

agreement with the work of Röntgen and Zehnder⁴ who measured the effect of temperature on the pressure coefficient of the refractive index. One may also determine from the calibration data above the extent to which the temperature of the instrument must be controlled in order to secure the desired accuracy.

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THE OSMOTIC PRESSURES OF CONCENTRATED SOLUTIONS OF SUCROSE AS DETERMINED BY THE WATER INTERFEROMETER.

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Received August 18, 1921.

Many difficulties are encountered in the direct measurement of the osmotic pressures of solutions among which are those involved in measuring the pressure. The limit of pressure that the glass manometer will stand as found by Frazer and Myrick is about 100 atmospheres. Among the uncertainties involved in the use of gas manometers are the deviation of gases from Boyle's law, and the fact that gas may be occluded between the mercury and the glass, both of which may become appreciable when measuring high pressures. The percentage error involved in reading the levels of the mercury menisci also increases with the compression of the gas and the change of form of the meniscus is not to be disregarded. So the higher the pressure the less accurate the gas manometer becomes.

Frazer and Myrick² by the use of the resistance pressure gage were able to obtain a constant sensitivity at all pressures, but owing to certain difficulties such as hysteresis in the resistance coils it was thought wiser to seek a method for measuring high pressures that would be less objectionable.

Berkeley and Hartley³ determined the osmotic pressure of several solutions up to pressures of 133 atmospheres by applying mechanical pressure and determining the equilibrium pressure by noting the point at which the solvent just ceases to pass through the semipermeable membrane.

In an article by Woods⁴ the objection is raised that the osmotic pressure of solutions as measured is not the true osmotic pressure, but of that layer of solutions in immediate contact with the semipermeable membrane

⁴ Röntgen and Zehnder, *Wied. Ann.*, **44**, 34 (1891).

¹ This work has been assisted by grants from the Carnegie Institution of Washington.

² Frazer and Myrick, *THIS JOURNAL*, **38**, 1907 (1916).

³ Berkeley and Hartley, *Phil. Trans.*, **206A**, 486 (1906).

⁴ Woods, *Trans. Faraday Soc.*, **11**, 29 (1915).

which is more concentrated than the solution proper, due to adsorption. This criticism applies more particularly to dilute solutions and has been partly answered by the work of Minter and Frazer.⁵ They used a stirring device which could be operated during the time the measurements were being made.

The same osmotic pressure was also obtained by allowing the pressure to rise by the diffusion of solvent through the membrane as was obtained by submitting the solution to a hydrostatic pressure greater than the equilibrium pressure, which latter pressure is reached by the removal of solvent from the solution through the membrane.

Apparatus.

The water interferometer as adapted to the measurement of pressure⁶ was used in this work for measuring the osmotic pressures developed. The cells used were made by the method of Frazer and Myrick,² the membrane of copper ferrocyanide being deposited on the outside. The container of bronze was also the same as used in the above work.

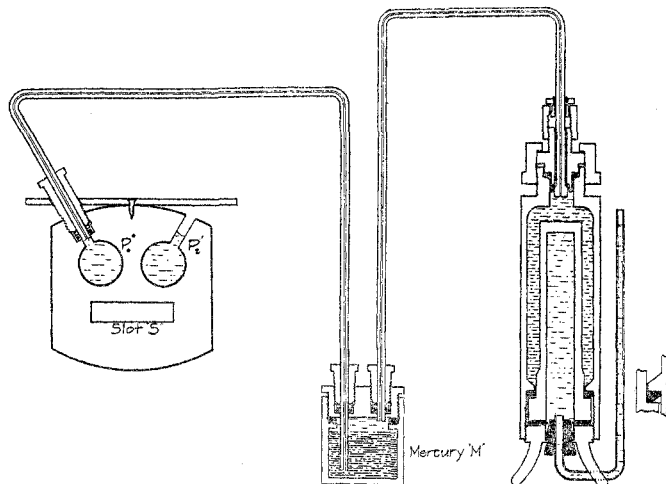


Fig. 1.

When attempting the measurements at 55.7° it was found necessary to modify the washer used between the cell shoulder and the cell container, due to the flowing of the rubber at this high temperature and pressure. This was prevented by inserting a bronze washer between the cell shoulder and washer as shown in insert Fig. 1.

Temperature Control.

In the 30° experiments the entire apparatus was placed in a 30° air-

⁵ Minter and Frazer, unpublished dissertation. Johns Hopkins University, 1917.

⁶ Van Doren, Parker and Lotz, *THIS JOURNAL*, 43, 2497 (1921).

bath which varied but 0.05° . In the 57.7° experiments the cell and container were placed in a double-walled copper bath in which the constant temperature was maintained by boiling acetone in the outer compartment. The inner compartment containing the cell surrounded by water was cylindrical in shape, 10 cm. in diameter and 25 cm. high. With a bath of these small dimensions stirring was found unnecessary. Temperature varied from day to day about 0.1° with change in the atmospheric pressure but the time required to complete an experiment was very short, the maximum period required to obtain equilibrium being $2\frac{3}{4}$ hours, in which interval no changes in temperature could be detected.

