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OSMOTIC PRESSURE

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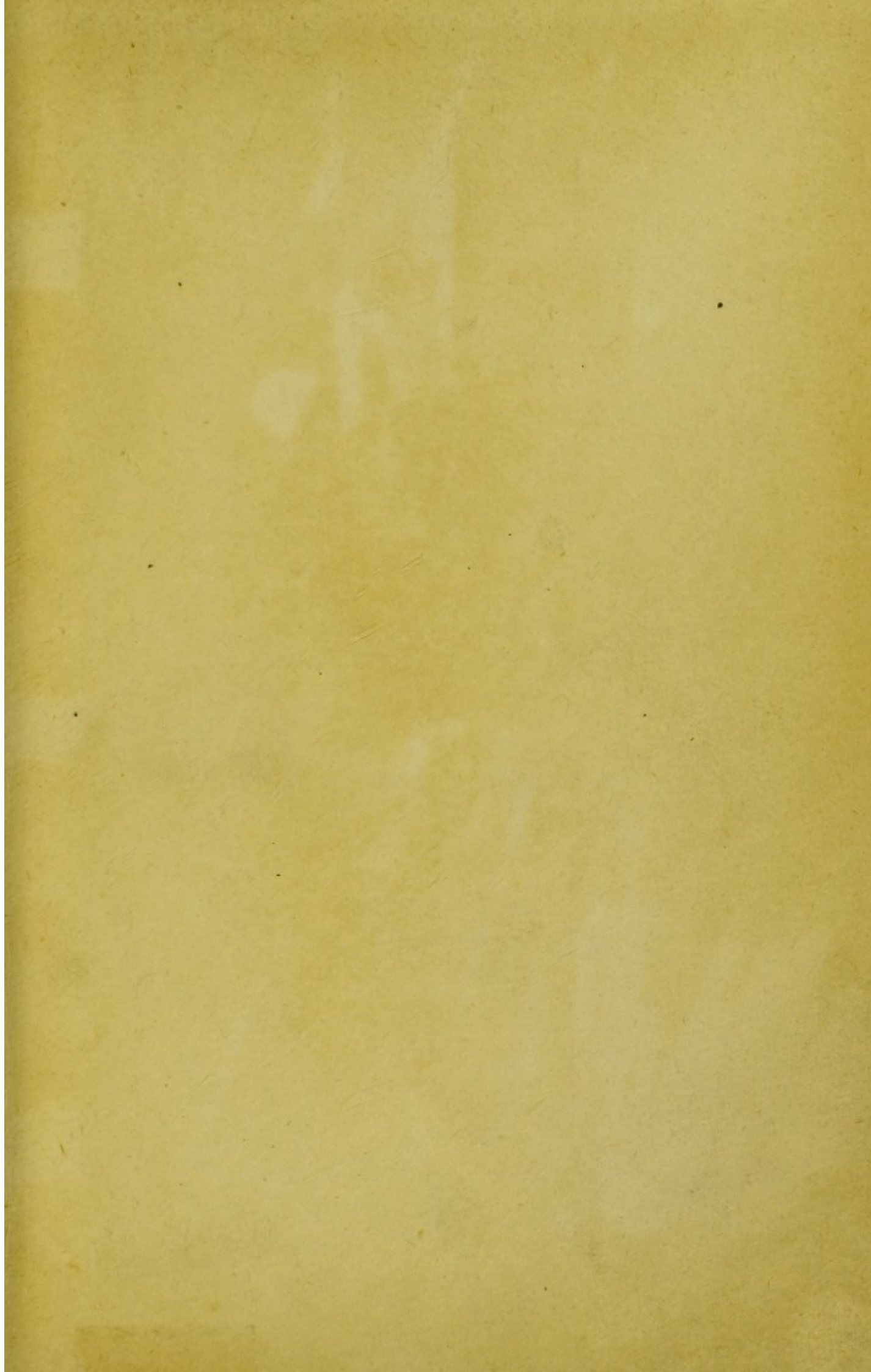
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# Monographs on Inorganic and Physical Chemistry

EDITED BY

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To those engaged in guiding the reading of advanced students of Chemistry, the difficulty of obtaining adequately summarised accounts of the progress made in recent years, more especially along certain of the more actively pursued lines of advance, becomes ever more acutely felt. So great has now become the volume of chemical investigation, and so numerous the channels of its publication, that not only the Honours Student but also the worker desirous of undertaking Research in one or other department of his subject, feels it a growing difficulty to become *au fait* with the present state of the more important and more strenuously cultivated regions of his Science. To assist these two classes of students—those reading for an Honours Degree, and those undertaking Research—is the main aim of the present Series of Monographs.

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# OSMOTIC PRESSURE

BY

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PERCY F. FRANKLAND, LL.D., F.R.S.  
PROFESSOR OF CHEMISTRY, UNIVERSITY OF BIRMINGHAM  
A TRIBUTE OF RESPECT

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## CHAPTER I.

### SEMI-PERMEABLE MEMBRANES AND OSMOTIC PRESSURE.

ALTHOUGH the process of osmosis,\* or diffusion of a liquid through a membrane, appears to have been discovered as early as 1748 by the Abbé Nollet,<sup>1</sup> and although many observations on the process of osmosis were made in later years by other investigators, who were attracted to the subject chiefly on account of its physiological interest, it was not till many years later, between 1826 and 1846, that quantitative measurements were carried out by Dutrochet<sup>2</sup> and by Vierordt.<sup>3</sup> By them it was found that when a salt solution is separated from water by means of a membrane of pig's bladder, the water diffused through the membrane more rapidly than the salt. The level of the solution therefore rose, and a hydrostatic pressure was produced; and since this pressure was brought about by osmosis, it was called an *osmotic pressure*.

By Dutrochet and by Vierordt it was established that the difference between the rates of osmosis of pure water and of salt solution depends not only on the nature of the salt but also on the concentration of the solution; and, as was found later, on the nature also of the membrane or permeable septum employed. This influence of the membrane, indeed, was utilized at a later time by Thomas Graham<sup>4</sup> for the separation of different substances by *dialysis*, and led to the characterization of substances as crystalloids and colloids.

The fact discovered by Graham that colloidal substances do not pass through colloidal membranes,† was seized on by Moritz

\* The terms *endosmosis* and *exosmosis*, applied to the oppositely directed diffusion currents, were first used by Dutrochet. The single term osmosis is now used to denote the whole process of diffusion through a membrane or permeable septum.

† It has been shown recently that diffusion does indeed take place but at a very slow rate comparatively, depending on the nature of the membrane and of the diffusing colloid,

Traube<sup>5</sup> as pointing to a method for imitating the behaviour of vegetable cells which, as was already known, are surrounded by a membrane through which osmosis can take place.

Hitherto, the process of osmosis had always been regarded as consisting of two diffusion currents in opposite directions; but the experiments of Graham now showed that in the case of colloidal solutions, at least, one of these diffusion streams, namely, the diffusion of the colloid, may vanish or become so slight as to be entirely negligible. In such cases, the osmosis was restricted to the passage of water through the membrane. If, however, unidirectional osmosis, as it might be called, is possible in the case of colloidal solutes, might it not be possible to find a membrane which would act in the same way with regard to crystalloid solutes? This question was first answered by Moritz Traube in 1867.

Inspired by the experiments of Graham and guided by the knowledge that the precipitate produced by the interaction of two colloids is also a colloid, Traube first carried out experiments with a non-setting glue\* and tannic acid. When a drop of concentrated glue solution carried on the end of a glass rod, was immersed in a solution of tannic acid, a precipitate was produced which formed a coating on the drop. A "cell" was thus obtained, and with such cells a number of osmotic phenomena were studied. The precipitation membrane which was obtained was found to be impermeable to the membrane-forming substances, but was permeable to water. It was also found to be permeable to ammonium chloride, ammonium sulphate, sulphuric acid, barium nitrate; but was impermeable to potassium ferrocyanide. This glue-tannic acid membrane was the first case known of an artificial membrane permeable to water but impermeable to a crystalloid.

Other precipitation membranes of a like nature were also prepared by Traube, e.g. lead tannate, copper tannate, lead silicate, copper silicate, tin silicate, copper ferrocyanide, and ferric ferrocyanide. These membranes, it was found, differed in their permeability to dissolved crystalloids; for, while the glue-tannic acid membrane was permeable to ammonium sulphate and barium

\* This was obtained by boiling glue with water for thirty hours. The liquid, on cooling, did not gelatinize except when the solution was very concentrated.

nitrate, the copper ferrocyanide membrane was impermeable to these salts. The membranes were, therefore, selective in their action.

The discovery by Traube of these precipitation membranes was one of most far-reaching importance for the quantitative study of osmosis. The importance of the membranes lay in the fact that, as was pointed out by Traube, they made it possible to determine experimentally the value of the "force" producing osmosis; a force which Traube assigned to the attraction of the solute for the solvent and called the "endosmotic force". So long as one was dealing with a membrane which was permeable both to the solvent and to the solute (as in the experiments of Dutrochet and Vierordt), the hydrostatic pressure obtained depended on the relative permeability of the membrane to solvent and solute. In proportion as the membrane becomes relatively less permeable to the solute, the observed hydrostatic pressure or osmotic pressure will increase; and it will attain a *maximum value* when the membrane is quite impermeable to the solute while still permeable to the solvent. Such a membrane which is permeable to only one component of a binary solution was afterwards called by van't Hoff a *semi-permeable membrane*.<sup>6</sup>

For the application of osmotic phenomena to the quantitative treatment of the properties of solutions, it is evident that the conception of a semi-permeable membrane is of supreme importance; for it is clear that the term "osmotic pressure of a solution" will have a definite meaning and value, independent of the nature of the membrane, only when regarded as measured by the *maximum* pressure obtainable with a *perfectly* semi-permeable membrane.

