½ hours	171.80	0.1058
(14)	1698.0	62.932	817.7248	1602.67	9 hours	167.60	0.1045
15	1698.0	62.932	817.7248	1597.00	16 hours	174.30	0.1091
22	1698.0	62.932	817.7248	1618.74	3 hours	175.80	0.1086
(16)	2037.6	67.079	888.3145	1932.91	17 hours	208.80	0.1080
17	2037.6	67.079	888.3145	1942.56	7 hours	220.40	0.11345
(18)	2037.6	67.079	888.3145	1982.40	5 hours	217.00	0.10946
21	2037.6	67.079	888.3145	1917.65	6 hours	216.10	0.11270
(23)	Supersaturated				7 hours	268.80	?

A summary of the results of the experiments is given in Table III. This also includes data on molar and tenth molar solutions previously determined in this laboratory. The results of Experiments Nos. 5 and 7 with glass manometers are given no importance, for they were not duplicated. No. 7 not even being completed. The results of Experiments Nos. 13, 14, 16 and 18 are also given slight consideration for these were the first times that the cells used were ever subjected to such pressures. It has long been recognized that even at much lower pressures cells must be seasoned at a given pressure before they will develop the maximum osmotic pressure of a solution and give concordant results. Hence those measurements with unseasoned cells are disregarded. All other measurements are with cells more thoroughly seasoned by being set up with strong sugar solutions in the apparatus shown in Fig. 1, having A sealed off instead of sealed to a manometer.

In the last Experiment (No. 23) a supersaturated solution of cane sugar was used, in hopes of measuring the osmotic pressure of a saturated solution. The excess sugar was more than sufficient to saturate the water that would be taken up by the solution during the measurement.

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[1] For previous work in this laboratory, see *Pub. Carnegie Inst.*, No. **198**.

The pressure developed reached the maximum during the first few hours and then gradually decreased as the excess sugar in solution gradually crystallized out. Evidently equilibrium between solid and dissolved sugar was not reached during the experiment. It was impossible to get a satisfactory analysis of the solution by the saccharimeter. There was considerable leakage of sugar through the membrane so the results of the experiment are of no value save to show the greatest pressure developed.

In Fig. 3, the data in Table III are shown graphically. The curve AB was obtained by plotting the pressures (P) against the concentrations (*c*). AC is a theoretical curve in which the calculated pressures obtained from the thermodynamic formula for osmotic pressure are plotted against the concentration. These calculations neglect association of the solvent and hydration of the solute so are of no theoretical importance but simply show the extent of the deviation from ideal conditions.

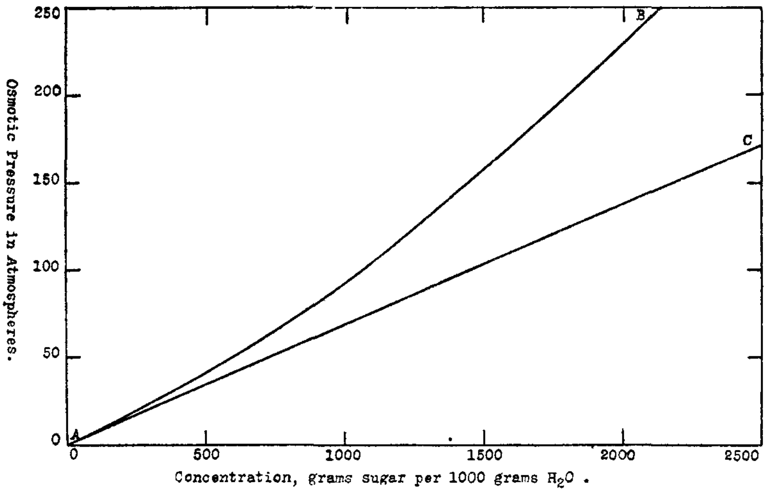

Fig. 3.

From the Curve AB, the actual osmotic pressure of a solution of sucrose of any concentration may be determined by interpolation. More exact values may be obtained from a curve made by plotting the ratio P/*c* (Table III) against *c*. The interpolated values given in Tables IV and V were obtained from such a curve.

