# On the Osmotic Pressures of Some Concentrated Aqueous Solutions

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# X. *On the Osmotic Pressures of some Concentrated Aqueous Solutions.*

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*Communicated by* W. C. D. Whetham, *M.A., F.R.S.*

## Introduction.

In a communication* to the Royal Society by one of us it was stated that an attempt would be made to determine directly the osmotic pressures of strong solutions. The purpose for which these determinations were required was to obtain data for the tentative application of Van der Waals' equation of state to solutions, but we propose, in this communication, to restrict ourselves to the actual results obtained, reserving for a future occasion the theory of the subject.

Some time ago, in the proceedings of the Royal Society,† we gave an account of some preliminary experiments. We there described the method and apparatus we used, and at the same time stated that we hoped to get more accurate results by modifying the apparatus. This hope has been fulfilled, and we trust that a somewhat full description of the methods used both in the actual determinations and in the preparation of the membranes will, therefore, not be out of place.

Before proceeding to describe these matters, it will be advisable to discuss briefly what is meant by osmotic pressure in the case of concentrated solutions, for it appears from recent discussions‡ that there is some ambiguity about the meaning of the expression.

There seem to be two methods of investigating directly the osmotic phenomena of a solution, and these will, in general, give two different results :—

(1) One, which we may call the osmotic "force" method, depends on the determination of the rate at which the solvent will flow through a semi-permeable membrane into a large quantity of solution when there is no pressure on the latter. A knowledge of this rate together with the frictional resistance to the flow will enable the osmotic "force" to be calculated in absolute units.

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* 'Phil. Trans. Roy. Soc.,' vol. 203, pp. 189–215.

† 'Roy. Soc. Proc.,' vol. 73, pp. 436–443.

‡ *Cf.* a letter in 'Nature,' vol. 74, p. 6.

(2) All other direct methods relate to what may be called equilibrium pressures ; they depend on the measurement of the pressure to be applied to the solution to bring about a state of equilibrium between it and the solvent, when the two are separated by a semi-permeable membrane.  The difference between the pressure on the solution and that on the solvent is the equilibrium pressure of the solution, under the conditions of the experiment.  It is evident that, in general, for the same solution the equilibrium pressure will vary, on account of the compression of the solution and solvent, according to the pressure on the solvent.  It is, therefore, necessary to state what pressure was on the solvent when the particular equilibrium pressure was observed.

We have made some attempts to obtain comparative values for the osmotic " force " by a method analogous to that indicated in (1), but these attempts, although not entirely unsuccessful, were not satisfactory, and will not be alluded to further. The following account refers only to equilibrium pressures, observed when there was a pressure of one atmosphere on the solvent.

### *General Description of the Method used.*

A gradually increasing pressure is placed upon the solution, which is separated from the solvent by a semi-permeable membrane, until the solvent, which at first flows into the solution, reverses its direction and is squeezed out.  The pressure, when there is no movement of the solvent, is considered to be the sum of the equilibrium pressure and a pressure equal to that on the solvent.

Owing to the difficulty of determining the exact point at which no movement takes place, and for other reasons, the experiments were arranged so as to enable an observation to be made of the rate of movement of the solvent both when the pressure on the solution was just below and when just above the turning-point pressure.  The turning-point pressure was deduced from these two rates, or, sometimes, from a series of rates corresponding to slightly different pressures both above and below the turning-point.

### *The Osmotic Apparatus.*

The apparatus used is shown in fig. 1.   AB is a porcelain tube*, 15 centims. long, 2 centims. external and 1·2 centims. internal diameter ; the vertical ends are glazed. This tube carries the semi-permeable membrane as close to the outer surface as possible.  CC is a gunmetal cage against the ends of which the dermatine rings DD are compressed, when the two parts E and F of the outer gunmetal vessel are screwed together.  The ends of this cage have shallow radial grooves cut out of them, so as to prevent the dermatine rings from rotating and rubbing the membrane during the operation of screwing E and F home.  The length of the cage is such that, when finally set up, the dermatine rings just overlap the ends of the porcelain tube.

* The porcelain tubes are similar in all respects to those described in our preliminary communication.

The outer gunmetal vessel (capacity about 250 cub. centims.) contains the solution which, when a pressure is applied to it, forces the dermatine rings against the bevelled faces GG, and thus causes a tight joint to be made with the porcelain tube. The joint between E and F is made good by another dermatine ring X, which is compressed between the metal ring I and the nuts JJ.
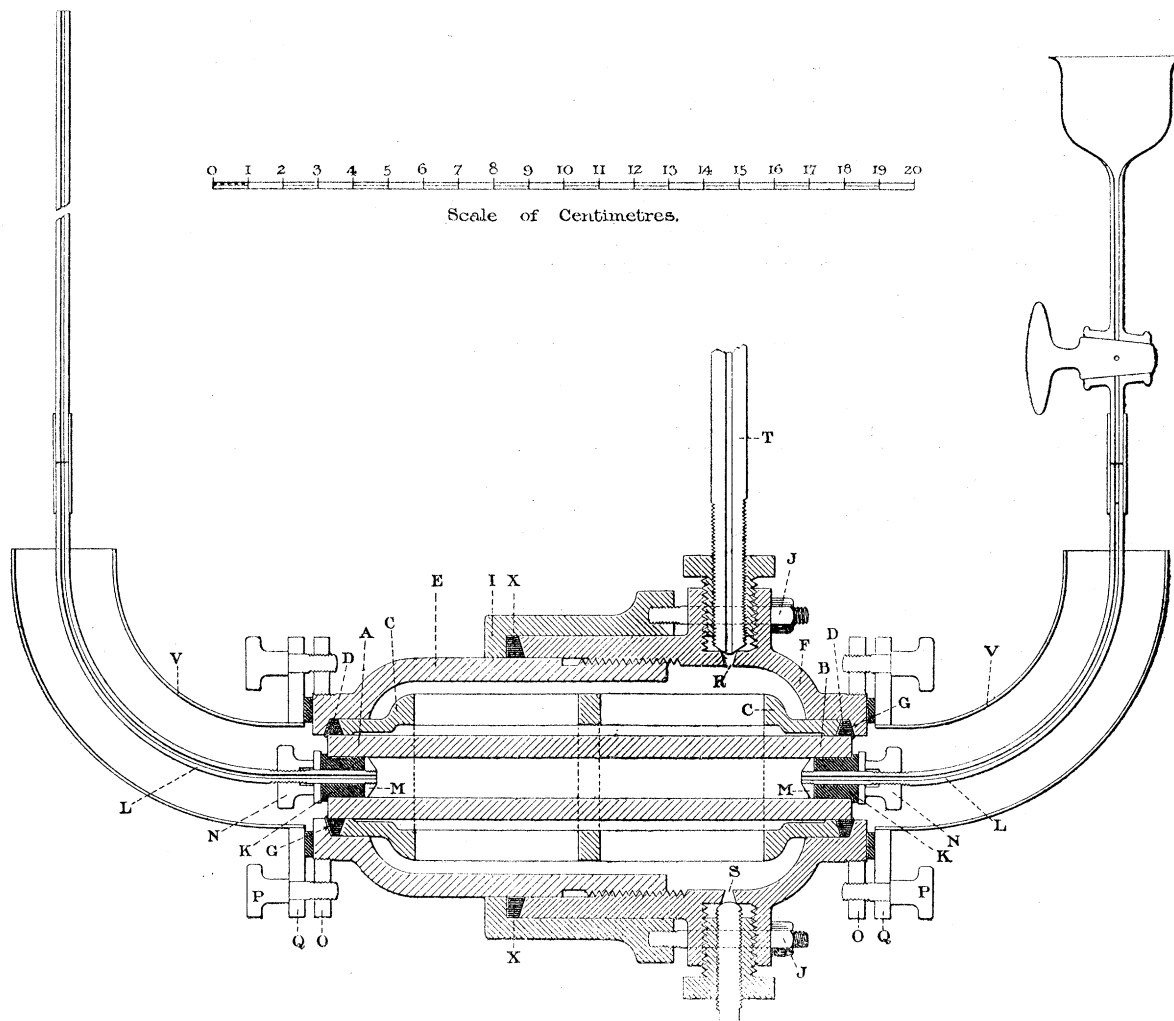


Scale of Centimetres.

Fig. 1.

The ends of AB are closed by pieces of thick-walled rubber tubing KK, through which the brass tubes LL are passed; a water-tight joint between LL and the inside of the porcelain tube is obtained by compressing the rubber between the metal washers MM and the nuts NN.* The brass tubes are joined by rubber tubing, one to a glass tap and the other to an open glass capillary—the latter, which we shall call the water gauge, was graduated in millimetres and calibrated; one centimetre of the bore contains 0·00312 cub. centim. The outer ends of E and F have threads cut on

* It seems advisable to point out that the rubber tubing KK is unaffected by the pressure put upon the solution.

them to receive the brass rings OO, which in their turn are perforated by screw holes to receive the thumb screws PP, by means of which, together with a rubber washer, a tight joint is made between the flanges QQ of the curved metal tubes VV and the ends of E and F. The uses of these tubes will be explained later.

The perforation R is for filling the apparatus with solution, and also for connecting to the pressure apparatus, while S serves to empty the vessel. The method of making a pressure-tight joint, shown at R, originated, we believe, at the Cambridge Scientific Instrument Co. It may be useful to call attention to it, as we have experienced no trouble, although the joint has been made and remade over a thousand times. It is scarcely necessary to describe the joint, as the diagram illustrates it sufficiently; the only point to emphasize is that the thread on the steel pressure tube T should be of a smaller pitch than that on the outside of the nut.