The osmotic pressure of a solution, therefore, in the sense indicated and in which we shall employ it here, may be defined as the equivalent of the hydrostatic pressure produced when the solution and solvent are separated by a perfectly semi-permeable membrane; or as the equivalent of the excess pressure which must be imposed on a solution in order to prevent the passage into it of solvent through a perfectly semi-permeable membrane.\*

\* In view of the misunderstandings and confusion of thought to which the use of the expression "osmotic pressure of a solution" has given rise, it may be emphasised here that the expression is, strictly speaking, incorrect. A solution does not, in itself, have any osmotic pressure; and the term is used, in a somewhat loose manner certainly, to denote the hydrostatic or mechanical



The question, of course, arises: Can such semi-permeable membranes as have been postulated here, be realized? It has been asserted by not a few chemists and physicists, e.g. Naccari,<sup>8</sup> Walden,<sup>9</sup> Tammann,<sup>10</sup> Meerburg,<sup>11</sup> Quincke,<sup>12</sup> Kahlenberg,<sup>13</sup> Ponsot,<sup>14</sup> that there is no membrane which is absolutely impermeable to the solute; no membrane which is perfectly semi-permeable. To such an assertion a philosophic assent must, of course, be given. But, in experimental science, the absolute is defined merely by the limits of experimental accuracy, so that in determinations of the osmotic pressure of a solution, the question of whether or not a membrane is semi-permeable is one which must be decided by experiment.

The first membranes found apparently to possess the property of semi-permeability are those surrounding animal and vegetable cells; and with these many valuable experiments were carried out by biologists such as de Vries,<sup>15</sup> Hamburger,<sup>16</sup> and others, on the relative osmotic pressures of different solutions. It can, however, scarcely be maintained that the semi-permeable character of such membranes has been adequately tested. In the precipitation membrane of copper ferrocyanide, however, which has been employed extensively in the direct measurement of osmotic pressures, more especially of solutions of cane sugar, we have a membrane which appears to be, for these solutions at least, truly semi-permeable. This has been shown most convincingly by Morse<sup>17</sup> in connexion with his experiments on the osmotic pressure of cane-sugar solutions. For the space of sixty days, at the temperature of 15°, a membrane of copper ferrocyanide maintained a pressure of over 12 atmospheres, without sign of leak. While, therefore, the truly semi-permeable character of the copper ferrocyanide membrane towards solutions of cane sugar may now be regarded as proved (up to pressures of 12

pressure *which would be produced* if the solution were separated from the pure solvent by a membrane or septum which is permeable only to the solvent. Recognition of this will prevent the confusion of thought which in the past prompted the objection that osmotic pressure acts in the wrong way, in that it causes a diffusion or osmosis from systems of lower to those of higher osmotic pressure.<sup>7</sup> It is osmosis that produces the osmotic pressure, not osmotic pressure which produces osmosis. Nernst, it is true (*Theor. Chem.*, English trans., revised by Tizard, p. 152), identifies the osmotic pressure with the expansive force which brings about diffusion; but it does not seem to the writer to be wise to use these two terms synonymously, although the "expansive force" can, of course, be measured by the osmotic pressure.

atmospheres), it must be remembered that the property of semi-permeability is a specific and not an universal one.

### Early Quantitative Measurements of Osmotic Pressure.

Although the discovery of semi-permeable precipitation membranes by M. Traube made it possible, in principle, to determine quantitatively the value of the osmotic pressure of a solution, a practical difficulty had still to be overcome. The membranes obtained by Traube were much too fragile to withstand the pressures produced with any but the most dilute solutions, and were, indeed, employed by Traube merely for comparative measurements. To overcome this practical difficulty, W. Pfeffer<sup>18</sup> introduced the device of forming the membrane in the wall of porous earthenware pots, whereby measurements of osmotic pressure amounting to several atmospheres were rendered practicable.

The apparatus used by Pfeffer was of a simple character. It consisted of a small cylindrical pot of porous ware in the walls of which a precipitate of copper ferrocyanide was allowed to form by diffusion of solutions of copper sulphate and potassium ferrocyanide from opposite sides of the cell walls. By means of a suitable collar this pot was connected with a closed manometer; and a tube was also provided to allow of the cell being filled with the solution, the osmotic pressure of which was to be determined. With this apparatus Pfeffer carried out a considerable number of osmotic pressure determinations, and although a number of precautions which have since been found to be necessary to secure accuracy, were not adopted, these measurements were the first, and for a long time remained the only quantitative determinations of osmotic pressure. As such they played a most important part in the history of solutions.

The results of the classical experiments of Pfeffer are familiar to all, and the following values of the osmotic pressure of solutions of cane sugar are given merely for convenience of reference.

TABLE I.—OSMOTIC PRESSURE OF SOLUTIONS OF CANE SUGAR AT TEMPERATURES BETWEEN 13.2° and 16.1°.

Grams of Cane Sugar in 100 c.c. of Water.	Pressure in cm. of Mercury.	Pressure Concentration.
1	53.8	53.8
2	101.6	50.8
4	208.2	52.1
6	307.5	51.3

These determinations showed that the osmotic pressure increases with the concentration of the solution, and indicated that the pressure was proportional to the concentration.

Moreover, the osmotic pressure was found to increase with rise of temperature, the values for a 1 per cent solution of cane sugar (1 gram in 100 grams of water) being as follows:—

TABLE II.

Temperature.	Osmotic Pressure.
6·8°	50·5 cm. Hg
13·7°	52·5 "
14·2°	51·0 "
22·0°	54·8 "
32·0°	54·4 "
36·0°	56·7 "

Although direct measurements of osmotic pressures were made at a later time by Ladenburg,<sup>19</sup> Adie,<sup>20</sup> Tammann,<sup>21</sup> Naccari,<sup>22</sup> and Ponsot,<sup>14</sup> the results obtained served merely to confirm those obtained by Pfeffer; and it is only in recent years that the accuracy of experiment and the range of investigation have been markedly increased and extended. These recent experiments and results will be described and discussed in the sequel (Chap. III). Reference may also be made to the experiments of P. S. Barlow,<sup>23</sup> and to those of E. Fouard.<sup>24</sup>

## CHAPTER II.

### VAN'T HOFF'S THEORY OF DILUTE SOLUTIONS.

ALTHOUGH many osmotic investigations have been carried out in recent years in connexion with problems of biological importance, the central point of interest in the quantitative study of osmotic pressure lies indubitably in the theory of solutions propounded by van't Hoff<sup>6</sup> in 1885. Previous to this time, van't Hoff had been engaged in the study of chemical equilibria, with a view to obtaining a quantitative expression for chemical affinity; and he had been led by these studies to recognize that the quantitative properties of gases are found in other systems, provided the matter in them is in an attenuated state.\* In his own words<sup>6</sup> we read: "In the course of an investigation which had as its chief object a knowledge of the laws of chemical equilibrium in solutions, it became gradually apparent that there is a profound analogy, indeed almost an identity, between them and gases, more especially also in physical properties, provided that for the ordinary pressure of gases one substitutes, in the case of solutions, the so-called osmotic pressure."

It is not merely in the recognition of this analogy (which had indeed been recognized apparently by Gay-Lussac<sup>26</sup>) but more especially in the recognition of the fact that the conception of osmotic pressure and of semi-permeable membranes allows solu-

\* An account of the genesis of the theory of dilute solutions has been given by van't Hoff himself (*Ber.*, 1894, 27, 1). For dilute gas systems, van't Hoff had already deduced the expression  $\frac{d \log_e K}{dT} = \frac{q}{RT^2}$ , and he had then turned his attention to dilute solutions. While his mind was engaged with this problem, with the problem, that is, of determining the maximum amount of work to be obtained by the addition of pure solvent to a solution, he was made acquainted by de Vries with the osmotic experiments of Pfeffer, and he recognized, as indeed M. Traube had recognized before him, that such determinations of osmotic pressure with the aid of semi-permeable membranes, afford a method by which the "water-attraction" of the solute could be measured; and he then applied the conceptions of semi-permeable membranes and osmotic pressure to the deduction of the quantitative laws of dilute solutions.

tions to be treated in a manner very similar to gases; and more especially allows of the second law of thermodynamics being applied with conspicuous ease and clearness to the theoretical investigation of the *quantitative* relations between the properties of solutions and their concentration, that the genius of van't Hoff becomes apparent.

The quantitative measurements of osmotic pressure, more especially of solutions of cane sugar, which had been carried out by Pfeffer, had pointed to the fact that the osmotic pressure is proportional to the concentration of the solution. On the kinetic explanation of osmotic pressure, the theoretical proof of this proportionality takes precisely the same form as in the case of gases. If, on the other hand, osmotic pressure be regarded as the outcome of an attraction between solvent and solute molecules, its value will, evidently, also be proportional to the number of attracting molecules in unit volume, provided (and this is taken for granted in sufficiently dilute solutions) the dissolved molecules exercise no attraction on each other, and that each one exerts its own special attractive action, uninfluenced by its neighbours.<sup>6</sup>

By the method of Carnot's thermodynamic cycle and by employing the conception of a perfectly semi-permeable membrane, van't Hoff deduced that the osmotic pressure must also be proportional to the absolute temperature.\* In making this deduction, however, *the important assumption was made that the solution was so dilute that the heat effect on further dilution is negligible.* This theoretical deduction was borne out by the experimental determinations of Pfeffer.