In Table IV the results of this work are compared with the data obtained by Berkley and Hartley[1] in their work on cane sugar. Their measurements were made at 0° (Col. 3), the concentrations being expressed in volume molar terms (Col. 1).

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[1] *Trans. Roy. Soc.*, (*A*) 206, 481 (1906).

By the help of the data in Table III the concentrations were transformed to the weight molar basis and are given in Col. 2. Assuming that the temperature coefficient of osmotic pressure is the same as for gas pressure, the values at 30° given in Col. 4 were calculated from the values of Berkley and Hartley determined at zero. In Col. 5 the data obtained in this laboratory are shown, these values being determined by interpolation as explained above. The concordance is really better than might be expected.

TABLE IV.

1.	2.	3. Berkley and Hartley.	4.	5. Frazer and Myrick.
Grams/1000 cc. solution.	Grams/ 1000 g. H_2O.	P_0.	P. $P_{30} = (1 + 0.00367t)P_0$.	P_{30}.
180.1	202	13.95	15.48	15.59
300.2	370	26.77	29.72	29.78
420.3	569	43.97	48.81	47.88
540.4	820	67.51	74.94	73.06
660.5	1133	100.78	111.87	109.10
750.6	1430	133.74	148.46	148.80

Discussion.

In calculating the theoretical values of osmotic pressure it has been customary in this laboratory to use the van't Hoff equation as modified by Morse and Frazer, *viz.*:

$$P = \frac{RT}{V} n \qquad (1)$$

where P is the osmotic pressure, R is the gas constant and T the absolute temperature. V represents the volume of the pure solvent in the solution at 4°, and n represents the number of mols of solute present. This does very well for dilute solutions, but for more concentrated solutions the more exact thermodynamic formula should be used.

As early as 1894 it was pointed out by van der Waals and his associates Boldingh and van Laar, especially the latter,[1] that the properties of solutions (vapor pressure, osmotic pressure, etc.) are functions not of the relation of solute particles to solvent particles, but of solute particles to the total number of particles present, or more exactly, that the properties are a function of the mol fraction of the solvent present. This view and its relation to van't Hoff's equation has also been discussed at length by many other writers, namely, Gibbs, Evans, Trevor, Lewis, and Washburn, in particular.

Van Laar's equation for the relation between osmotic pressure and concentration is

$$P = \frac{-RT}{V_0} \ln \frac{N}{N + n} \qquad (2)$$

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[1] Van Laar, *Zeit. Phys. Chem.*, 15, 457 (1894).

where V_0 = the molar volume of the solvent, N = the number of mols of the solvent and n = the number of mols of the solute. If the thermodynamic relation between vapor pressure and osmotic pressure expressed by the familiar equation,

$$P = \frac{RT}{V_0} \ln \frac{p_0}{p} \qquad (3)$$

is accepted, then Equation 2 follows directly from a consideration of Raoult's law.

In other words, Raoult's law states that the vapor pressure of a solution is a function of the mol fraction of the solvent present, so if there *is* a direct relation between vapor pressure and osmotic pressure, the latter must also be a function of the mol fraction of solvent present.

The above mentioned writers also point out that the value of Equation 1 lies in its being an approximation of Equation 2 for if x is used to represent the mol fraction of the solute present, Equation 1 may be expressed,

$$P = \frac{RT}{V_0} (x + x^2 + x^3 + \ldots\ldots\ldots) \qquad (4)$$

Equation 2 upon expansion becomes,

$$P = \frac{RT}{V_0} (x + {}^1/_2x^2 + {}^1/_3x^3 + \ldots\ldots.) \qquad (5)$$

and it will be seen that the two equations differ only in the higher powers of x. If this factor is small the higher powers may be neglected and the two equations become identical.

Equation 1, as an approximation of Equation 2, gives values practically identical with those obtained from the latter in the case of dilute solutions. However, as the concentration of the solution increases, the values as calculated from the two equations differ more and more. Hence Equation 2 alone can be used correctly in the case of concentrated solutions. This has been done in all calculations in this paper.