### The Beam Pressure Apparatus.

The pressure apparatus described briefly in our preliminary communication had to be modified because it was found that the dermatine-ring stuffing box therein mentioned was unsatisfactory, and also because the necessarily somewhat large leak past the stuffing box (this was unavoidable, for, if checked, the plunger was no longer free) made it imperative to adjust the beam continuously—a labour which sometimes lasted without intermission from 10 A.M. to 7 P.M.

The new form was made for us by the Cambridge Scientific Instrument Co., and is shown in elevation and plan in Diagrams 1 and 2 respectively.



Diagram 2.

Diagram 1.

Dead weight standard pressure gauge.

To osmotic apparatus.
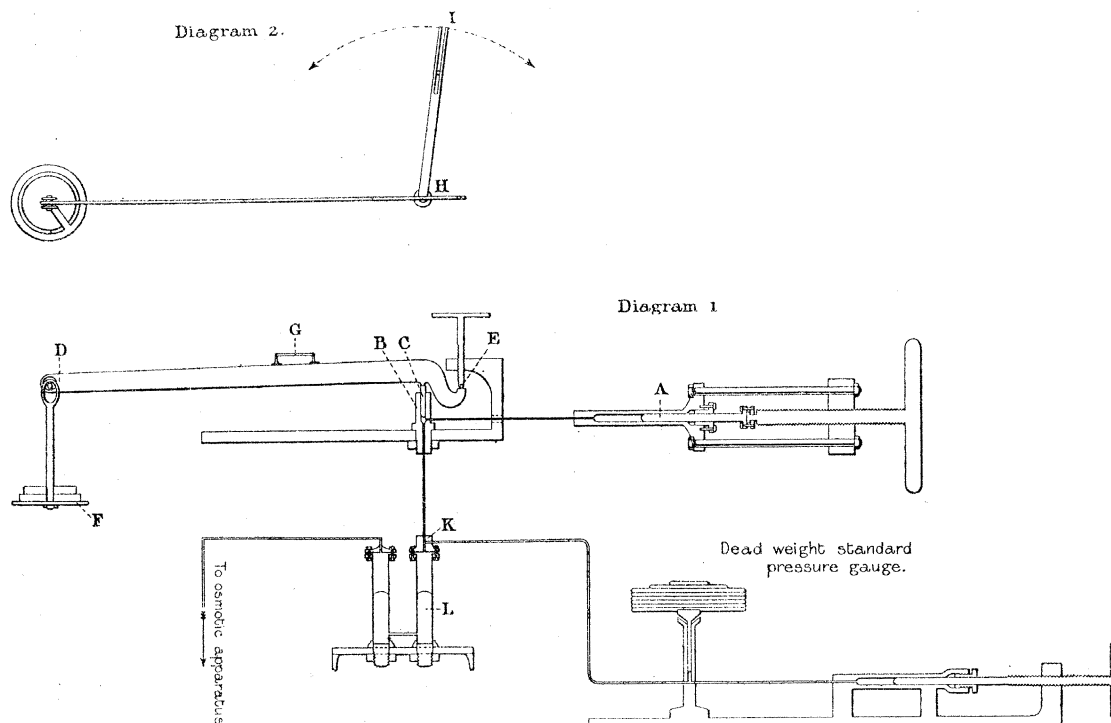
A plunger A, working through a stuffing box in a cylinder, compresses a thick "steam cylinder" oil. The pressure is communicated to another cylinder B by steel pressure tubing, and a steel plunger C works vertically in B and actuates the beam DE, which has a fulcrum at E. A pan F, suspended on knife edges, carries the weights, and a sensitive level is provided at G. The beam, on account of small leakages, does not remain horizontal, but has to be relevelled at intervals by means of the plunger A.

A horizontal arm HI (see plan) is secured to the top of the plunger C (elevation) and is constrained to move to and fro by means of an oscillating system (not shown) worked from the laboratory shafting. Although the plunger works in its cylinder without any stuffing box, and the viscosity of the oil is the only preventive of large leakage, it was found advisable to move it continuously about its vertical axis—otherwise the pressure registered by the weights on the beam was not quite the same as the pressure delivered to the osmotic apparatus.

Knowing the weights on the pan, the ratio of the arms of the beam and the diameter of the plunger, the pressure can be calculated—it was noticed, however, that, when big pressures were used, the calculated values did not quite agree with those shown by a standard pressure gauge—doubtless this was caused by a slight flexure in the beam.

The cylinder B is in communication with a ∪ tube L, and the pressure is delivered on to the surface of the mercury—the mercury in the other limb of the ∪ tube passes on the pressure to the solution in the osmotic apparatus.

### The Dead-Weight Standard Pressure Gauge.

During the course of the experiments it was found that more concordant results could be obtained than had been anticipated. The beam apparatus already described only gave pressures agreeing among themselves to about 1 per cent.; this was surmised to be due to the fact that the hardened steel balls at the fulcrum and at the top of the plunger gradually crushed the metal under them so as to form a depression, thus slightly altering the effective ratio of the arms of the beam every time it was put up. That some such effect was produced is shown by the fact that the oscillation of the arm HI (Diagram 2) caused a vertical oscillation in the beam, especially when the movable metal piece at the top of the plunger (not shown in the diagram) was worn into a depression.

It was therefore decided to substitute one of Messrs. SCHÄFFER and BUDENBERG's dead-weight standard plunger gauges for the final determination of the equilibrium pressures; this apparatus was connected to the ∪ tube at K, and a tap (not shown) was provided in the ∪ tube head so that the beam apparatus could be cut off when required.

The dead-weight gauge, which is a commercial article, need only be described briefly; it consists of two plungers, one supporting the weights, while the other,

actuated by a screw and wheel, compresses the "steam cylinder" oil which lies between them. The plunger supporting the weights may be regarded as the pressure gauge of the instrument; it was kept slowly rotating by hand whenever it was in use. The apparatus can be worked up to 136 atmospheres. The sensibility throughout the whole range is about 0·12 atmosphere, consequently at low pressures the percentage error is considerable.

The apparatus was compared with a standard Bourdon gauge and found correct. It should be borne in mind that the total pressure on the solution is the pressure registered by the dead weight together with that of the atmosphere.

### The Semi-Permeable Membranes.

The membranes were deposited on the surface of the porcelain tubes by the following means. The porcelain tube is placed in a copper sulphate solution (50 grammes in a litre) in a desiccator and the air exhausted, until no more bubbles come off from the tube—this takes place only after several days—the tube is withdrawn, wiped inside and outside with a clean linen duster, and allowed to dry for $\frac{3}{4}$ hour. The ends are then closed by rubber plugs, perforated for the passage of glass rods; then, holding the tube horizontal and spinning it rapidly between the fingers, it is plunged into a solution of potassium ferrocyanide (42 grammes in a litre). By this means an even deposit of copper ferrocyanide, very close to the outer surface of the porcelain, is obtained. The tube is allowed to soak in the ferrocyanide, after which it is set up for electrolysis. The same solutions and of the same strength are used; the tube is plugged at one end, and at the other is fitted with a perforated plug and thistle funnel, through which a copper electrode dips into the copper sulphate solution, while a platinum electrode is immersed in the ferrocyanide surrounding the porcelain tube. It was found best to place the platinum electrode in a porous pot suspended in the ferrocyanide solution, in order to prevent the alkali from attacking the membrane, and the solution in the pot was frequently changed during the experiment.

The current is passed (from the copper to the platinum electrode) until the resistance becomes constant; this generally takes about 2 hours. We found, as noted by Messrs. MORSE and HORN*, that apparently the best voltage to apply is a hundred volts. When the resistance has risen to a steady value, the tube is taken out, washed and allowed to soak in distilled water for about ten days; care should be taken that the last traces of copper sulphate are not washed away. Experiment showed that unless this substance be present, the colloid copper ferrocyanide begins to dissolve. It may be mentioned that, before the necessity of this precaution was realised, we spoilt nearly the whole of our membranes; only one of them regained its efficiency and that only after several months' work on it.

* 'American Chem. Jour.,' vol. 26.

After this washing, any copper ferrocyanide which is only loosely adhering to the tubes, and not deposited in the pores, is rubbed off with pumice-stone, and the tube is remade electrolytically.   In general the resistance increases; when steady, the tube is again washed, and the operation repeated after the lapse of a few days, and so on until there appears to be no further rise in the resistance.   If the tube is a good one, the resistance should now be of the order of 50,000 ohms.

It is then set up in the osmotic apparatus and tested with a solution of 660 grammes of cane sugar in the litre—a solution whose equilibrium pressure is about 100 atmospheres; the tube will probably give a turning point somewhat lower than this pressure, on account of a leak of solution through the membrane.   The tube is then taken down, electrolytically remade, soaked in water for two or three days, and tested again with the cane sugar.   It will be found that although there has been no apparent rise in the resistance, the turning-point pressure has perceptibly increased.   The whole process is again repeated until a final steady value of the turning point is reached.   A determination of the amount of sugar that has come through the membrane during an experiment will help to indicate whether the tube is likely to be of any use or not.

The following table shows the progress of a certain tube which will be called N; the membrane was originally deposited on it about March 8, 1904.