Since, therefore, the osmotic pressure of dilute solutions is proportional to the concentration, or inversely proportional to the volume of the solution; and since, also, the pressure is proportional to the absolute temperature, we can write  $PV = K.T$ , an expression analogous to that found to express the behaviour of perfect gases.

But a step farther was taken by van't Hoff. By the application of thermodynamics to the case of a gaseous solute, and by postulating the existence of semi-permeable membranes, one of which is permeable only to the gaseous solute, while the other is

\* This deduction will be found in the ordinary text-books on Physical Chemistry, and more especially in van't Hoff's *Lectures on Theoretical Chemistry*.

permeable only to the solvent, van't Hoff deduced the important generalization that *the osmotic pressure of a solution is equal to the pressure which the dissolved substance would exercise in the gaseous state if it occupied a volume equal to the volume of the solution.* In other words, the theorem of Avogadro applies also to dilute solutions. The same law was also deduced at a later time by Lord Rayleigh.<sup>26</sup> This deduction, however, is valid, in the first instance only in the case of infinitely dilute solutions, and in the case of gaseous solutes which obey Henry's law, i.e. which exist in the same molecular state as a gas as in solution; and it involves also the assumption that the vapour of the solvent obeys the gas laws. By reason, however, of the fact that the analogy between dilute solutions and gases extends to the laws of Boyle and of Gay-Lussac, the possibility immediately suggested itself that Avogadro's theorem would apply not only in the case of gaseous, but also in the case of other solutes; and that therefore the value of the constant  $K$  in the osmotic equation  $PV = K.T$ , would have the same numerical value as the constant  $R$  of the gas equation. This remarkable and unexpected deduction found confirmation in the determinations of osmotic pressure by Pfeffer, as well as in the indirect determinations of osmotic pressure which had already been carried out by de Vries<sup>15</sup> and by Raoult.<sup>27</sup>

Just as the expression  $\frac{pv}{T} = R$  represents, in the case of gases, the work done in moving a piston through the gram-molecular volume  $v$  under a pressure  $p$  and at the absolute temperature  $T$ , so the analogous expression in the case of a dilute solution represents the work done in separating from the solution at the temperature  $T$  the gram-molecular volume  $V$  of the solvent against the opposing osmotic pressure  $P$ .

It must again be emphasised that the theory of solutions which finds its expression in the equation  $P = \frac{nRT}{V}$ , where  $n$  is the number of gram-molecules of solute in the volume  $V$  of solution, was put forward by van't Hoff explicitly as expressing the quantitative relationships *only in the case of infinitely dilute solutions*; for only in the case of such solutions are the assumptions valid which were made in the thermodynamic deduction. It was, however, as van't Hoff<sup>28</sup> has remarked, a fortunate chance that the disability under which the theory thus laboured was not felt too

sorely, on account of the fact that in the chief applications of the theory, its applications, namely, to the determination of molecular weights and to the investigation of physiological problems, the errors involved were not sufficiently great, or the solutions dealt with were, in any case, sufficiently dilute. It may, however, also be argued that it was just this fact, combined, no doubt, with the extraordinary simplicity of the theory, which led to a too extended application of the theory and to many false deductions being drawn regarding the constitution of solutions; while, doubtless, it also delayed the experimental study and dulled the appreciation of the mathematical investigation of concentrated solutions.

It should be borne in mind that the term "osmotic pressure" as used by van't Hoff represents the maximum limiting pressure which would be obtained with a perfectly semi-permeable membrane, and this is the only sense in which the term should be used when discussing the quantitative theories of solutions.\* Granted a perfectly semi-permeable membrane, however, the laws of osmotic pressure deduced by van't Hoff are quite independent of the nature of the semi-permeable membrane or of the process by which the osmotic pressure is produced. It is quite true that van't Hoff, in view of the analogy with gases, considered that osmotic pressure could most plausibly be explained as due to the bombardment of the membrane by the solute molecules, but he also recognized that it might be attributed to the attraction between solvent and solute. Of the cause and mechanism of the production of osmotic pressure, the van't Hoff theory is quite independent. Further, as has been pointed out by Larmor,<sup>29</sup> the principles of thermodynamics necessitate the osmotic laws even when there is a formation of complexes between solvent and solute, "provided the solution is so dilute that each such complex is for very much the greater part of the time out of range of the influence of the other complexes".

\*The experimental values of osmotic pressure will differ more or less from this theoretical value, according as the membrane is more or less permeable to the solute; that is, according to the degree to which the membrane deviates from semi-permeability. Failure to recognize this, and the use of the term "osmotic pressure" to signify both the theoretical osmotic pressure deduced on the basis of thermodynamics, and the experimental osmotic pressure which varies with the membrane employed and is not an equilibrium pressure, have led to much confusion. (See remarks by A. Findlay and by Whetham, *Trans. Faraday Soc.*, 1907, 3, 30, 34.)

## CHAPTER III.

### DIRECT DETERMINATION OF THE OSMOTIC PRESSURE OF CONCENTRATED SOLUTIONS.

AS the first to carry out direct quantitative determinations of the osmotic pressure of solutions, W. Pfeffer will always be honoured. The precipitation membranes previously obtained by M. Traube, which rendered such measurements possible, were much too fragile to withstand the pressures produced with any but the most dilute solutions; and it is to Pfeffer that we owe the device of forming the membrane in the wall of porous earthenware pots, whereby measurements of osmotic pressure amounting to several atmospheres were rendered practicable. As is well known, a considerable number of such measurements were carried out by Pfeffer, and these afforded valuable confirmation of the theory of van't Hoff. The experiments of Pfeffer, even when supported by the indirect measurements of osmotic pressure available at that time, were, however, too few in number and insufficient in accuracy and in the extent of concentration covered, to yield a satisfactory experimental control of the deductive theory, or to define the limits of concentration within which such theory could, in any given case, claim validity. It was therefore of the greatest importance that further measurements of a more extended and exact character, should be carried out.

As will be pointed out later, determinations of the osmotic pressure of concentrated solutions can be carried out, most satisfactorily, by indirect methods; but in view of the historical development of the theory of solutions and of the rôle which the conception of osmotic pressure has played in that development, direct measurements of the pressure possess a large amount of interest. Such measurements, however, are surrounded by great difficulties, so that, although they were undertaken by several investigators (p. 6), it is only within the past few years that the numerous experimental difficulties have been overcome at all.



satisfactorily. The success which has been achieved in this direction is due chiefly to the most painstaking care and ingenuity of H. N. Morse<sup>30</sup> (assisted by various co-workers) in America, and of the Earl of Berkeley and E. G. J. Hartley<sup>31</sup> in England. The work of these investigators merits somewhat fuller discussion.

We shall consider, in the first place, the experimental work of the American chemists, who, during a protracted course of investigation have so perfected the experimental method introduced by Pfeffer, that direct determinations of osmotic pressures of nearly 30 atmospheres can now, in their hands, be carried out with a considerable degree of accuracy.

As we have indicated, the apparatus employed is, in principle, the same as that used by Pfeffer, and consists, therefore, of a pot or cell of porous ware on the walls of which the semi-permeable membrane of copper ferrocyanide was formed. To the mouth of the pot was attached a closed manometer of capillary tubing, by which the pressure produced could be determined. In detail, however, the apparatus differs considerably from that used by Pfeffer; and it is to the perfecting of the details of the apparatus and method of manipulation, that the success of Morse and his collaborators is due. Improvement of the material and construction of the pots, of the manometer tube and the manner of its attachment to the pot, as well as increased accuracy of temperature regulation, are some of the more important factors in the successful determination of osmotic pressures by this method.

The most recent form of apparatus employed by Morse and his collaborators,<sup>32</sup> is represented in section in Figure 1. The porous pot, prepared in the manner to be described later, is closed by means of a conical brass plug (4) over which a rubber tube (12) has been passed. To prevent distortion of this rubber under pressure, it is tightly wound with twisted shoemakers' thread (13, 14). The brass cone is firmly fixed in position by means of a brass collar (1) and a brass nut (2), the glaze on the cell being protected by means of a lead washer (3). The brass cone (4) has two holes passing entirely through it, one for the glass tube (5) to which the manometer is afterwards sealed, and the other for a hollow needle (6). The glass tube and needle are fastened securely in the cone by means of Wood's metal (7). The hollow