At the pressures measured in this work the compressibility of the solution is no doubt an important factor. However, no data was available so this factor was neglected.

In the case of aqueous solutions the degree of association of the solvent must be considered as well as the hydration of the solute.

For weight normal solutions $N = \frac{1000}{18.015.a}$ where a is the degree of association of the solvent. If we represent the degree of hydration of the solute by W, then

$$N = \frac{1000}{18.015.a} - \frac{W}{a} n$$

and the mol fraction of solvent present

$$\frac{N}{N+n} = \frac{\dfrac{1000}{18.015.a} - \dfrac{W}{a}n}{\left(\dfrac{1000}{18.015.a} - \dfrac{W}{a}n\right) + n}$$

The molecular volume of the solvent is equal to the volume (v) of one gram of the solvent at the temp. (t) multiplied by its molecular weight.

$$V_o = v.\ 18.015.a$$

The value of R in cc. atmospheres is 82.07. Making these substitutions and introducing the factor for transference from natural to Briggsian logarithms we have as the final working form of the equation

$$P = \frac{-82.07(273.1 + t^{\circ})2.303}{v.\ 18.015a} \log \frac{\dfrac{1000}{18.015a} - \dfrac{W}{a}n}{\left(\dfrac{1000}{18.015a} - \dfrac{W}{a}n\right) + n} \qquad (6)$$

No reliable data are available for the degree of association of water. However, it is the consensus of opinion[1] that water is a ternary mixture of mono-, di- and tri-hydrol, the di-hydrol predominating. The equilibrium, however, is greatly influenced by temperature and pressure. Increases in the former shift the equilibrium towards the mono-hydrol and increases in pressure shift the equilibrium toward the di-hydrol. So in the absence of exact figures the degree of association has been taken as 2.

Using the factors indicated in Equation 6, n must be expressed as the weight molar concentration in terms of O = 16.

Table V gives a comparison of the experimental values of osmotic pressure compared with the calculated values, assuming the various degrees of hydration indicated.

TABLE V.

Osmotic Pressures of Cane Sugar.

Concentration. Wt. molar. H = 1.	Observed. P.	Observed. M. p.	Observed. Equation 1. $a = 1.$ $w = 0.$	Calculated. Equation 6. $a = 1.$ $w = 0.$	Calculated. Equation 6. $a = 1.$ $w = 6.$	Calculated. Equation 6. $a = 2.$ $w = 6.$	Calculated. Equation 6. $a = 2.$ $w = 5.$	Calculated. Equation 6. $a = 2.$ $w = 4.$
0.1	2.472	24.72	2.47	2.44	2.47	*2.48*	2.48	2.47
1	27.22	27.22	24.72	24.4	27.28	*26.99*	26.45	25.98
2	58.37	29.19	49.43	48.32	61.19	*59.89*	*57.41*	55.1
3	95.16	31.72	74.15	71.85	104.65	100.95	*94.03*	88
4	138.96	34.74	98.86	94.80	162.25	153.7	*138.2*	125.5
5	187.3	37.46	123.58	117.7	242.6	224.2	*192.5*	*168.8*
6	232.3	38.7	148.3	140.1	361.7	323.9	*261.4*	*219.3*
6.5	252.8	38.9	173.0	151.2	446.9	391.75	303.4	*247.9*

In Column 2 are found the experimental values of osmotic pressure P and in Column 3 are shown the values of "molecular pressure" at each

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[1] Walden, *et al.*, *Trans. Far. Soc.*, 6, 71 (1910).

concentration (*i. e.*, the pressure per mol of sugar, neglecting hydration). It will be noted that these figures approach a constant value as saturation is approached.

In Columns 4 and 5 a comparison is made of the values of P as calculated by Equation 1 and by Equation 2, association and hydration both being neglected.