## TABLE I.

| Date. | Resistance. | Temperature. | Turning point. | Temperature. |
|---|---|---|---|---|
| | ohms | | atmospheres | |
| March 11, 1904 . . . . . | 2,700 | Laboratory | — | Laboratory |
| November  4, 1904 . . . | 29,000 | ,, | — | ,, |
| „    15, 1904 . . . | 38,000 | ,, | — | ,, |
| December 12, 1904 . . . | 70,000 | ,, | — | ,, |
| August 11, 1905 . . . . | 45,000 | ,, | — | ,, |
| September 21, 1905 . . . | 60,000 | ,, | — | ,, |
| December  6, 1905 . . . | 65,000 | ,, | 95·5 | ,, |
| „    10, 1905 . . . | 300,000 | 0° C. | 96·3 | 0° C. |
| „    13, 1905 . . . | 250,000 | 0 | 96·7 | 0 |
| „    30, 1905 . . . | 250,000 | 0 | 99·4 | 0 |
| January 11, 1906. . . . | 200,000 | 0 | 100·0 | 0 |
| „    22, 1906. . . . | 270,000 | 0 | 100·0 | 0 |
| February  9, 1906  . . . | 200,000 | 0 | 100·4 | 0 |
| „    25, 1906  . . . | 170,000 | 0 | | |
| March  6, 1906  . . . . | 170,000 | 0 | | |
| „    10, 1906  . . . . | 170,000 | 0 | These numbers refer to the resistance of the tube when "remade" after experiments with other solutions. | |
| „    14, 1906  . . . . | 170,000 | 0 | | |
| „    24, 1906  . . . . | 170,000 | 0 | | |
| April  2, 1906. . . . . | 170,000 | 0 | | |
| „    17, 1906. . . . . | 100,000 | 0 | | |
| „    25, 1906. . . . . | 100,000 | 0 | | |

The second column gives the resistances which the tube reached when remade—the order of number only is given; they were measured by means of an ordinary Weston ammeter.   It should be mentioned that we are not quite sure that the first four

entries really belonged to tube N—the record was unfortunately mixed up with that of other tubes; the numbers give, however, the usual course of events. The third column states the temperature at which the tube was remade.

The fourth column gives the turning point, obtained shortly after "remaking," when using a solution of 660 grammes of cane sugar in the litre, and the fifth column gives the temperature at which this was determined.

Out of some 100 tubes of various makes only two reached the state of efficiency shown by N, although over 400 electrolyses were made. Some of the tubes could be discarded immediately after first depositing the membrane upon them; others could never be made to reach a resistance of even 50,000 ohms, while a small percentage always allowed a fairly large amount of sugar solution to pass through them when tested in the osmotic apparatus, although their resistances appeared to be high enough.

In the course of the experiments it was found that better results were obtained if the membranes were electrolytically remade after every osmotic pressure determination, and also that, for observations at $0°$ C., to which this communication is restricted, it was best to remake the membrane at $0°$ C., and to keep the tubes in water surrounded by ice during the time elapsing between "remaking" and setting up for an experiment.

### Remaking the Membranes under Pressure.

All the tubes (except N) which, judging by their resistances, seemed promising, were also remade electrolytically under pressure. The object aimed at was to break down the weak places in the membrane while the current was passing, so that any small holes would be filled up at once by the interaction of the copper and ferrocyanide ions. It is probable that the pressure alone causes a considerable part of the improvement by forcing the membrane into the pores of the porcelain. It will have been noticed that in the previous table the resistance of N on December 10, 1905, suddenly rose from 65,000 ohms to 300,000 ohms; this may be due to either of the two changes in the conditions, i.e., to having previously been subjected to pressure, or to the change in the temperature at which the membrane was remade; we have found that both causes improve the membranes.

The apparatus for remaking the membranes under pressure is shown in Diagram 3. AB is a strong wrought-iron cylinder* which can be connected to the U tube mentioned on page 485 by means of the steel pressure tubing C. The apparatus is filled with a strong solution of cane sugar,† in which the usual quantity of potassium ferrocyanide has been dissolved; the equilibrium pressure of the solution should be about 130 atmospheres. The porcelain tube, M, filled with the copper sulphate solution,

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* It is capped by a lead washer, as indicated in the diagram.

† The object of the sugar solution was (1) to preserve such parts of the membrane as were already good by preventing a great flow of water through them, (2) to prevent, by its great viscosity, the alkali, which is found at the walls of the cylinder, from reaching the membrane.

is suspended in the sugar solution by means of the arrangement shown at D; this consists in a glass capillary EF, furnished with a thistle funnel at H, and down which a platinum wire is threaded. The lower end of the platinum is connected to a



Diagram 3.

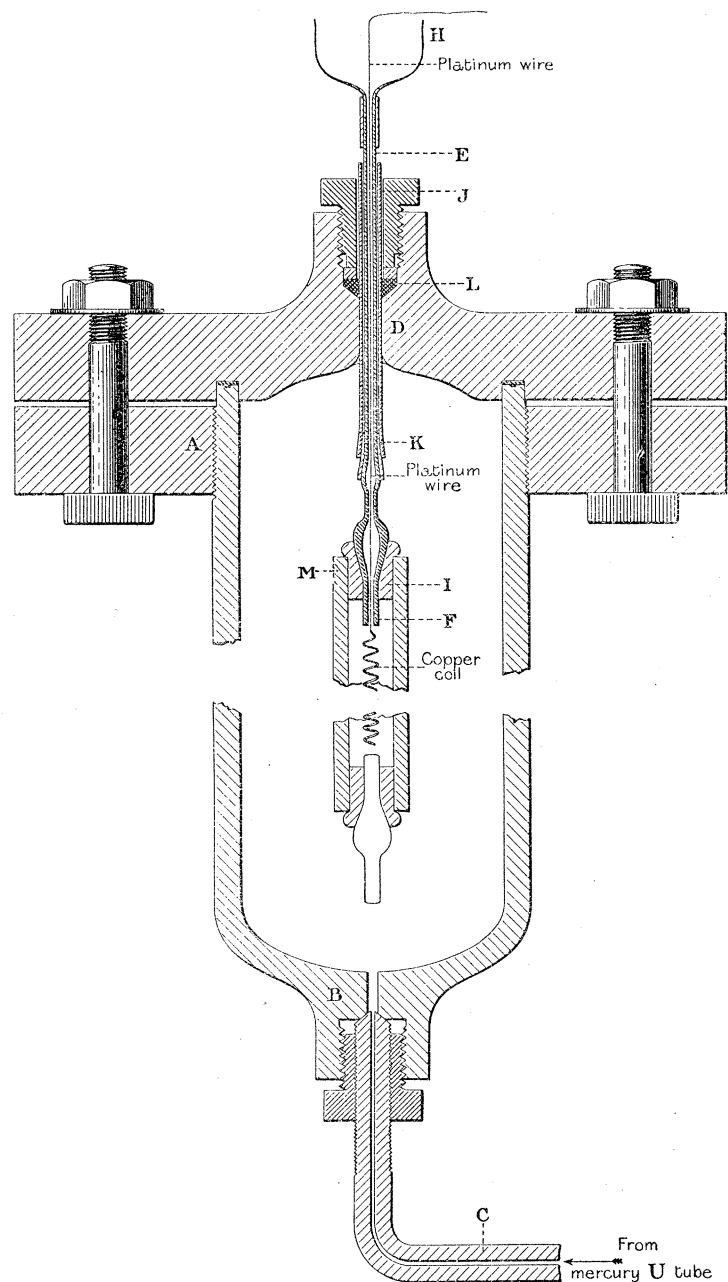copper coil. A tight joint between the glass capillary and the porcelain tube is made by blowing a conical bulb in the former and inserting the taper end into the rubber plug I. The bottom of the tube is closed in a similar manner.

A brass tube JK surrounds the capillary, and the joint between the two, at K, is made by slipping a piece of rubber tubing over a slight thickening in the capillary.

The brass tube serves to protect the glass from the pressure exerted by the dermatine ring L, when it is compressed by the nut and washer.

It will be observed that by this arrangement the outside surface of the porcelain can be subjected to pressure while the inside is only under atmospheric pressure, and if the wrought-iron vessel be connected to one terminal of the battery and the platinum wire to the other, a current can be passed through the porcelain and the solutions.

Pressures of about 130 atmospheres were used.

### The Operation of Determining the Equilibrium Pressure.

There are three separate operations required for the purpose of determining the equilibrium pressure.

(1) *Guard-ring Leak.*—As explained in our preliminary paper, the semi-permeable membrane is never quite on the surface of the tube, and, therefore, it is impossible to get perfect contact between the dermatine rings (see fig. 1) and the membrane. The result of this is that a small quantity of solution is forced out at this point. In the old apparatus there was always a noticeable part of the membrane not subjected to pressure, over which this solution flowed and, therefore, abstracted water from the interior. In the new apparatus, by arranging that the dermatine rings overlap the ends of the tube, we have reduced the exposed membrane to a minimum; there are, however, minute cracks in the glaze at the ends of the tubes, and the solution, flowing over these, draws water from the interior. To ensure that the rate at which the water is abstracted is constant during an experiment, the metal tubes VV (see fig. 1) were provided and were filled with enough solution to cover the ends of the porcelain.

The amount abstracted, that is, the guard-ring leak, was determined before every observation in the following manner. The tube was set up in the osmotic apparatus and the latter was filled with water, filling the porcelain tube as well; the pressure tube T (see fig. 1) was replaced by an open glass tube, which was filled with water to the same level as that of the water in the capillary gauge; the whole apparatus was then placed in ice, and some of the solution whose equilibrium pressure was afterwards to be determined was poured into VV.