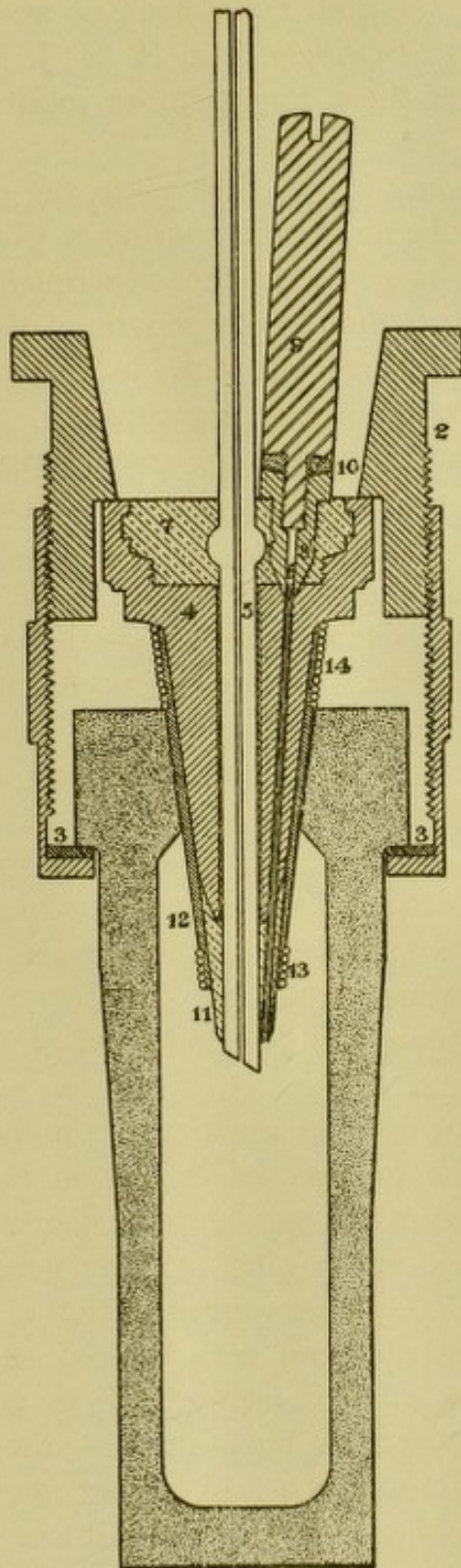
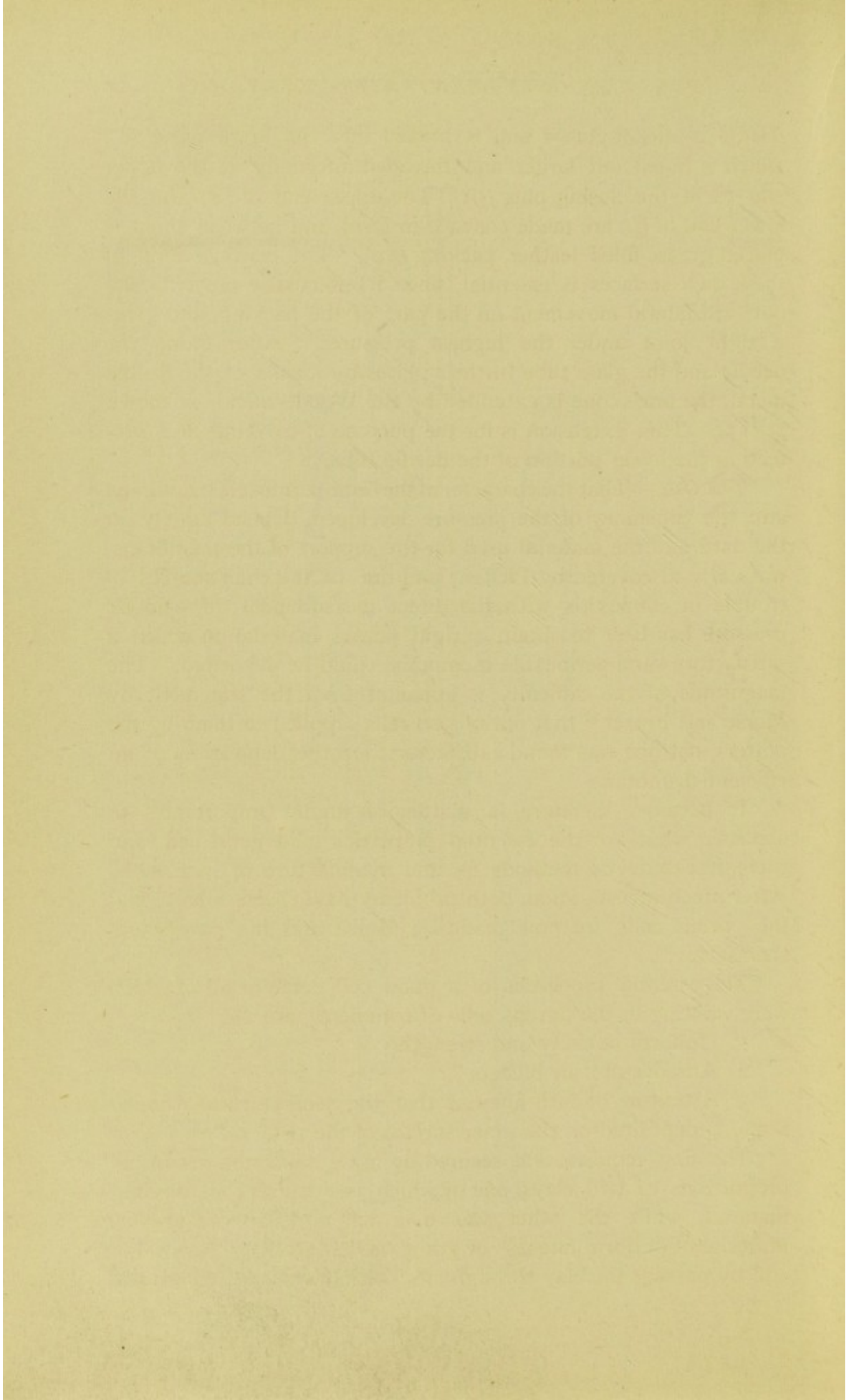


FIG. 1.



needle is nickel-plated and is brazed into the brass piece (8), which is bored out larger and threaded internally at the upper end to fit the closing plug (9). The upper end of (8) and the lower end of (9) are made concave in form, and between them is placed grease-filled leather packing (10). The concave form of these two surfaces is essential, since it effectually prevents any outward lateral movement on the part of the packing, and gives a tight joint under the highest pressures. After fixing the needle and the glass tube in their places by means of the fusible metal, the brass cone is extended by the Wood's metal, as shown at (11). This extension is for the purpose of covering and protecting the lower portion of the needle tube.

*The Cell.*—That the character of the semi-permeable membrane and the constancy of the pressure developed, depend largely on the nature of the material used for the support of the membrane, was early discovered by Pfeffer; and one of the chief sources of trouble in connexion with the direct measurement of osmotic pressure has been to obtain a rigid porous material on which a satisfactory semi-permeable membrane could be deposited. The magnitude of the difficulty is apparent from the statement by Morse and Frazer<sup>33</sup> that out of 500 cells supplied to them by the potters, not one was found satisfactory for the deposition of an efficient membrane.

It became, therefore, a matter of urgent importance to ascertain what are the essential properties of a good cell, and thereafter to devise methods for the manufacture of such cells. After much investigation, both problems have been solved, and the porous cells are now made by Morse and his co-workers themselves<sup>32</sup>.

The essential properties of a good cell, some or all of which were wanting in the porous cells of commerce, are :—

1. Uniform porosity and strength.
2. Absence of "air blisters".
3. A texture of such fineness that the semi-permeable membrane is deposited on the inner surface of the pot.

The first requisite was secured by using mixtures in proper proportions of two clays, one of which was deficient in binding material, while the other was over-rich in that constituent. Material of uniform fineness of grain was obtained by elutriation and by passing the clay through silk bolting-cloth having 16,000

holes to the square inch. The clays were then very carefully mixed and sifted, churned with water and filtered through bolting cloth. The moist clay was then kneaded till, through loss of water, it had attained the requisite consistency.

To secure absence of "air blisters" and the necessary fineness of texture, the moist clay was placed in a steel press and subjected to a total pressure of about 200 tons for fourteen to sixteen hours, the excess water draining away through plates of porous, hard-burned clay or of asbestos. The cylinder of compact clay was then cut and hollowed on a lathe and fired carefully in an electric furnace. After being baked, the end of the cell was ground and flanged so as to take the brass collar by means of which the conical plug used for closing the cell was afterwards fixed in position. The neck, also, of the cell was ground to the exact taper of the brass plugs to be employed. The ends of the cells were then glazed, both externally and internally.

*The Hollow Needle.*—The purpose of the hollow needle, to which reference was made above, is to facilitate the closing of the cell at the beginning, and the opening of it at the end of an experiment. When closing the cell, the solution escapes through the hollow needle, and the outflow can be stopped at any moment by means of the screw plug (9). This is of advantage, as it is important to arrange that the mechanical pressure imposed on the solution by the closing of the cell should be nearly equal to the osmotic pressure, so as to avoid any appreciable dilution or concentration of the cell contents during the measurement. When opening the cell, air passes in through the needle and so facilitates removal of the stopper.

The *Manometers*<sup>34</sup> employed were U-shaped, and closed. They were filled with nitrogen and carefully calibrated. To protect them as far as possible from the danger of being broken, the manometers were not attached direct to the brass plugs by which the cells were closed, but were sealed, as occasion required, to short pieces of tubing of the same kind which were fixed in the brass cones, as described previously.

*The Membrane.*—Membranes of copper ferrocyanide were employed. Their production is, of course, an all-important matter. The simple method, employed by Pfeffer, of allowing solutions of copper sulphate and potassium ferrocyanide to diffuse from opposite sides of the cell wall, does not yield a membrane

of sufficient strength to withstand the higher pressures developed in the case of concentrated solutions. It was found, however, by Morse and Horn<sup>35</sup> that the quality of the membrane could be greatly improved by assisting the process of diffusion by the electrical transport of the ions. The method adopted was therefore as follows: The cell was filled with and placed in a dilute solution (0.5 gram per litre) of potassium sulphate and an electrical current passed between electrodes placed inside (cathode) and outside (anode) the cell. By this means a streaming of the liquid (electrical endosmose) was caused to take place, whereby the air held in the pores of the cell, was swept out. The cell was then freed from salts by repeated washing with distilled water, accompanied by electrolysis, which was continued until the conductivity of pure water was reached. It was thereafter filled with a solution of potassium ferrocyanide and placed in a solution of copper sulphate. A current of electricity is then passed from a copper anode, placed in the solution of copper sulphate, to a platinum cathode immersed in the solution of ferrocyanide. As the membrane forms and thickens, the resistance increases considerably (up to 100,000 ohms) but the efficiency of the membrane cannot be gauged entirely by the resistance. Since alkali is produced in the ferrocyanide solution during electrolysis, the latter must be renewed from time to time to prevent the harmful action of the alkali on the membrane.