The curve AC in Fig. 3 is of the values in Column 5 and shows by comparison with the experimental curve AB how greatly the complications of the associations of solvent and the hydration of the sugar cause the results to deviate from ideal conditions.

Column 6 gives the values obtained when the assumption is made that a hexahydrate of constant composition is formed and that the effect of association on the results obtained is negligible. It is upon these assumptions that Washburn[1] bases his consideration of calculated osmotic pressures. While the concordance with the observed values is fair at lower concentrations it is obvious that the errors are considerable at higher concentrations.

Columns 7, 8 and 9 show the values obtained from Equation 6, assuming the degree of association of water as 2 and assuming the formation of the hexa-, penta- and tetrahydrates, respectively. From a consideration of Column 7 it will be seen that even when the degree of association is taken into account, the assumption that a hexahydrate is formed which is stable throughout the entire range, is unwarranted. Similarly, from Column 8, it will be seen that the assumption of Callendar,[2] that a stable pentahydrate exists throughout the range, is also open to objection. Both of these assumptions, however, seem to hold over limited ranges, but now that the entire range of solubility has been studied, the evidence indicates a change in the degree of hydration with changes in concentration. Up to concentrations of 2 molar, calculations based on the assumption of the formation of the hexahydrate, give results most concordant with the experimental values. At two molar concentration the experimental value is a mean between values obtained theoretically, considering the formation of hexa- and pentahydrates, respectively.

For 3 and 4 molar concentrations the assumptions of the existence of the pentahydrate gives values concordant with experimental results. At 5 and 6 molar concentrations the experimental values are intermediate between those obtained assuming the degree of hydration as five, and those assuming the hydration as four.

The extrapolated experimental value for 6.5 molar (which is practically a saturated solution) concords well with the calculated value

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[1] "Principles of Phys. Chem.," McGraw-Hill, 1915.

[2] *Proc. Roy. Soc.*, (*A*) 80, 466 (1908).

for the tetrahydrate. Hence it would seem that the degree of hydration of cane sugar in aqueous solutions decreases gradually with increase in concentration. This is in harmony with the newer hydrate theory of Jones.[1] Findlay,[2] in his discussion of osmotic pressure considers the experimental data formerly available as evidence against Jones' hydrate theory and harmonizing with the older one of Mendeleef. His conclusions, as well as those of Washburn and Callandar were simply based on considerations of too limited ranges of concentration.

Summary.

I. In this article the authors describe a modification of the Morse and Frazer method of measuring Osmotic Pressures. The principal features of the new apparatus are: first, the reversal of the position of the semipermeable membrane such that the pressure is developed around the outside of the porous clay cell; second, the use of an electrical resistance gage for measuring the magnitude of the pressures developed.

II. It is pointed out that this apparatus is a decided improvement over the old, and that it is much stronger and much quicker in its action. Pressures of at least 270 atmospheres can be measured and equilibrium is reached in a few hours so that measurements are completed in from 12 to 24 hours. These features make the method applicable to a study of concentrated solutions, and, it is hoped, to a study of solutions of certain electrolytes.

III. Measurements of the osmotic pressures of cane sugar solutions over the complete range of solubility are given and the results compared with those of other investigators over limited ranges.

IV. In the theoretical discussion the Morse and Frazer modification of van't Hoff's equation is compared with van Laar's thermodynamic equation, using the mol fraction basis. The necessity of using the latter in calculating the osmotic pressures of concentrated solutions is recognized by the authors, as has been done by others.

The experimental values obtained are compared with the theoretical values calculated by means of van Laar's equation, assuming various degrees of hydration of the dissolved sugar. It is pointed out that, although the theoretical calculations are based on assumptions and neglect certain factors, the evidence indicates that the hydrates of cane sugar formed in aqueous solutions are not of constant composition, as some have thought, but are of variable composition. The degree of hydration decreases with increase in the concentration of the sugar.

JOHNS HOPKINS UNIV.,
BALTIMORE, MD.

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[1] *Am. Chem. J.*, 33, 584 (1905).

[2] Alexander Findlay, "Mon. on Inorganic and Physical Chem."