When the temperature, indicated by a thermometer placed in mercury in a hole bored some distance into the osmotic apparatus, had fallen nearly to 0° C., and was constant at that point, repeated measurements of the rate at which the water in the gauge fell were made until constant rates were obtained; the latter were taken to be due to the guard-ring leak.

The guard-ring leak, which in our previous work had been equivalent to a rate such as would be produced by a pressure of two or three atmospheres on the solution, was now found to be very nearly negligible and corresponded to about 0·15 of an atmosphere; it was also nearly constant for any one tube, as will be seen on reference to the table of results,

(2) *Determination of the Turning Point.*—As already explained, a gradually increasing pressure is put upon the solution until the level of the water in the gauge ceases to fall and begins to rise. If there were no corrections to apply, the pressure at which this turning point takes place would give the equilibrium pressure; but on account of the guard-ring leak, and the solution leak (see later), the turning point is not, in general, the pressure required.

The method therefore adopted is to take rates of movement of the level in the gauge, corresponding to slightly differing pressures, both below and above the turning point; any small correction can then easily be applied.

The operation, then, is first to determine the guard-ring leak; after this the apparatus is withdrawn from the ice and the water outside the porcelain tube run out, and, after washing with a portion of the solution, it is filled with that solution—with very viscous solutions it is advisable to use a force pump. The washing and the filling should be carried out as rapidly as possible, for it must be remembered that until the equilibrium pressure can be put on the solution, the latter is in contact with the membrane and is diluting itself by abstracting water from the inside of the tube. When full, the apparatus is replaced in ice and connected to the beam pressure apparatus. Weights are then put on the pan, and at the same time the beam is kept horizontal by means of the wheel and screw and its plunger. The weights are put on the pan by increments of 2 and 3 kilos—this represents 8 or 12 atmospheres—at short intervals of time; a very rapid addition of weights might strain the membrane, while the sudden application of the equilibrium pressure would almost certainly damage it. When within about 10 per cent. of the equilibrium pressure, the weight increment is reduced and the length of time between the changes is increased; for it is found that the water, which had been sucked into the solution during the filling, will, on account of imperfect diffusion, now be squeezed out again, and it was feared that a rapid flow of water through the membrane might be detrimental. The weights are added in this manner until the turning point is about reached; then an interval of an hour is allowed to elapse to give time for the temperature throughout the apparatus to become steady at 0° C., and also for the more dilute stratum of solution near the membrane to diffuse.

In the later experiments we proceeded as follows:—The dead-weight gauge, previously adjusted to give a pressure close to that already on the solution, is turned on and the beam apparatus cut off. The weights are then rapidly adjusted until the rate of movement in the water gauge is as nearly as possible equal to the guard-ring leak. If the exact pressure cannot be applied by the weights we use (the increment of weight is equivalent to 0·34 atmosphere), a rate slightly above or slightly below the turning point is taken. The dead-weight gauge is then cut off and the beam apparatus turned on.

At intervals of an hour the same process is repeated until we are satisfied that no further change in the rate corresponding to a given pressure will take place. Two

rates, one above and one below the turning point, are then considered to be sufficient to enable that point to be calculated.

With viscous solutions, such as 660 grammes of cane sugar, it was necessary to lengthen the interval of time considerably; in fact, a constant rate was generally only attained after the apparatus had been set up for some 5 or 6 hours.

In the earlier experiments, before we realised that the method was susceptible of greater accuracy, we used somewhat larger increments of pressure. It was found that there were slight differences in the rate corresponding to a given pressure according as that pressure had been reached from above or below. A moment's consideration will show the cause of this.

It is evident that for any definite pressure, unless it be exactly the turning-point pressure, the solution near the membrane must be changing in concentration; the change is brought about by the water which is either squeezed out or sucked into the solution. This layer of abnormal concentration is prevented from merging rapidly into the remainder of the solution, because it is entangled in the pores of the porcelain tube lying outside the membrane, so that on taking off weights, when working above the turning point, the observed rate is that due to a slightly more concentrated solution than normal, while when working below it is due to a more dilute one.

The following table gives an example of the kind of effect produced. It is extracted from the laboratory notebook, and gives part of the experiment of August 23, with 420 grammes of cane sugar.

## TABLE II.

| | Temperature of osmotic apparatus. | Pressure on the solution in atmospheres. | Gauge readings. | Rate of movement in millimetres per 15 minutes.* |
|---|---|---|---|---|
| | ° C. | | | |
| 5.10 P.M. | 0·13 | 41·80 | — | — |
| 5.12 ,, | — | 41·80 | 276·6 | − 12·2 |
| 5.20 ,, | — | 42·77 | 270·1 | |
| 5.22 ,, | — | 42·77 | 271·4 | − 5·1 |
| 5.30 ,, | — | 43·74 | 268·7 | |
| 5.32 ,, | — | 43·74 | 270·8 | + 0·9 |
| 5.40 ,, | — | 44·71 | 271·3 | |
| 5.42 ,, | — | 44·71 | 274·4 | + 7·1 |
| 5.50 ,, | 0·15 | 45·68 | 278·2 | |
| 5.52 ,, | — | 45·68 | 282·2 | +13·9 |
| 6.0 ,, | — | 44·71 | 289·6 | |
| 6.2 ,, | — | 44·71 | 288·1 | + 6·4 |
| 6.10 ,, | — | 43·74 | 291·5 | |
| 6.12 , | — | 43·74 | 289·8 | + 0·2 |
| 6.20 ,, | — | 42·77 | 289·9 | |
| 6.22 ,, | — | 42·77 | 287·3 | − 5·6 |
| 6.30 ,, | — | 41·80 | 284·3 | |
| 6.32 ,, | — | 41·80 | 281·0 | −11·6 |
| 6.40 ,, | 0·18 | 42·77 | 274·9 | |
| 6.42 ,, | — | 42·77 | 276·2 | − 4·3 |
| 6.50 ,, | — | 42·77 | 273·9 | |

* The rate of movement is placed opposite the pressure causing it.

We give this example in detail, as we thought at first that the error introduced from this cause might be considerable; but even in this case it is evident that it is quite small, and in our later experiments, where care has been taken not to work far from the turning point and the increment of pressure is smaller, the error is quite negligible.

(3) *Solution Leak.*—The turning point having been satisfactorily determined, the osmotic apparatus is taken apart, and the porcelain tube, with the brass tubes LL (see fig. 1) untouched, and therefore still containing the water used in the experiment, is placed in distilled water. After an interval of two or three days, about 100 cub. centims. of water are run through the tube and the content of sugar analysed. If enough sugar is found, another 100 cub. centims. are run through at the end of two more days, and this process is repeated until there is practically no more sugar in the tube. It is then remade electrolytically at 0° C., and kept in water at that temperature.

We would like to point out that even with the best membranes there is always, or nearly always, an indication of a very small quantity of sugar as having come through the membrane,* and we would therefore emphasize the necessity of always testing the water inside the tube.

The analyses were made by means of FEHLING's solution; the equivalent value, in terms of sugar, of the resulting copper oxide, together with a standard method of working, being obtained by the analysis of dilute solutions of sugar of known content.

In our preliminary paper we stated that, on certain assumptions, a satisfactory correction for the solution leak could be applied to the apparent turning point so as to give concordant results; at that time the membranes were new, and a fairly large amount of sugar came through during the whole time an experiment lasted. We now find that with the very much improved membranes—membranes it must be remembered which undoubtedly have given way some scores of times, and been remade in probably a different layer of the porcelain—there is only a rough connection between the amount of solution leak and the lowering of the turning point. It is evident that, apart from the difficulties of analysis, with such small quantities of sugar no exact connection could be expected; the extremely minute holes in the membrane, indicated by the smallness of the leak, may easily close up or open out during the course of the experiment. All attempts, therefore, to correct for the "solution leak" were given up, and the value of an experiment was based on the amount of sugar found inside the tube; practically this resolved itself into rejecting, for the final computation of the equilibrium pressure, all the experiments done with tubes other than those we call X and N, and only accepting these when it had been proved that no more sugar than 0·0003 gramme had come through in the experiment.

The following table, copied from the laboratory notebook, gives examples of the

* *Cf.* Table VI., Column VII.

experiments—they cover the whole range of pressures.    The first of the two columns headed pressure gives the approximate pressure in atmospheres corresponding to the weights on the beam ; the second gives the accurate pressure delivered by the dead-weight standard gauge.    The next column gives the height of the level of the water in the glass capillary at the times shown.    The seventh column gives the rate of movement of the water level for 15 minutes, and the numbers are placed opposite to the pressures causing the movement.

The process pursued will be clear from the following example.    Referring to the experiment with dextrose, begun May 17, at 12.5 P.M., the height of the water was 236·3 millims. ; immediately this level had been noted, the pressure was altered to 28·92 atmospheres, and a short interval of time allowed for a steady state to be reached ; at 12.10 the level was at 234·9 millims.    Ten minutes after, at 12.20, the level had fallen to 233·2.    The difference between the last two readings gives the rate corresponding to 28·92 atmospheres pressure.