After it has been formed in this way, the membrane is tested by carrying out a determination of the hydrostatic pressure developed, with a sugar solution. The membrane is again subjected to the above "making" process, and again tested osmotically; and this procedure is continued until no further increase in osmotic pressure is obtained.

It is important that the membrane be deposited as close as possible to the inner surface of the cell, since otherwise inequalities in the concentration of the solution at the membrane occur.

For the efficient action of the membrane, it is advisable to add to the liquids, on either side of the membrane, a small quantity of the membrane-forming salts in osmotically equivalent amounts. Through the presence of these, any slight ruptures which might occur in the membrane during use, are "healed"; and it seems also that when they are absent the membrane tends to dissolve and to allow the sugar to escape,<sup>31</sup>

As has already been mentioned (p. 4) the membrane of copper ferrocyanide appears to be truly semi-permeable to aqueous solutions of cane sugar. The difficulty, however, of preparing membranes sufficiently impermeable to the solute, appears to increase as the molecular weight of the solute diminishes, so that a membrane which may not be sensibly permeable to cane sugar may allow glucose<sup>36</sup> and mannite<sup>31</sup> to pass.

In connexion with the determinations of osmotic pressure carried out by Morse and his collaborators, it may be said that the elimination of sources of error has proceeded continuously and the accuracy of the measurements has been increased progressively during the period over which the investigation has extended. More especially has attention been paid to the elimination of "thermometer effects," by the very careful regulation of the bath and air temperature;<sup>37</sup> and the corrections for changes in the barometric height during the progress of an experiment (which may extend over a period of ten days or more although equilibrium is, in some cases, attained in one day or even less) have been carefully considered.

Although it has been objected by Kahlenberg<sup>38</sup> that the osmotic pressure measurements carried out by Morse and his co-workers must be defective on account of the fact that the solutions were not stirred, and that therefore the layer of liquid in contact with the membrane is not of the same concentration as in the body of the solution, Morse<sup>39</sup> has expressed the conviction that failure to stir the contents of the cell does not invalidate the results obtained.

In the following Tables, III, IV, and V, are collected the results of the measurements of osmotic pressure so far carried out by Morse and his collaborators. In connexion with these attention must be drawn to the fact, to which reference will again be made later, that the concentration of the solutions is expressed in terms of gram-molecules of solute in 1000 grams of water (weight-normal concentration) instead of in terms of gram-molecules of solute in 1000 c.c. of solution (volume-normal concentration). In connexion also with Table IV, it should be mentioned that the calculated gas pressure is that which would be shown by the given amount of solute in the form of gas at the temperature of experiment and occupying a volume equal to the volume *not* of the solution but of the water in the solution at the temperature

of 4° C. Moreover, the gram-molecular volume of hydrogen at N.T.P. has been taken as 22·28 litres.

TABLE III.—OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS.

Weight Normal Concentration.	Mean Osmotic Pressure in Atmospheres at											
	0°	5°	10°	15°	20°	25°	30°	40°	50°	60°	70°	80°
0·1	(2·46)	2·45	2·50	2·54	2·59	2·63	2·47	2·56	2·64	2·72	—	—
0·2	4·72	4·82	4·89	4·99	5·06	5·15	5·04	5·16	5·28	5·44	—	—
0·3	7·09	7·20	7·33	7·48	7·61	7·73	7·65	7·84	7·97	8·14	—	—
0·4	9·44	9·61	9·79	9·95	10·14	10·30	10·30	10·60	10·72	10·87	—	—
0·5	11·90	12·10	12·30	12·55	12·75	12·94	12·98	13·36	13·50	13·67	13·99	—
0·6	14·38	14·61	14·86	15·14	15·39	15·62	15·71	16·15	16·32	16·54	16·82	—
0·7	16·89	17·21	17·50	17·82	18·13	18·43	18·50	18·93	19·20	19·40	19·57	—
0·8	19·48	19·82	20·16	20·54	20·91	21·25	21·38	21·80	22·12	22·33	22·57	23·06
0·9	22·12	22·48	22·88	23·31	23·72	24·13	24·23	24·74	25·12	25·27	25·56	25·92
1·0	24·83	25·28	25·69	26·19	26·64	27·05	27·22	27·70	28·21	28·37	28·62	28·00

TABLE IV.—OSMOTIC PRESSURE OF GLUCOSE SOLUTIONS AT 0°.

Weight Normal Concentration.	Temp.	Osmotic Pressure. Atm.	Calculated Gas Pressure.	Ratio of Osmotic Pressure to Gas Pressure.
0·1	0·26°	2·40	2·23	1·074
0·2	0·13°	4·65	4·45	1·045
0·3	0·22°	7·01	6·68	1·050
0·4	0·17°	9·30	8·91	1·044
0·5	0·21°	11·65	11·14	1·046
0·6	0·10°	14·01	13·36	1·048
0·7	0·07°	16·37	15·59	1·050
0·8	0·13°	18·77	17·82	1·053
0·9	0·16°	21·25	20·05	1·060
1·0	0·17°	23·59	22·28	1·057
Mean . . . . .				1·052

TABLE V.—OSMOTIC PRESSURE OF GLUCOSE SOLUTIONS AT 10°.

Weight Normal Concentration.	Temp.	Osmotic Pressure. Atm.	Calculated Gas Pressure.	Ratio of Osmotic Pressure to Gas Pressure.
0·1	10·15°	2·39	2·31	1·035
0·2	10·30°	4·76	4·62	1·030
0·3	10·00°	7·11	6·92	1·027
0·4	10·10°	9·52	9·24	1·030
0·5	10·15°	11·91	11·55	1·031
0·6	10·05°	14·31	13·85	1·033
0·7	10·00°	16·70	16·16	1·033
0·8	10·00°	19·05	18·46	1·032
0·9	10·05°	21·39	20·78	1·030
1·0	10·00°	23·80	23·08	1·031
Mean . . . . .				1·031



Before passing to the discussion of these results we shall consider those obtained by the Earl of Berkeley and E. G. J. Hartley.<sup>31</sup> The method employed is essentially different from that of Morse, and is based on a method first employed by Tammann.<sup>40</sup> Instead of measuring the pressure developed in a cell by the passage inwards of the solvent, Lord Berkeley and E. G. J. Hartley subjected the solution, separated from the solvent by a semi-permeable membrane, to a gradually increasing pressure, until the solvent, which at first flows into the solution, reverses its direction and is squeezed out. The turning-point at which the pressure on the solution is just sufficient to prevent the inflow of solvent, is taken as the equivalent of the osmotic pressure of the solution.

The apparatus is represented in section in Fig. 2. "AB is a porcelain tube, 15 cm. long, 2 cm. external and 1.2 cm. 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 gun-metal cage against the ends of which the dermatine rings DD are compressed when the two parts E and F of the outer gun-metal 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 outer gun-metal vessel (capacity about 250 c.c.) 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.