This form of apparatus fulfilled all expectations, proving convenient, strong, and of quick action, as the results in Table I show. Equilibrium was obtained in from 12 minutes for the lower concentrations to $3\frac{3}{4}$ hours for the measurements at high concentrations. In the $2 M$ measurements at 55.7° the final reading obtained after adjusting the apparatus was maintained throughout the experiment showing that equilibrium had been obtained even before the time recorded in the table.

In the 30° work all solutions used were at 30° , in the 55.7° work the solutions were cooled somewhat below 55.7° in order to lessen the effect of dilution of the solution being measured.

Experimental.

Preparation and Analysis of Solutions.—Aqueous solutions of cane sugar were studied over the complete range of solubility. The sucrose used was carefully purified "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 $O=16$ scale. The sugar in each instance was dissolved in distilled water made $0.01 N$ with potassium ferrocyanide. The solvent against which the osmotic pressures were measured was $0.01 N$ copper sulfate.

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 for 1000 g. of water was obtained.

In the work on dilute solutions carried on in this laboratory, corrections for changes in concentration are made by changing the observed pressure the same percentage 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

considerable. 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 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 any of our measurements except in Expt. 11. The cell used here was an old one that had not been used for several years and was set up without seasoning. All of the other cells used had been well seasoned at high pressures and gave very satisfactory results.

TABLE I.
OSMOTIC PRESSURES.

Expt.	Sugar/1000 cc. of solution. G.	Sugar/1000 g. of water. G.	Equilibrium time. Min.	Osmotic pressure. Atmospheres.
30°.				
1	478.3	680	90	57.5
2	472.0	665	12	56.6
3	597.0	958	90	87.2
4	605.4	980	150	90.4
5	608.5	990	165	92.0
6	700.2	1260	195	129.5
7	695.0	1242	225	127.4
8	781.4	1549	180	169.1
9	781.4	1549	225	168.6
10	777.3	1533	90	164.1
11 ^a	831.5	1758	300	198.2
12	826.2	1737	195	200.2
13	839.8	1796	165	206.1
55.7°.				
14	477.2	674	22	61.0
15	481.4	685	20	63.1
16	610.6	996	35	97.4
17	612.7	1000	16	98.7
18	702.3	1270	30	132.4
19	706.4	1284	55	133.5
20	782.5	1556	75	170.6
21	791.9	1590	90	178.7
22	856.5	1877	120	222.0
23	842.9	1810	135	213.8
24	900.2	2112	165	259.3
25	910.6	2190	135	265.6
26	No analysis.		135	273.0

^a Unseasoned Cell.

Results.

Table I summarizes the experiments. Some were lost and not recorded, due to the washers breaking; and hence no analysis could be made of these solutions. In Expt. 26 the upper washer was broken and the ex-

periment was incomplete. No importance is attached to the result obtained in Expt. 11, as we found that the results obtained with unseasoned membranes as shown by solute leakage are invariably low and the true equilibrium pressure is not reached.

Frazer and Myrick report sugar leakage after reaching concentrations of 5 *M* and greater. We should therefore expect to find their results at these higher concentrations somewhat low. On plotting a curve with their results, *i. e.*, osmotic pressure against concentrations—a decided drop in the curve is noticed after passing 5 *M* concentrations. In comparing their results for corresponding concentrations with the results of Expts. 12 and 13 our predictions are found to be correct, since we obtained 200.2 and 206.1 as compared with 192.0 and 200.0, respectively, found by Frazer and Myrick.

The results obtained in this work for 6 *M* sucrose when substituted in the above curve of Frazer and Myrick give a continuous and regular curve at 30°.

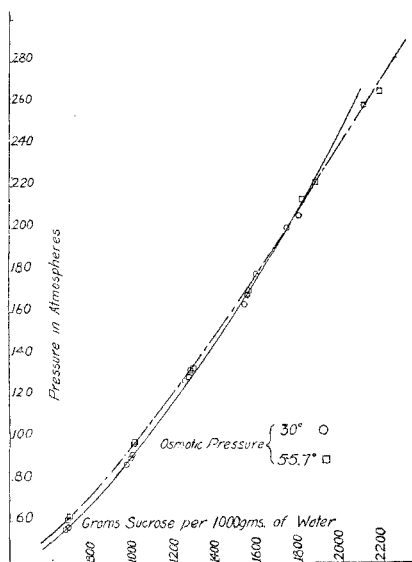


Fig. 2.

In Fig. 2 the data in Table I are shown graphically. Here the concentration expressed in g. of sucrose for 1000 g. of water is plotted against the osmotic pressure in atmospheres. It will be noticed that the curve for 55.7° cuts the extrapolated 30° curve at a concentration of 2000 g. of sucrose to 1000 g. of water. Above this concentration the osmotic pressure of solutions at 55.7 is less than that of like concentration at 30°.