TABLE III.—Experiment with 200 grammes of Dextrose in the litre with Tube X.
(R = 111,000 ohms.)

| I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. |
|---|---|---|---|---|---|---|---|---|
| | | | Pressure. | | Reading of water level in gauge. | Rate of movement of water in millims. per 15 minutes. | Rate corrected for G.R.L. | |
| Date. | Time. | Temperature of osmotic apparatus. | Pressure given by beam in atmospheres. | Dead-weight pressure in atmospheres. | | | | Remarks. |
| | | ° C. | | | | | | |
| March 17 . | 5.0 P.M. | — | — | — | — | — | — | Set up for G.R.L. in ice. |
| „ 18 . | 5.15 „ | 0·05 | — | — | 258·2 | — | — | |
| | 6.20 „ | — | — | — | 255·5 | 0·6 | — | |
| | 7.5 „ | — | — | — | 253·7 | 0·6 | — | |
| | 9.35 A.M. | — | — | — | — | — | — | Set up for O.P. in ice. |
| | 9.38 „ | — | 29·4 | — | — | — | — | |
| | 10.47 „ | 0·04 | — | 28·92 | — | — | — | Cut off beam apparatus. |
| | 10.50 „ | — | — | 28·92 | 230·9 | − 3·0 | — | |
| | 10.55 „ | — | — | 29·26 | 229·9 | — | — | |
| „ 19 | 11.0 „ | — | — | 29·26 | 230·7 | +0·3 | — | |
| | 11.5 „ | — | 29·4 | — | 230·8 | — | — | Cut off dead weight. |
| | 11.50 „ | 0·04 | — | 29·26 | — | — | — | Cut off beam apparatus. |
| | 11.55 „ | — | — | 29·26 | 235·9 | +0·6 | +1·2 | |
| | 12.5 P.M. | — | — | 28·92 | 236·3 | — | — | |
| | 12.10 „ | — | — | 28·92 | 234·9 | − 2·5 | − 1·9 | |
| | 12.20 „ | — | — | 28·92 | 233·2 | — | — | Took down and set up for "solution leak." |
| „ 21 . | 9.0 A.M., 100 cub. centims. run through the tube gave 0·0007 gramme of sugar. | | | | | | | |

The rate for a pressure of 29·26 atmospheres is +0·6 millim. in 15 minutes.
,,        ,,        ,,        28·92        ,,                −2·5 millims.        ,,

Therefore a difference of pressure of 0·34 atmosphere causes a difference in the rate of 3·1 millims., hence the correction to be subtracted from 29·26 atmospheres to obtain the pressure at which no movement of the water would have taken place, that is, the apparent turning point, is 0·6 × 0·34/3·1 = 0·06 atmosphere. The apparent turning point is, therefore, 29·20 atmospheres. As the "guard-ring leak" is also 0·6 millim. in 15 minutes, the correction to be subtracted from the apparent turning point will also be 0·06 atmosphere, and the corrected turning point is 29·14 atmospheres.

TABLE IV.—Experiment with 540 grammes of Cane Sugar in the litre with Tube X. (R = 143,000 ohms.)

| I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. |
|---|---|---|---|---|---|---|---|---|
| | | | Pressure. | | | Rate of movement of water in millims. per 15 minutes. | | |
| Date. | Time. | Temperature of osmotic apparatus. | Pressure given by beam in atmospheres. | Dead-weight pressure in atmospheres. | Reading of water level in gauge. | | Rate corrected for G.R.L. | Remarks. |
| | | °C. | | | | | | |
| Oct. 22 | 10.0 A.M. | — | — | — | — | — | — | Set up for G.R.L. in ice. |
| | 5.0 P.M. | — | — | — | 310·5 | — | — | |
| | 5.10 ,, | — | — | — | 309·8 | 1·0 | — | |
| ,, 23 | 8.20 A.M. | — | — | — | 256·8 | — | — | |
| | 8.30 ,, | — | — | — | 256·3 | 0·8 | — | |
| | 9.28 ,, | — | — | — | — | — | — | Set up for O.P. in ice. |
| | 10.55 ,, | 0·15 | 67·1 | — | — | — | — | |
| | 12.5 P.M. | 0·06 | — | 67·37 | — | — | — | Cut off beam apparatus. |
| | 12.7 ,, | — | — | 67·37 | 358·7 | −1·7 | — | |
| | 12.15 ,, | — | — | 68·05 | 357·8 | — | — | |
| | 12.17 ,, | — | — | 68·05 | 359·4 | +3·4 | — | |
| | 12.25 ,, | — | — | 67·37 | 361·2 | — | — | |
| | 12.27 ,, | — | — | 67·37 | 359·8 | −2·1 | — | |
| | 12.35 ,, | 0·06 | 67·5 | — | 358·7 | — | — | Cut off dead weight. |
| | 3.5 ,, | 0·04 | — | 67·37 | — | — | — | Cut off beam apparatus. |
| | 3.10 ,, | — | — | 67·37 | 364·9 | −2·0 | −1·2 | |
| | 3.20 ,, | — | — | 68·05 | 363·6 | — | — | |
| | 3.22 ,, | — | — | 68·05 | 365·0 | +3·4 | +4·2 | |
| | 3.30 ,, | — | — | 67·37 | 366·8 | — | — | |
| | 3.32 ,, | — | — | 67·37 | 365·1 | −2·1 | −1·3 | |
| | 3.40 ,, | — | — | 68·05 | 364·0 | — | — | |
| | 3.42 ,, | — | — | 68·05 | 365·6 | +3·2 | +4·0 | |
| | 3.50 ,, | — | — | 67·37 | 367·3 | — | — | |
| | 3.52 ,, | — | — | 67·37 | 365·8 | −2·1 | −1·3 | |
| | 4.0 ,, | — | — | 67·37 | 364·7 | — | — | Took down and set up for "solution leak." |
| ,, 26 .. | 7.30 A.M., 100 cub. centims. run through the tube gave no trace of sugar. | | | | | | | |

In a manner similar to that detailed in the previous experiment, the apparent turning point is 68·08 − 3·2 × 0·68/5·3 = 67·67 atmospheres, and the corrected turning point is 67·67 − 0·8 × 0·68/5·3 = 67·56 atmospheres.

TABLE V.—Experiment with 750 grammes of Cane Sugar in the litre with Tube X.
(R = 111,000 ohms.)

| I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. |
|---|---|---|---|---|---|---|---|---|
| | | | Pressure. | | | Rate of move-ment of water in millims. per 15 minutes. | | |
| Date. | Time. | Tem-perature of osmotic appa-ratus. | Pressure given by beam in atmo-spheres. | Dead-weight pressure in atmo-spheres. | Reading of water level in gauge. | | Rate cor-rected for G.R.L. | Remarks. |
| | | ° C. | | | | | | |
| March 27 . | 5.0   P.M. | — | — | — | — | — | — | Set up for G.R.L. in ice. |
| | 9.6   A.M. | — | — | — | 242·9 | — | — | |
| | 9.26   ,, | 0·05 | — | — | 242·2 | − 0·5 | — | Set up for O.P. in ice. |
| | 9.55   ,, | — | — | — | — | — | — | |
| | 10.5   ,, | — | 132·0 | — | — | — | — | |
| | 10.50   ,, | — | 134·0 | — | — | — | — | |
| | 11.45   ,, | 0·04 | — | 132·69 | — | — | — | Cut off beam apparatus. |
| | 11.50   ,, | — | — | 132·69 | 258·0 | − 1·5 | − 1·0 | Cut off dead weight. |
| | 11.55   ,, | — | 134·0 | — | 257·5 | — | — | Cut off beam apparatus. |
| | 12.35 P.M. | — | — | 133·37 | — | — | — | |
| ,,    28 | 12.40   ,, | — | — | 133·37 | 274·4 | + 1·5 | + 2·2 | Cut off dead weight. |
| | 12.45   ,, | — | 134·0 | — | 274·7 | — | — | Cut off beam apparatus. |
| | 2.40   ,, | — | — | 133·37 | — | — | — | |
| | 2.45   ,, | — | — | 133·37 | 308·7 | + 0·1 | + 0·6 | |
| | 2.55   ,, | — | 134·0 | — | 308·8 | — | — | Cut off dead weight. |
| | 5.0   ,, | — | — | 133·37 | — | — | — | Cut off beam apparatus. |
| | 5.5   ,, | — | — | 133·37 | 342·2 | − 0·1 | + 0·5 | |
| | 5.15   ,, | — | — | 133·03 | 342·1 | — | — | |
| | 5.20   ,, | — | — | 133·03 | 341·0 | − 1·3 | − 0·8 | |
| | 5.30   ,, | — | — | — | 340·1 | — | — | Took down and set up for " solution leak." |
| ,,    30 . | 9.0   A.M., 100 cub. centims. run through the tube gave 0·0009 gramme of sugar. | | | | | | | |
| April 1 . . | 9.0   ,,   100   ,,   ,,   ,,   ,,   0·0013   ,,   ,, | | | | | | | |

NOTE.—The " solution leak " was not pursued any further on account of our absence from the laboratory.

The apparent turning-point pressure is 133·42 atmospheres.

The corrected turning point is 133·23 atmospheres.

This experiment was selected so as to give an idea of the influence that a small solution leak has on the experiments. It will be noticed on examining the tabular statement of results that the experiment gives a value of the turning-point pressure slightly below another experiment where there was practically no leak.

### Substances Used.

For the cane-sugar solutions, " double refined " loaf sugar was used; it was tested for invert sugar and only a trace found; tests were also made of the solution at the end of an experiment, and the quantity of invert sugar showed a scarcely appreciable increase.

The solutions, both for cane sugar and for the other substances, were always made up the night before an experiment.