"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

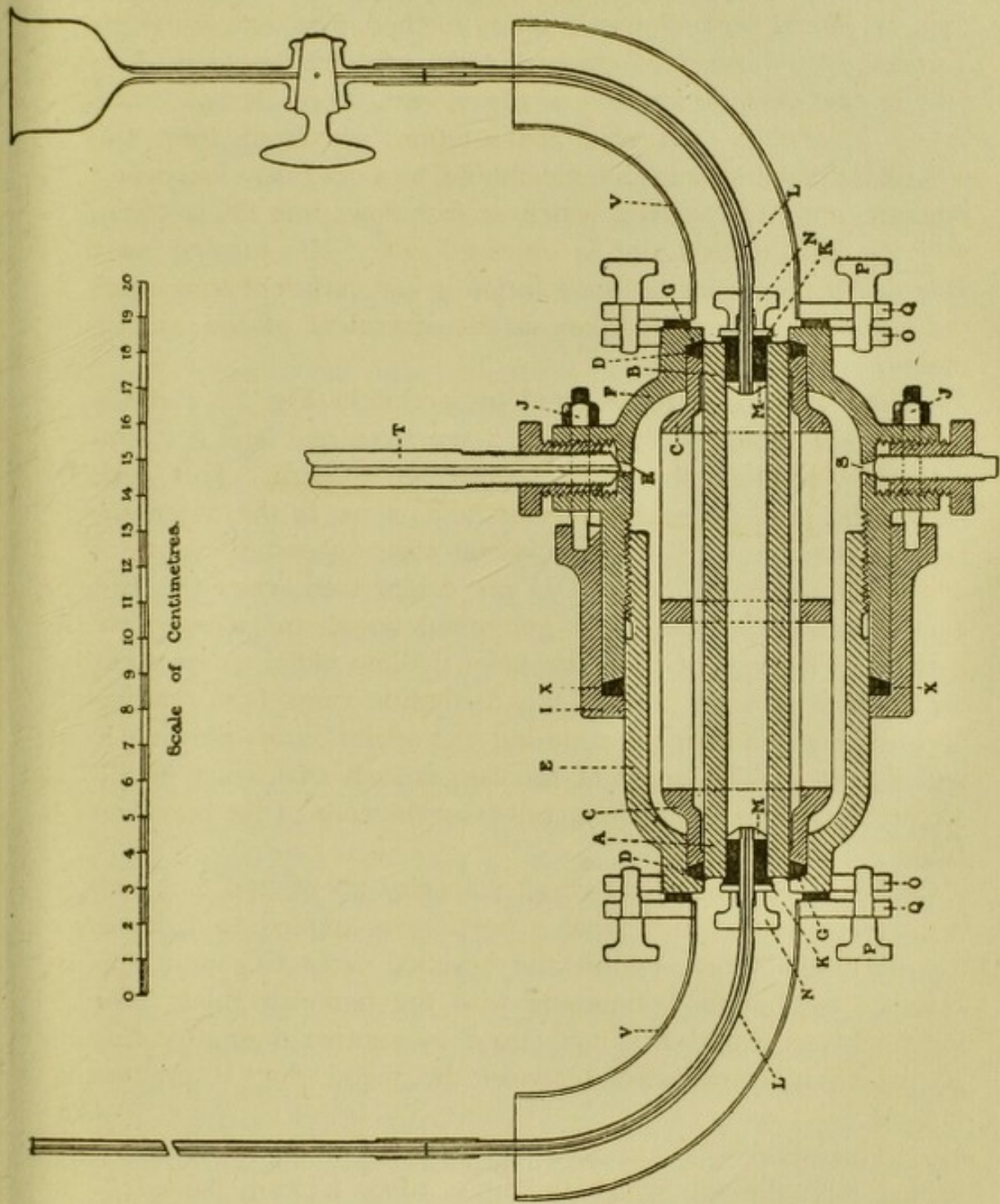
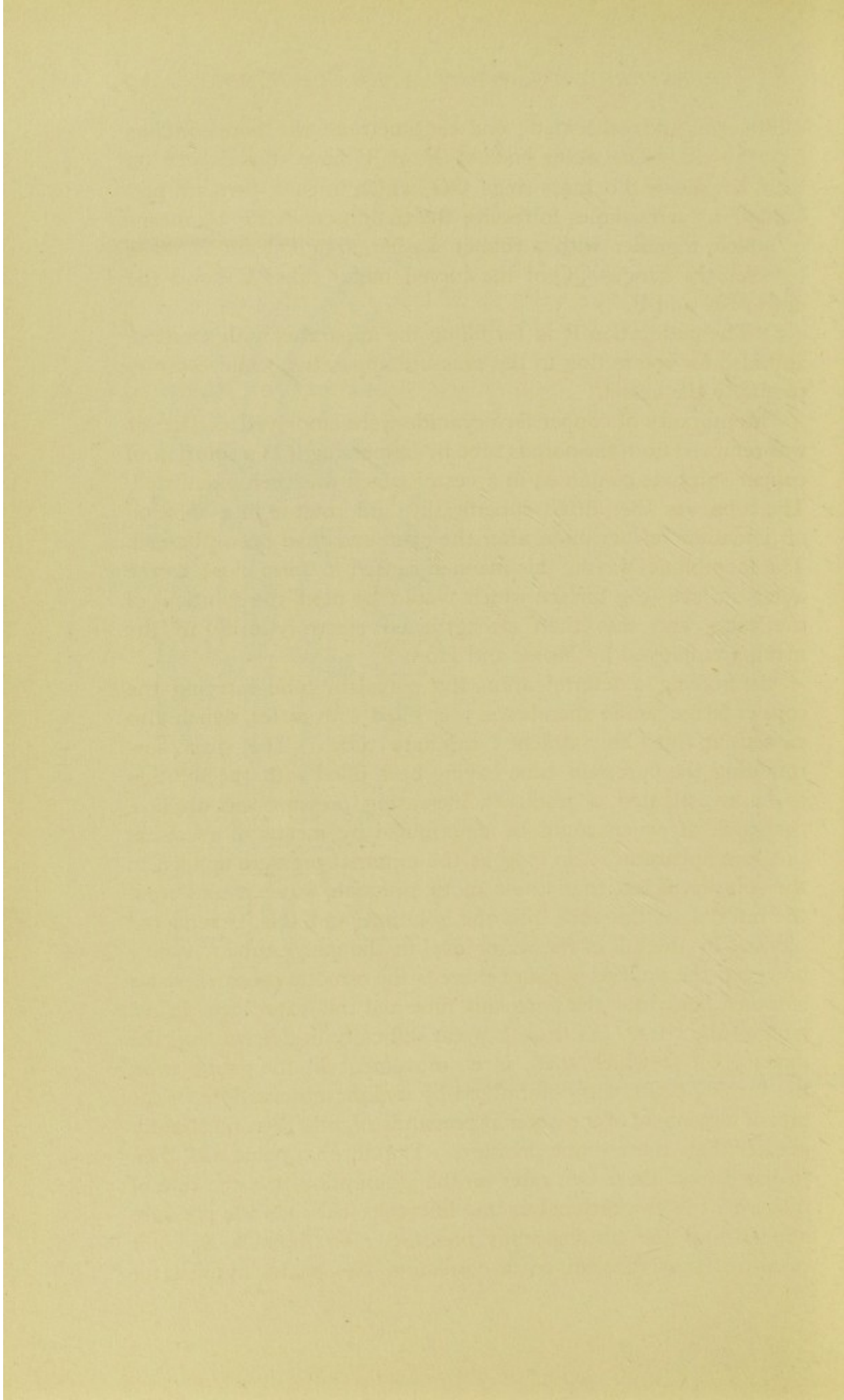


FIG. 2.



millimetres and calibrated; one centimetre of the bore contains 0.00312 c.c. The outer ends of E at F have threads cut on them to receive the brass rings OO, which in their turn are perforated by screw-holes to receive the thumbscrews 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 perforation R is for filling the apparatus with solution, and also for connecting to the pressure apparatus, while S serves to empty the vessel.”

Membranes of copper ferrocyanide were employed. The air was removed from the porous tube by immersing it in a solution of copper sulphate contained in a vessel which was then exhausted. The tube was then dried superficially and rotated in a solution of potassium ferrocyanide, after the open ends had been plugged. The membrane was in this manner caused to form close to the outer surface (the surface which would be next the solution) of the tube, and was then strengthened electrolytically in the manner employed by Morse and Horn.<sup>35</sup>

In making a determination, the porcelain tube carrying the copper ferrocyanide membrane was filled with water, which also passed up into the attached capillary tubes. The space surrounding the porcelain tube having been filled with the solution to be investigated, a gradually increasing pressure was applied, the value of which could be determined by means of a special pressure apparatus. So long as the external pressure applied to the solution is less than the osmotic pressure, water passes from the interior of the tube into the solution and this is rendered obvious by the fall of the water-level in the gauge tube. When, however, the applied pressure exceeds the osmotic pressure, water is forced back into the porcelain tube and the water level in the gauge-tube rises. As there is great difficulty in determining the exact point at which there is no movement in the gauge tube, the turning-point was determined by making observations of the rate of movement of the water at pressures slightly less and slightly greater than the osmotic pressure. The turning-point was then deduced from these two rates on the assumption that the rate of movement is proportional to the difference between the pressure applied and the turning-point pressure. To the turning-point pressures thus determined, a correction has to be applied for

what is called the guard-ring leak. This leak is due either to the fact that (in the older apparatus) the semi-permeable membrane does not lie quite on the surface of the tube, and consequently it is impossible to get perfect contact between the dermatine rings and the membrane; or to the fact that (in the case of the tubes with glazed ends) there are cracks in the glaze through which the solution flows and abstracts water from the interior.

As the sensitiveness of the pressure gauge was only about 0.12 atm., and the guard-ring leak corresponded to about 0.15 atm., the method described could not be used for measuring osmotic pressures of less than 12 atm. with sufficient accuracy. The time, however, required for carrying out a determination is much less than with the method employed by Morse.

The following tables give the results obtained by Lord Berkeley and E. G. J. Hartley, at the temperature 0°, the concentrations being expressed in grams of solute in 1 litre of solution.

TABLE VI.—OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 0°.

Concentration.	Osmotic Pressure Observed. Atm.	Osmotic Pressure Calculated according to van't Hoff. Atm.
180.1	13.95	11.79
300.2	26.77	19.66
420.3	43.97	27.52
540.4	67.51	35.38
660.5	100.78	43.24
750.6	133.74	49.15

TABLE VII.—OSMOTIC PRESSURE OF GLUCOSE SOLUTIONS AT 0°.

Concentration.	Osmotic Pressure Observed. Atm.	Osmotic Pressure Calculated according to van't Hoff. Atm.
99.8	13.21	12.42
199.5	29.17	24.82
319.2	53.19	39.72
448.6	87.87	55.83
548.6	121.18	68.27

TABLE VIII.—OSMOTIC PRESSURE OF GALACTOSE SOLUTIONS AT 0°.

Concentration.	Osmotic Pressure Observed. Atm.	Osmotic Pressure Calculated according to van't Hoff. Atm.
250	35.5	31.1
380	62.8	47.29
500	95.8	62.22

TABLE IX.—OSMOTIC PRESSURE OF MANNITOL SOLUTIONS AT 0°.

Concentration.	Osmotic Pressure Observed. Atm.
100	13·1
110	14·6
125	16·7

The experiments with mannitol are not satisfactory, as there seemed to be no doubt that the copper ferrocyanide membrane is slightly more permeable to this substance than to the sugars.

The accuracy of the above measurements may be estimated from the fact that the equilibrium pressure obtained between two solutions of cane sugar containing 750 grams and 540 grams respectively in the litre, was 66·0 atm. This agrees very well with the difference between the equilibrium pressures of these two solutions when measured against water, viz. 66·23 atm. (see Table VII).