Discussion.

Woods⁴ calculated the value for osmotic pressure from the vapor-pressure measurements obtained by him for concentrated solutions of sucrose by using the Porter equation which connects the osmotic pressure and the vapor pressure of the solution and solvent. Data for 3 solutions of concentrations 92.0, 156.6 and 224.3 g. of sucrose to 100 g. of water respectively were obtained at temperatures from 60° to 90°.

He noticed that in the two more concentrated solutions the osmotic pressure as calculated showed a distinct tendency to diminish with rise in temperature.⁷ The results obtained in this work indicate that, while

⁷ Results obtained in this laboratory on sugar solutions up to *M* concentrations showed the same tendency, *i. e.*, to increase less than the theoretical value.

the calculated values obtained by Woods may be high, the relative values are not far from correct.

From a perfect solution the osmotic pressure would increase with rise in temperature according to the gas laws. Here, however, the increase is much less than the theoretical increase. This is quite evident even with the less concentrated solutions, while on approaching concentrations of 6 *M* the osmotic pressure at 55.7° becomes actually less than the values obtained at 30°.

It has been firmly established that these sugar solutions warm when diluted adiabatically. If we were then to accept the suggestion made by Woods that negative heats of dilution imply an association of solute molecules, the amount of which becomes greater at the higher temperatures, then the dynamical explanation would be that the increased association more than balanced the increase of kinetic pressure due to the rise in temperature.

Callender⁸ has elaborated the vapor-pressure theory of Poynting and according to his view, when the heat of dilution is small, as it is, at any rate, with moderately strong solutions,

$$\Pi_{\pi} = \frac{N - an}{N - an + n} \pi_0$$

where *a* is a hydration factor representing the number of solvent molecules associated with each molecule of solute; Π_{π} , the vapor pressure of the solution; Π_0 , the vapor pressure of the solvent; *N*, the mol fraction of the solvent; *n*, the mol fraction of the solute. If, on the other hand, Callender's hydration factor *a* changes, owing to the formation of simpler hydrates at the higher temperature, then one might consider the increase in effective dilution due to the liberation of the water previously attached to the sugar molecules to be responsible for the decrease in the osmotic pressure.

Woods also integrates the equations of Porter as applied to the results of Berkeley and Hartley

$$P = \frac{nRT}{V - nb}$$

and obtains $\frac{dP}{dT} = \frac{P}{T} \left(1 + \frac{P}{R} \frac{db}{dT} \right)$

which makes *P* independent of the temperature when $db/dT = -R/P$. Then, for a solution whose osmotic pressure is 180 atmospheres, a loss of 1 molecule of water for each 40° rise of temperature would suffice in order that the osmotic pressure remain unchanged with rise in tem-

⁸ Callender, *Proc. Roy. Soc.*, **80A**, 466 (1908).

perature. A greater rate of dehydration than this would involve a decrease of the osmotic pressure with rise of temperature.

Woods, however, believes that this stage is not reached in the cases he studied and attributes the apparent decrease in his calculated values to a too rapid variation of the ratio of Π_0/Π_π with temperature. This conclusion seems unjustified. The loss by dehydration must reach such a magnitude at concentrations of 6 *M* and over that the increase in solvent due thereto more than balances the increase of kinetic pressure due to rise in temperatures.

Summary.

1. In this article the authors describe a modification of the method used by Frazer and Myrick for measuring the osmotic pressure. The principle feature of the new apparatus is the use of the water interferometer in determining the magnitude of the pressures developed.

2. The apparatus affords a decided improvement over the method of Frazer and Myrick, being somewhat quicker in action and more dependable. Pressures up to 273 atmospheres have been measured, while the pressure chambers have been calibrated up to 330 atmospheres.

3. Measurements over the entire range of solubility are given for 30° and 55.7°.

4. Attention is called to the results of Woods as calculated for vapour-pressure measurements, and it is shown that his results, showing a decrease in osmotic pressure with rise in temperature with concentrated solutions, are relatively correct although his actual values for the osmotic pressure seem to be high as compared with these direct measurements.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, No. 1, 7.]

THE EQUILIBRIUM IN MIXTURES OF BINARY ELECTROLYTES.

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Received August 24, 1921.

1. Introduction.

The determination of the equilibrium in a mixture of electrolytes is a problem of considerable practical importance since many of the reactions with which we have to deal are carried out in mixtures of this kind. If the law of mass action is applicable to the resulting equilibrium, then the problem is in general soluble, provided intermediate ions are not formed. In all likelihood this condition is fulfilled in mixtures of binary electrolytes, but, as Harkins¹ has pointed out, when higher types of salts are present, intermediate ions are probably formed. The following discussion will therefore be limited to mixtures of binary electrolytes.

¹ Harkins, *THIS JOURNAL*, 33, 1807 (1911); 38, 2679 (1916).