The dextrose was purchased from Messrs. KAHLBAUM, and was described by them as their purest anhydrous; no tests as to purity were made except to determine the amount of moisture* in the various quantities sent. The amount was found to be very small and practically constant. The galactose was also KAHLBAUM'S purest anhydrous; the amount of moisture was found to be constant. Some of the galactose was recovered by crystallizing from a saturated solution and digesting with methyl alcohol for 10 days. Solutions of 500 grammes of this recovered galactose in the litre gave equilibrium pressures (see table of results) which were about 2 per cent. higher than those obtained with similar solutions of the original substance. As the purification of galactose is a very lengthy process, and our main object in making experiments with this substance was to see if it be suitable for osmotic pressure measurements, no further steps have yet been taken in the matter. The mannite came from KAHLBAUM, and was only tested for moisture.

A considerable number of organic substances which are not likely to be dissociated in aqueous solutions were tried, but without success, as they all passed through the membranes to a greater or less degree.

### *Results.*

In the following tables we give all the experiments that we have made at 0° C., with the exception of those which were carried out merely for the purpose of testing the membranes. The concentration of the solution is placed at the head of each table; the numbers are the weights of the substance in one litre of solution made up at 15° C. :—

Column (I.) gives the date of the experiments; these are tabulated in chronological order.

Column (II.) gives the name of the tube used.

Column (III.) gives the apparent turning-point pressure, in atmospheres, as derived from the dead-weight standard pressure gauge. It is the pressure for which there would have been no movement of the water in the capillary gauge.

A blank in the column means that the true turning-point pressure was exactly that on the solution, and therefore it was not necessary to take rates above and below it; in other words, this pressure gave a rate which exactly equalled the "guard-ring leak" rate.

Column (IV.). In this and the other columns where rates are given it is to be noted that they all represent the movement of the level of the water in the capillary

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* The "moisture" was determined by the loss of weight of the substance on heating at 100° C.; but we have evidence that there were traces of methyl alcohol present.

in millimetres per 15 minutes.   The rates in this column are those caused by the "guard-ring leak."

Column (V.) gives the apparent turning-point pressure corrected for the "guard-ring leak" (see explanation of column X.).   As already pointed out, the pressures registered by the dead weights are not the total pressures on the solution ; the pressure of the atmosphere must be added to them.   On the other hand, the water inside the tube is under atmospheric pressure, so that if there had been no "solution leak" the pressures noted in this column would be equilibrium pressures.

Column (VI.) gives the length of time the solution was under pressure.

Column (VII.) gives the total amount, in grammes, of solid which came through the membrane during the experiment.   The letters j.v.t. mean "just visible trace."

Column (VIII.).   Assuming that the amount of solid given in (VI.) represents a corresponding volume of solution, then the numbers in this column give the rate at which the water would rise in the gauge, on the further assumption that the solution came through the membrane at a uniform rate.

Column (IX.) gives the increment of pressure, in atmospheres, which was used in the experiment.   Column (X.) gives the difference between the rates corresponding to the two pressures separated by this increment, the one just above and the other just below the turning point.   The numbers are therefore the rates due to these increments of pressure near the turning point.   It is from these rates that the correction for the "guard-ring leak" is derived by assuming that it bears the same ratio to the increment of pressure as the numbers in (IV.) do to those in (X.).

### Table VI.

| I. Date. | II. Name of tube. | III. Apparent turning-point pressure in atmospheres. | IV. Rate of movement of water-level due to guard-ring leak. | V. Turning-point pressure in atmospheres. | VI. Time. h. m. | VII. Solution leak. | VIII. Rate of movement of water-level due to solution leak. | IX. The increment of pressure used in the experiment. atmospheres | X. Rate of movement of water-level caused by increment of pressure. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 180 Grammes Cane Sugar. | | | | | |
| Nov. 15 | X | 14·03 | 0·5 | *13·96 | 3  35 | trace | — | 0·34 | 2·5 |
| „ 24 | X | — | 0·8 | *13·95 | 4  40 | j.v.t. | — | 0·34 | — |
| | | | | 300 Grammes Cane Sugar. | | | | | |
| Oct. 4 | B | 26·35 | 0·9 | 26·28 | 5  45 | 0·0023 | 1·1† | 0·68 | 8·3 |
| „ 6 | G | 26·16 | 0·8 | 26·07 | 6  15 | 0·0016 | 0·7† | 0·68 | 5·9 |
| „ 9 | X | 26·78 | 0·8 | *26·69 | 7  40 | j.v.t. | — | 0·68 | 6·0 |
| „ 17 | X | 26·85 | 0·8 | *26·76 | 5  35 | none | — | 0·68 | 5·8 |
| Nov. 14 | G | 26·37 | 0·4 | 26·32 | 5  0 | 0·0014 | 0·7† | 0·34 | 2·8 |
| | | | | 420 Grammes Cane Sugar. | | | | | |
| Aug. 10 | X | 42·8 | 0·0 | 42·8 | 8  45 | 0·0035 | 0·8 | 0·97 | 5·8 |
| „ 13 | B | 40·7 | 0·0 | 40·7 | 7  30 | 0·0090 | 4·7 | 0·97 | 6·9 |
| „ 18 | G | 39·8 | 0·2 | 39·8 | 3  0 | 0·0247 | 15·7 | 0·97 | 6·2 |
| „ 23 | X | 43·7 | 0·7 | 43·6 | 3  20 | trace | — | 0·97 | 7·1 |
| „ 25 | B | 41·8 | 0·6 | 41·7 | 5  10 | 0·0162 | 5·9 | 0·97 | 7·7 |
| „ 29 | X | 44·09 | 0·6 | *44·00 | 6  40 | trace | — | 1·36 | 9·0 |
| Sept. 3 | G | 40·3 | 0·2 | 40·2 | 5  10 | 0·0181 | 6·6 | 0·97 | 6·0 |
| „ 7 | X | 43·49 | 0·5 | 43·40 | 5  30 | 0·0006 | — | 1·36 | 7·5 |
| „ 12 | B | 43·52 | 0·9 | 43·42 | 5  30 | 0·0035 | 1·2† | 1·36 | 12·0 |
| „ 20 | G | 42·50 | 0·2 | 42·46 | 6  0 | 0·0083 | 2·6† | 1·36 | 7·6 |
| „ 29 | X | 44·14 | 0·7 | *43·95 | 8  0 | none | — | 1·36 | 10·6 |
| Nov. 23 | G | 43·39 | 0·6 | 43·32 | 5  25 | 0·0043 | 1·5† | 0·34 | 2·9 |
| | | | | 540 Grammes Cane Sugar. | | | | | |
| Oct. 19 | G | 67·26 | 0·3 | 67·22 | 5  55 | 0·0015 | 0·4† | 0·68 | 4·8 |
| „ 23 | X | 67·67 | 0·8 | *67·56 | 6  30 | none | — | 0·68 | 5·3 |
| „ 27 | V | 66·34 | 0·0 | 66·34 | 7  30 | undetermined | — | 0·34 | 1·8 |
| „ 28 | X | 67·54 | 0·8 | *67·43 | 3  0 | j.v.t. | — | 0·34 | 2·4 |
| | | | | 660 Grammes Cane Sugar. | | | | | |
| Nov. 2 | X | 100·72 | 0·7 | *100·61 | 7  45 | j.v.t. | — | 0·34 | 2·3 |
| „ 3 | G | 100·21 | 0·2 | 100·19 | 8  0 | 0·0036 | 0·5† | 0·34 | 2·4 |
| „ 7 | B | 100·32 | 0·2 | 100·30 | 6  0 | 0·0171 | — | 0·34 | 3·0 |
| „ 9 | X | 100·91 | 0·9 | *100·86 | 5  55 | none | — | 0·34 | 3·4 |
| Jan. 30 | V | 99·48 | 0·4 | 99·42 | 7  40 | 0·0077 | 1·2† | 0·34 | 2·4 |
| Feb. 14 | B | 100·32 | 0·9 | 100·22 | 6  45 | 0·0047 | 0·8† | 0·34 | 3·2 |
| | | | | 750 Grammes Cane Sugar. | | | | | |
| Nov. 17 | V | 133·45 | 0·1 | 133·44 | 7  10 | 0·0044 | 0·6† | 0·34 | 2·0 |
| March 22 | N | 133·88 | 0·5 | *133·74 | 7  45 | 0·0002 | — | 0·34 | 1·2 |
| „ 28 | X | 133·42 | 0·5 | 133·28 | 7  35 | 0·0022 | 0·3† | 0·34 | 1·2 |

NOTE.—The experiments marked * are dealt with on p. 503, and those marked † in Appendix A.

*Remarks.*—The experiment of August 23 is rejected for the final result. It was carried out solely with the beam apparatus, and, as already stated, the degree of accuracy obtainable with that apparatus is not sufficiently good for the purpose.

The total quantity of sugar found in the experiment of November 7 is quite anomalous. We can offer no satisfactory explanation of this.