The Earl of Berkeley and E. G. J. Hartley have also suggested<sup>41</sup> a dynamic method of determining osmotic pressure. Instead of determining the hydrostatic pressure which must be applied to the solution to prevent the inflow of water, they have also measured the rate of flow of solvent into the solution. Assuming that this rate of flow is the same as would occur if the water were caused to pass through the membrane under a mechanical pressure numerically equal to the osmotic pressure of the solution, they find that if the *initial* rate of flow only is considered, it yields values for the osmotic pressure which agree well with the values measured directly (or calculated by the Boylevan't Hoff law from the osmotic pressure of more concentrated solutions) in the case of dilute solutions. In the case of concentrated solutions, however, the discrepancy is somewhat large. In the case of dilute solutions, Lord Berkeley and E. G. J. Hartley believe that fairly accurate determinations of the osmotic pressure can thus be made more easily than by employing the direct equilibrium (statical) method.\*

The dynamical method is, however, applicable only when the initial rate is measured, since the rate of flow gradually diminishes,

\* In this connexion the recent investigations of H. C. Ross (*Proc. Roy. Soc.*, 1909, B., 81, 97), on the diffusion of stains into bacteria and other cells, and of A. J. Brown (*Proc. Roy. Soc.*, 1912, B. 85, 546), on the diffusion of water into the seeds of barley (*Hordeum vulgare*) are of interest and importance.

as was shown by Vegard.<sup>42</sup> The velocity of osmosis and its dependence on the osmotic pressure has also been investigated by Šebor.<sup>43</sup>

Reference may also be made to the determinations by Lord Berkeley and E. G. J. Hartley<sup>44</sup> of the osmotic pressure of concentrated and dilute solutions of calcium, strontium and potassium ferrocyanides (see Chap. VII.). From the results obtained it is concluded that these salts exist as ionized double molecules in solution.

The method of determining osmotic pressures suggested by Trouton<sup>134</sup> has been adversely criticised by Lord Berkeley.<sup>135</sup>

In recent years, also, measurements of osmotic pressure in non-aqueous solutions have been carried out with pyridine solutions by Kahlenberg,<sup>45</sup> Cohen and Commelin,<sup>46</sup> and Wilcox,<sup>47</sup> using membranes of rubber. The results are, however, too conflicting to justify further discussion here.

## CHAPTER IV.

### DISCUSSION OF THE RECENT DETERMINATIONS OF OSMOTIC PRESSURE AND OF THE VAN'T HOFF THEORY.

IN view of the fact that recent investigation of the osmotic pressure of solutions was inspired by the theory of van't Hoff, we turn naturally to inquire how far this theory is in harmony with the results so recently obtained. The theory of van't Hoff postulates direct proportionality between the osmotic pressure of the solution and its concentration expressed in grams or gram-molecules in unit volume of solution; and also direct proportionality between osmotic pressure and absolute temperature. The osmotic pressure, moreover, according to this theory, is equal to the pressure which the dissolved substance would exercise if in the state of a gas occupying a volume equal to the volume of the solution.

In considering the recent determinations of osmotic pressure we must ask, in the first place, to what extent the results obtained by Morse and his collaborators, on the one hand, and by Lord Berkeley and E. G. J. Hartley on the other, are in agreement with one another. Unfortunately a close comparison of the two sets of results is not possible, on account, first of all, of the fact that the measurements of the English investigators are limited to one temperature ( $0^{\circ}$ ), and in the second place because the range of concentration investigated is, for the most part, very different in the two cases. The numbers given in Table X will, however, allow of such comparison being made as is possible under the circumstances.

TABLE X.

Concentration (Moles. of Cane Sugar in 1 Litre of Solution).	Osmotic Pressure, in Atm., at $0^{\circ}$ as determined by	
	Morse.	Lord Berkeley and Hartley.
0.527	—	13.95
0.534	14.38	—
0.686	19.48	—
0.828	24.83	—
0.877	—	26.77



If one takes the value 13.95 atm. for the solution of concentration 0.527 as correct, and calculates by proportion the value for the solution of concentration 0.534, we obtain the pressure 14.14 atm. On the other hand, if the osmotic pressure of the solution of concentration 0.828 is calculated from the value for the solution of concentration 0.877, one obtains the pressure 25.27. That is to say, the measurements of Morse yield at the lower concentrations higher values, and at higher concentrations lower values of the osmotic pressure than do those of Lord Berkeley and E. G. J. Hartley. The agreement is, however, probably as satisfactory as one could expect.

Let us see now how the matter stands with regard to the validity of the Boyle-van't Hoff law. In Table XI are tabulated the values of the osmotic pressure of solutions of cane sugar at 20°, as determined by Morse and his collaborators, together with the values calculated according to the van't Hoff theory and also according to the method of Morse.

TABLE XI.

Weight Normal Concentration.	Volume Normal Concentration.	Osmotic Pressure Observed. Atm.	Osmotic Pressure in Atm. Calculated according to	
			van't Hoff.	Morse.
0.1	0.098	2.59	2.34	2.39
0.2	0.192	5.06	4.59	4.78
0.3	0.282	7.61	6.74	7.17
0.4	0.369	10.14	8.82	9.56
0.5	0.452	12.75	10.81	11.95
0.6	0.533	15.39	12.72	14.34
0.7	0.610	18.13	14.58	16.73
0.8	0.684	20.91	16.36	19.12
0.9	0.756	23.72	18.08	21.51
1.0	0.825	26.64	19.73	23.90

On glancing at the numbers in the above table we are at once struck by the fact that even in deci-normal solutions of cane sugar the experimental value of the osmotic pressure is appreciably higher than the value calculated according to the theory of van't Hoff; and as the concentration of the solution increases, the deviation from the calculated values increases still further. That the deviation becomes increasingly great at higher concentrations is very evident from Table VI (p. 20), where we see that when the concentration is increased from 180.1 to 750.6 grams per

litre (a ratio of 1 to 4.2), the osmotic pressure increases from 13.95 atm. to 133.74 atm. (a ratio of 1 to 9.5). At the higher concentration, instead of the osmotic pressure being 49.15 atm., as calculated according to the van't Hoff theory, it amounts to 133.74 atm.

It was, however, pointed out by Morse that better agreement is obtained between the experimental values of the osmotic pressure and the theoretical values, if these are calculated on the assumption that the osmotic pressure is equal to the pressure which the substance would exercise if it existed as a gas in the volume occupied by the *solvent*, not by the solution as according to the van't Hoff theory. That this is so is seen from Table XI, where the values calculated in this way are given in the last column of the table. But even so, it will be seen that the values obtained still deviate appreciably from the experimental numbers. Such deviations are found also at other temperatures, as is shown by Table XII, which gives the ratios of the experimentally determined osmotic pressures to the gas pressures, calculated according to the method which has just been mentioned.<sup>48</sup>

TABLE XII.—RATIOS OF OSMOTIC PRESSURE TO GAS PRESSURE IN THE CASE OF CANE SUGAR SOLUTIONS.

Weight Normal Concentra- tion.	Ratio of Osmotic Pressure to Gas Pressure at											
	0°	5°	10°	15°	20°	25°	30°	40°	50°	60°	70°	80°
0.1	(1.106)	1.082	1.082	1.082	1.084	1.084	1.000	1.003	1.000	1.000	—	—
0.2	1.061	1.063	1.060	1.061	1.062	1.059	1.020	1.011	1.002	1.001	—	—
0.3	1.061	1.058	1.059	1.061	1.060	1.060	1.031	1.024	1.009	0.999	—	—
0.4	1.060	1.059	1.060	1.059	1.060	1.059	1.040	1.038	1.017	1.000	—	—
0.5	1.069	1.067	1.066	1.068	1.067	1.065	1.050	1.046	1.025	1.006	1.000	—
0.6	1.077	1.074	1.073	1.073	1.073	1.071	1.060	1.054	1.032	1.015	1.002	—
0.7	1.083	1.084	1.083	1.083	1.084	1.083	1.069	1.059	1.041	1.020	0.999	—
0.8	1.093	1.093	1.092	1.093	1.093	1.093	1.081	1.067	1.049	1.027	1.008	1.001
0.9	1.104	1.102	1.102	1.102	1.103	1.102	1.089	1.076	1.059	1.033	1.015	1.000
1.0	1.115	1.115	1.113	1.115	1.115	1.113	1.101	1.085	1.071	1.044	1.023	1.000

From the above table it will be seen that the deviations of the calculated from the observed pressures are found in all cases at temperatures below 25°, and that they are greater in the case of concentrated than in the case of dilute solutions. It will be observed, however, that at higher temperatures, the deviations

gradually disappear, so that at  $80^{\circ}$  the deviations no longer exist even in the case of the most concentrated solutions.

With regard to the validity of the Gay-Lussac-van't Hoff law, it will be seen from Table XII that for any given concentration the ratio of osmotic pressure to gas pressure is constant (up to  $25^{\circ}$ ). This implies that the osmotic pressure of solutions varies with temperature in the same way as the pressure of a gas, *provided one calculates the osmotic pressure in terms of volume of solvent at  $4^{\circ}$  instead of volume of solution at the temperature of the experiment.* At temperatures above  $25^{\circ}$ , however, as is seen from Table XII, even the Gay-Lussac-Morse law ceases to be valid, the ratio of osmotic pressure to gas pressure (calculated according to Morse) being no longer constant for a given concentration of solution.

From what has just been said it follows that the Boyle-van't Hoff law and the Gay-Lussac-van't Hoff law do not hold with any accuracy over the range of concentration and temperature investigated. Nor, indeed, was it to be expected that they would. Since, in the deduction of the van't-Hoff theory, simplifying assumptions were introduced which could be valid only in the case of infinitely dilute solutions, the theory made no claim to be a general theory of solutions applicable to all concentrations; and the experimental investigation of osmotic pressures could serve the purpose only of defining the limits within which the simplifying assumptions could be regarded as still applicable. That the range of validity of the van't Hoff theory is comparatively small, in the case at least of solutions of cane sugar, is shown by the determinations of Morse and his co-workers as well as, more strikingly, by the experiments of Lord Berkeley and E. G. J. Hartley. Although better agreement is obtained when the osmotic pressures are calculated according to the method of Morse, still the need is felt for an expression which shall represent the quantitative properties of a solution over a wider range of concentration. The question therefore arises: What form shall this expression for a general theory of solutions take?