TABLE VII.

| I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. | X. |
|---|---|---|---|---|---|---|---|---|---|
| Date. | Name of tube. | Apparent turning-point pressure in atmospheres. | Rate of movement of water-level due to guard-ring leak. | Turning-point pressure in atmospheres. | Time. | Solution leak. | Rate of movement of water-level due to solution leak. | The increment of pressure used in the experiment. | Rate of movement of water-level caused by increment of pressure. |
| | | | | | h. m. | | | atmospheres | |
| 100 GRAMMES DEXTROSE. | | | | | | | | | |
| May 16 | X | 13·24 | 0·5 | *13·21 | 3  0 | none | — | 0·34 | 3·9 |
| 200 GRAMMES DEXTROSE. | | | | | | | | | |
| March 10 | X | 29·25 | 0·7 | *29·18 | 2 15 | 0·0002 | — | 0·34 | 3·2 |
| ,,  19 | X | 29·20 | 0·6 | 29·14 | 2 45 | 0·0007 | 1·0 | 0·34 | 3·1 |
| 320 GRAMMES DEXTROSE. | | | | | | | | | |
| Feb.  26 | N | 50·94 | 0·8 | 50·81 | 3  5 | 0·0034 | 2·8 | 0·34 | 1·8 |
| March  6 | X | 53·51 | 1·5 | *53·33 | 2 40 | 0·0001 | — | 0·34 | 2·8 |
| ,,  16 | N | — | 0·5 | 52·40 | 2 20 | 0·0011 | 1·2 | 0·34 | — |
| ,,  24 | X | 53·09 | 0·5 | *53·04 | 2 45 | 0·0002 | — | 0·34 | 3·2 |
| 450 GRAMMES DEXTROSE. | | | | | | | | | |
| Jan.  19 | G | — | 0·4 | 86·36 | 2 45 | 0·0054 | 3·5 | 0·34 | — |
| Feb.  8 | X | 87·48 | 0·9 | *87·34 | 3 25 | 0·0001 | — | 0·34 | 2·2 |
| ,,  12 | X | 87·84 | 1·1 | *87·70 | 3 10 | none | — | 0·34 | 2·4 |
| 550 GRAMMES DEXTROSE. | | | | | | | | | |
| Feb.  28 | X | 121·09 | 2·8 | 120·66 | 3 10 | 0·0021 | 0·9 | 0·34 | 2·2 |
| Mar.  8 | N | 121·08 | 0·2 | *121·02 | 2 50 | 0·0002 | — | 0·34 | 1·2 |
| May  5 | X | 121·46 | 0·9 | *121·35 | 2 10 | j.v.t. | — | 0·34 | 2·6 |
| ,,  12 | X | 121·26 | 0·7 | *121·17 | 2 10 | 0·0002 | — | 0·34 | 2·5 |

*Remarks.*—Part of the solution of May 5 was kept for a week and its equilibrium pressure redetermined on May 12. The small difference between the two results shows that no change had taken place in the interval.

## TABLE VIII.

| I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. | X. |
|---|---|---|---|---|---|---|---|---|---|
| Date. | Name of tube. | Apparent turning-point pressure in atmospheres. | Rate of movement of water-level due to guard-ring leak. | Turning-point pressure in atmospheres. | Time. | Solution leak. | Rate of movement of water-level due to solution leak. | The increment of pressure used in the experiment. | Rate of movement of water-level caused by increment of pressure. |
| | | | | | h. m. | | | atmospheres | |
| **100 GRAMMES MANNITE.** | | | | | | | | | |
| Jan. 18 | X | 13·3 | 0·3 | *13·3 | 2 10 | 0·0014 | 5·0 | 0·34 | 1·9 |
| ,, 26 | X | — | 0·5 | *12·9 | 2 10 | 0·0008 | 2·8 | 0·34 | — |
| **110 GRAMMES MANNITE.** | | | | | | | | | |
| Jan. 9 | X | 14·7 | 0·5 | *14·6 | 2 0 | 0·0017 | 6·2 | 0·34 | 4·1 |
| **125 GRAMMES MANNITE.** | | | | | | | | | |
| Dec. 5 | X | 16·71 | 0·5 | *16·64 | 3 45 | 0·0009 | 1·5 | 0·34 | 2·4 |
| ,, 7 | G | — | 0·5 | 15·9 | 2 30 | 0·0066 | — | 0·34 | — |
| ,, 14 | X | 16·82 | 0·8 | *16·71 | 2 0 | 0·0014 | 4·4 | 0·34 | 2·6 |

*Remarks.*—The experiments with mannite are not satisfactory; there seems to be no doubt that the membranes are slightly more permeable to this substance than to the sugars. The numbers under the heading "solution leak" are not reliable; they were obtained by evaporating down the contents of the tube and weighing the residue. Small quantities of copper sulphate left in the tube from the previous electrolytic "remaking" would help to produce higher and erratic results. No higher osmotic pressures are obtainable with mannite, as 125 grammes in the litre is about the limit of solubility.

TABLE IX.

| I. | II. | III. | IV. | V. | VI. | VII. | IX. | X. |
|---|---|---|---|---|---|---|---|---|
| Date. | Name of tube. | Apparent turning-point pressure in atmospheres. | Rate of movement of water-level due to guard-ring leak. | Turning-point pressure in atmospheres. | Time. | Solution leak. | The increment of pressure used in the experiment. | Rate of movement of water-level caused by increment of pressure. |
| | | | | | h. m. | | atmospheres. | |
| 250 GRAMMES GALACTOSE. | | | | | | | | |
| Feb.      2 | X | 35·58 | 0·7 | *35·47 | 3  35 | 0·0002 | 0·34 | 2·8 |
| 380 GRAMMES GALACTOSE. | | | | | | | | |
| March 14 | X | 62·86 | 0·6 | *62·79 | 2  35 | none | 0·34 | 2·9 |
| 500 GRAMMES GALACTOSE. | | | | | | | | |
| March 12 | N | — | 0·3 | 94.59 | 3  10 | 0·0006 | 0·34 | — |
| „       26 | N | — | 0·3 | 96·63 | 2  12 | 0·0004 | 0·34 | — |
| May     3 | N | — | 0·4 | *97·31 | 4  15 | j.v.t. | 0·34 | — |
| „       11 | N | 94·92 | 0·7 | *94·75 | 2  30 | 0·0003 | 0·34 | 1·5 |

*Remarks.*—The experiments of March 26 and May 3 were with the recovered galactose mentioned on page 497.

No higher osmotic pressures were determined, as it was found that a solution of 500 grammes in the litre was already supersaturated at 0° C.

### The Experimental Errors.*

Unfortunately we are not in a position to evaluate the experimental errors. The approximate constancy of the guard-ring leak, with different tubes, seems to justify the assumption that no great variable error enters through this cause, but it should be pointed out that we have no means of proving that there is not a constant error introduced thereby. The errors due to " solution leak " are mentioned in the next section, and are obviated by discarding those experiments which showed a leak ; in this connection it should be remembered that analyses of very small quantities of sugar are far from reliable, and it may be that even the results given by those experiments which showed no trace of sugar are really too low.

It was feared that the use of a somewhat more viscous oil than the dead-weight apparatus is designed for (the makers recommend glycerine) might in cold weather vitiate the results; special experiments, however, showed this cause of error to be absent. It is scarcely necessary to point out that a sensibility of 0·12 atmosphere in the dead-weight gauge, taken in conjunction with a " guard-ring leak " rate

* See Appendix B.

equivalent to about 0·15 atmosphere, showed that equilibrium pressures of less than 12 atmospheres could not be measured with any degree of accuracy with this apparatus.

### Discussion of the Results.

On looking over the tables it will be noticed that the experiments which give the highest values for the turning point are always those in which there was no "solution leak"; and the difference between these and the other results follows roughly the ratio* that the "solution leak" rate bears to the rate per increment of pressure. (In other words, the larger the "solution leak" the lower the equilibrium pressure.) No satisfactory method of correcting for these deviations was found;† so it was decided to use, for the final computation, only those experiments (marked by an asterisk) in which there was little or no "solution leak."

It has been stated already that the turning-point pressures in these experiments are the equilibrium pressures, and therefore the arithmetical mean would give the best value; but we have felt justified in giving double weight to experiments which showed no "solution leak" whatever.

The following tabular statement gives the final values for the equilibrium pressures at 0° C. of the various solutions when there is a pressure of one atmosphere on the solvent.

### TABLE X.

#### CANE SUGAR.

180·1 grammes in the litre gives a pressure of  13·95 atmospheres.
300·2       „                „                „          26·77        „
420·3       „                „                „          43·97        „
540·4       „                „                „          67·51        „
660·5       „                „                „         100·78        „
750·6       „                „                „         133·74        „

#### DEXTROSE.

 99·8 grammes in the litre gives a pressure of  13·21 atmospheres.
199·5       „                „                „          29·17        „
319·2       „                „                „          53·19        „
448·6       „                „                „          87·87        „
548·6       „                „                „         121·18        „

#### GALACTOSE.

250    grammes in the litre gives a pressure of  35·5   atmospheres.
380       „                „                „          62·8        „
500       „                „                „          95·8        „

#### RECOVERED GALACTOSE.

500    grammes in the litre gives a pressure of  97·3   atmospheres.

#### MANNITE.

100    grammes in the litre gives a pressure of  13·1   atmospheres.
110       „                „                „          14·6        „
125       „                „                „          16.7        „

* The ratio is not tabulated, as it was not considered of sufficient importance.

† See Appendix A.

The number of grammes in the litre are, for the cane-sugar and dextrose solutions, reduced to a vacuum, the dextrose being further corrected for the small quantity of "moisture" found in the "anhydrous" substance. Neither of these corrections are applied to the galactose and mannite; in the former case because the substance is presumably slightly impure, and in the latter because the experiments are not very accurate.

In the following set of curves the final values are plotted against concentrations, and it is interesting to observe that all four substances show considerable deviations from the straight lines which represent the theoretical osmotic pressures.*   It is also



Galactose.

Cane sugar.

Dextrose.

Mannite.
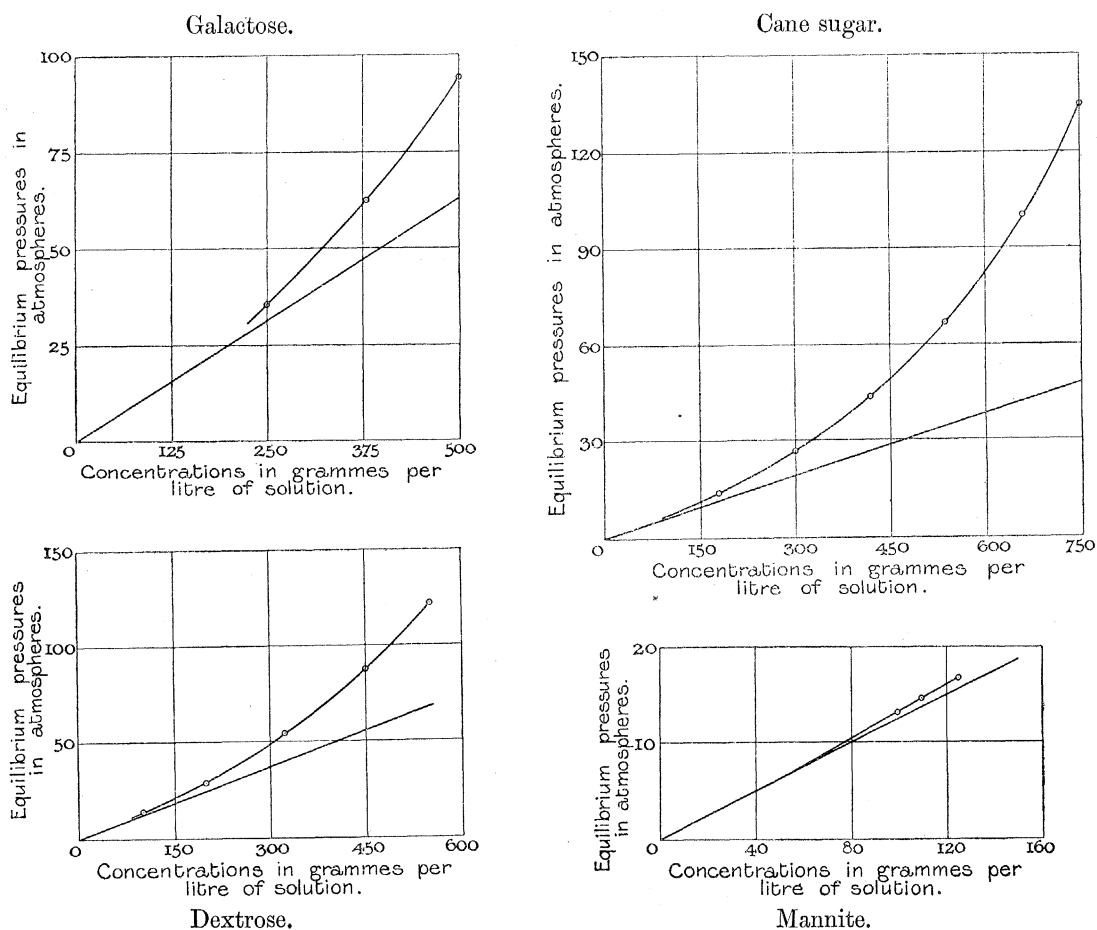
to be noticed that on extrapolating the various curves towards the origin they appear to merge in the straight lines before the origin is reached; this means that dilute solutions will give pressures corresponding to the BOYLE-AVOGADRO law, the gradients at the origin being inversely as the molecular weights of the dissolved substances.†

* The straight lines are drawn on the usual assumption that 1 gramme molecular weight of solute per litre should give an osmotic pressure of 22·4 atmospheres.

† Further consideration of the theoretical bearing of the forms of these curves is deferred.

We think that, for the purpose of comparison, it may be of use to append a table of the results (some of which have already been published) of the determination of the osmotic pressures of cane-sugar solutions by way of their vapour pressures.    For the discussion of the theoretical connection and the details of the method and apparatus, we would refer to the original paper,* but would mention that a slight modification in the apparatus has enabled us to obtain more concordant values.   We hope to give full details on another occasion.

TABLE XI.

| Concentration in grammes per litre solution. | Temperature. | Osmotic pressure in atmospheres derived from vapour pressure. | Measured equilibrium pressure at 0° C. in atmospheres. |
|---|---|---|---|
| | ° C. | | |
| 420 | 12·6 | 44·3 | 43·97 |
| 420 | 14·2 | 45·9 | — |
| 420 | 15·7 | 46·6 | — |
| 420 | 19·5 | 47·3 | — |
| 660 | 19·0 | 105·7 | — |
| 660 | 19·4 | 103·2 | — |
| 660 | 19·5 | 107·0 | — |
| LATER EXPERIMENTS. | | | |
| 540 | 0° C. | 69·4 | 67·51 |
| 660 | 0 | 101·9 | 100·78 |
| 750 | 0 | 136·0 | 133·74 |

We would draw attention to the fact that our results for cane sugar, where they overlap those obtained by Messrs. MORSE and FRASER,† are somewhat higher.   For instance, a solution containing 282 grammes in the litre is given by them as having an equilibrium pressure of 22·49 atmospheres, while we obtain 25 atmospheres, this value being taken from the curve.

There seems to be no mention in Messrs. MORSE and FRASER's account of their work of any steps taken to determine the amount of solution which came through the membranes.   A small "solution leak" would make a considerable difference to the pressure they obtained, not so much on account of "back" osmotic pressure, but because the passage of a small volume of solution would have a large effect on the level of the mercury in the manometer, the more so as the diameter of the latter is only 0·5 millim. and it is a closed one.   The general excellence of their work, however, makes it improbable that this hypothetical explanation is correct; it may be that future experiments will clear up the discrepancy.

* 'Roy. Soc. Proc.,' A, vol. 77, 1906, and also 'Nature,' vol. 74, p. 6.
† 'American Chemical Journal,' vol. 34, pp. 1–99.

## APPENDIX A.

[*August* 15.—An empirical method of making the correction for "solution leak" (see p. 498, explanation of Column VIII.; also p. 503) can be applied by assuming that during the passage of the solution through the minute holes in the membrane the solute has been partially filtered off from the solvent, and that this action is proportional to the concentration; if so, the rates tabulated in Column VIII. of Tables VI. and VII. must be multiplied by a factor which is proportional to the concentration.*

In the case of cane sugar, it is easy to see that this factor, for a solution of 300 grammes in the litre, is 3, and therefore for the other concentrations it will be 4·2, 5·4, 6·6, and 7·5 respectively. Then, proceeding in a manner similar to that explained at the top of p. 495, but adding the resulting pressure correction, we get, for the observations (marked †) done with the dead-weight pressure gauge, the following table, of which the results are to be compared with the numbers in Table X., where no "solution leak" is present :—

| Date of experiment. | Turning-point pressure in atmospheres. | Solution-leak correction in atmospheres. | Final corrected turning-point in atmospheres. | Date of experiment. | Turning-point pressure in atmospheres. | Solution-leak correction in atmospheres. | Final corrected turning-point in atmospheres. |
|---|---|---|---|---|---|---|---|
| 300 GRAMMES CANE SUGAR. (Equilibrium pressure from Table X. = 26·77 atmospheres.) | | | | 660 GRAMMES CANE SUGAR. (Equilibrium pressure = 100·78 atmospheres, see Table X.) | | | |
| Oct. 4 . . . | 26·28 | 0·27 | 26·55 | Nov. 3 . . | 100·19 | 0·45 | 100·64 |
| „ 6 . . . | 26·07 | 0·24 | 26·31 | Jan. 30 . . | 99·42 | 1·12 | 100·54 |
| Nov. 14 . . | 26·32 | 0·51 | 26·83 | Feb. 14 . . | 100·22 | 0·56 | 100·78 |
| 420 GRAMMES CANE SUGAR. (Equilibrium pressure = 43·97 atmospheres, see Table X.) | | | | 750 GRAMMES CANE SUGAR. (Equilibrium pressure = 133·74 atmospheres, see Table X.) | | | |
| Sept 12 . . | 43·42 | 0·57 | 43·99 | Nov. 17 . . | 133·44 | 0·76 | 134·20 |
| „ 20 . . | 42·46 | 1·95 | 44·41 | March 28 . . | 133·28 | 0·63 | 133·91 |
| Nov. 23 . . | 43·32 | 0·74 | 44·06 | | | | |
| 540 GRAMMES CANE SUGAR. (Equilibrium pressure = 67·51 atmospheres, see Table X.) | | | | | | | |
| Oct. 19 . . | 67·22 | 0·31 | 67·53 | | | | |

We propose to investigate this matter more closely. It may throw some light on the molecular structure of solutions.]

* Almost as good an agreement is obtained if we assume that this factor is proportional to the pressure on the solution. Unfortunately the experiments with dextrose (Table VII.) are not numerous enough to differentiate between the two.

## APPENDIX B.

[*August* 15.—An experiment with 750 grammes of cane sugar in the litre was made with tube N filled with a solution of 540 grammes in the litre. This experiment was carried out in a manner similar to that described in the text. The equilibrium pressure between the two solutions we found to be 66·0 atmospheres, and the difference between their equilibrium pressures as given in Table X. is 66·23 atmospheres. The agreement between these two numbers is a confirmation of the validity of the method of work.]