## CHAPTER V.

### THE GENERAL THEORY OF IDEAL SOLUTIONS.

ATTEMPTS to obtain a general theory of solutions, that is to say, an expression which will represent the quantitative relationships of solutions of any concentration, have been made in various directions. The striking analogy which was shown by van't Hoff to exist between dilute solutions and gases seemed to point quite naturally to the view that the van't Hoff laws, when applied to concentrated solutions, would have to be modified in much the same way as the laws for gases under high pressures. In other words, it was thought that the quantitative relationships between osmotic pressure and concentration should be expressed by an equation similar to that of van der Waals for gases.

Equations more or less of that form have been put forward by Bogdan,<sup>49</sup> Bredig,<sup>50</sup> Noyes,<sup>51</sup> Abegg,<sup>52</sup> Ewan,<sup>53</sup> Wind,<sup>136</sup> Sackur,<sup>137</sup> and others; and, recently, Lord Berkeley and E. G. J. Hartley<sup>54</sup> have attempted to find an expression to cover the range of determinations carried out by them. Out of some fifty modifications of the van der Waals equation, two were found to express, with fair accuracy, the experimental relationships. These two equations are:

$$(A/v - p + a/v^2)(v - b) = RT \quad . \quad . \quad . \quad (1)$$

$$(A/v + p - a/v^2)(v - b) = RT \quad . \quad . \quad . \quad (2)$$

In these two equations  $a/v^2$  is a factor intended to correct for a mutual attraction of the solute molecules, while the term  $A/v$  is a correction for the attraction between solvent and solute. In the equation (1),  $v$  represents the volume of the *solvent* which contains one gram-molecule of solute; and in (2),  $v$  represents the volume of the *solution* which contains the gram-molecular weight. The following Tables XIII and XIV give the results obtained on applying these equations to the calculation of the osmotic pressures of solutions of cane sugar and of glucose,

TABLE XIII.—CANE SUGAR SOLUTIONS.

Concentration (Grams of Sugar in 1 Litre of Solution).	$v$ (Equation 1).	$v$ (Equation 2).	Calculated Osmotic Pressure (Equation 1).	Calculated Osmotic Pressure (Equation 2).	Observed Osmotic Pressure.
850	0.18270	0.39722	(183.0)	(183.0)	183.0
760	0.23656	0.45025	(133.7)	(133.7)	133.7
660	0.29883	0.51177	(100.8)	(100.8)	100.8
540	0.41431	0.62570	68.4	67.7	67.5
420	0.59471	0.80492	45.0	43.4	44.0
300	0.91883	1.12764	27.7	25.4	26.8
180	1.67368	1.88094	14.6	12.2	14.0

The constants of equation (1) are,

$$A = 45.3689, a = 3.5696, b = 0.05266.$$

and of equation (2) they are,

$$A = 6.7166, a = 7.2960, b = 0.25139.$$

TABLE XIV.—GLUCOSE SOLUTIONS.

Concentration.	$v$ (Equation 1).	$v$ (Equation 2).	Calculated Osmotic Pressure (Equation 1).	Calculated Osmotic Pressure (Equation 2).	Observed Osmotic Pressure.
549	0.21326	0.32435	(121.2)	(121.2)	121.2
449	0.28601	0.39664	(87.9)	(87.9)	87.9
319	0.44838	0.55824	(53.2)	(53.2)	53.2
200	0.78438	0.89357	28.8	28.4	29.2
100	1.67913	1.78789	12.9	12.4	13.2

The constants for equation (1) are,

$$A = 43.0512, a = 3.0089, b = 0.06069,$$

and for equation (2) they are,

$$A = 3.3845, a = 2.9706, b = 0.10762.$$

On comparing the agreement between the calculated and observed osmotic pressures, there seems to be but little difference between the applicability of the two equations. On the whole, equation (1) appears to be the more satisfactory over the present range; though it is probable, according to Lord Berkeley and E. G. J. Hartley, that the second one, having the positive sign for  $p$ , may replace it at higher dilutions. It appears, however, that these equations will hold good only over a limited range of values.

Moreover, as Callendar<sup>55</sup> has stated, the above method of taking account of the discrepancy between the values of the

osmotic pressure determined experimentally and calculated according to the van't Hoff theory cannot be regarded as satisfactory, because so many different types of equation are possible, and the empirical constants cannot be interpreted, or predicted from other properties of the substances concerned.\*

Similar ideas underlie the modification of the van't Hoff theory suggested by Morse.<sup>56</sup> During the course of their experiments, Morse and his collaborators found that better agreement was obtained between the experimental and the calculated values, if the assumption is made that the osmotic pressure is equal to the pressure which the substance would exercise if it existed as a gas in the volume occupied by the *solvent*, not by the solution, as according to the van't Hoff theory. This modification of the van't Hoff theory was considered as equivalent to the use of the term  $(v - b)$  instead of  $v$ , where  $v$  is the volume of the solution and  $b$  is a correction term for the volume of the solute molecules; a correction which is especially large in the case of a substance with high molecular weight, like cane sugar. In other words, according to the theory of Morse, the concentration of the solution is expressed in terms of *weight normality*, instead of volume normality. That better agreement is thereby obtained is seen from Table XI (p. 24).

Such attempts at a general theory of solutions, however, offer little hope of success. To regard, as some have done, the van't Hoff theory as a general theory of solutions (although explicitly recognized by van't Hoff as not being so), and to attempt to bring it into harmony with the results of experiments in the case of concentrated solutions by the addition of various terms in order to "correct" the equation in accordance with particular views regarding the constitution of solutions, is scarcely a logical method of procedure. The great simplicity of the van't Hoff equation was attained owing to the introduction of simplifying assumptions, which are not valid in the case of con-

\* Otto Stern (*Zeitschr. physikal. Chem.*, 1912, 81, 441) has quite recently deduced an expression based on the van der Waals equation for gases, in which the simple equation is modified by the introduction of terms in order to correct for the volume of the solute and also for the attractions between the solvent and the solute molecules. In the case of solutions of carbon dioxide in several organic solvents, Stern found that the osmotic pressure of concentrated solutions obeyed the law of ideal gases deduced on the above basis.

centrated solutions. At the very outset, therefore, from the purely mathematical point of view, there is a very good reason for the invalidity of the van't Hoff equation in the case of concentrated solutions.

To obtain a general theory of solutions, therefore, it will be better to go back once more to the general thermodynamic equation; but instead of introducing the simplifying assumption that the solution is infinitely dilute, we shall introduce the assumption that the solution is "perfect" or "ideal". By this means, the thermodynamic equation can be simplified, just as the general gas equation is simplified by introducing the assumption of a perfect gas.

This method of obtaining an expression for the quantitative relationships of solutions, was first followed by the Dutch physicists Boldingh,<sup>57</sup> van der Waals,<sup>58</sup> and van Laar,<sup>59</sup> who as long ago as 1893-4 had deduced exact equations for the physical properties of solutions, which were independent of the concentration. Similar equations have also been deduced by Willard Gibbs,<sup>60</sup> T. Ewan,<sup>61</sup> J. E. Trevor,<sup>62</sup> G. N. Lewis,<sup>63</sup> and E. W. Washburn.<sup>64</sup> A good account of the theory of ideal solutions, with applications to different solutions, is given by K. Ikeda.<sup>65</sup>

The complete thermodynamic equation for solutions will involve factors the value of which will vary from case to case, and will depend on the number of components forming the solution, on the molecular state of the components, on the change of volume which occurs on mixing, on the heat of dilution, compressibility of the solution, etc. The expression would therefore be a very complicated one, and it is necessary to introduce some simplification. Such simplification can be introduced if we assume that we are dealing with a solution of only two completely miscible components and that these components have normal molecular weight, that is, they undergo neither dissociation nor association. Further, it will also be assumed that the components do not interact with each other, and that there is neither change of the total volume nor any heat effect when the solution is diluted. By the introduction of these assumptions we obtain the simplest case of a homogeneous mixture of two components, namely that of which the properties are intermediate between the properties of the pure components and can be calcu-

lated from these properties by means of the mixture formula. Such a solution is called an *ideal* or *perfect* solution.

For such a solution, the general equation, valid for any concentration, has been obtained:—

$$P = p - p_0 = \frac{RT}{V_0} [-\log_e(1-x)] - \frac{1}{2}aP^2 \quad . \quad . \quad (3)$$

In this expression  $p$  represents the pressure on the solution and  $p_0$  that on the solvent, when the solvent and solution are in equilibrium through a membrane permeable only to the solvent. In other words,  $P$ , the osmotic pressure, is put equal to the additional pressure which must be placed on the solution in order to prevent the inflow of solvent through a perfectly semi-permeable membrane;  $x$  is the molar fraction of the solute, or the ratio of the number of molecules of solute to the total number of molecules present;  $V_0$  is the molecular volume of the solvent under the standard pressure; and  $a$  is the coefficient of compressibility of the solvent.

The coefficient of compressibility is open to experimental determination, but it is obvious that the compressibility factor will be negligible except under very high pressures. In most cases, therefore, this factor can be omitted, and the general equation can thereby still further be simplified, so that we obtain as the general equation for the osmotic pressure:—

$$P = \frac{RT}{V_0} [-\log_e(1-x)] \quad . \quad . \quad . \quad (4)$$

By expanding the term  $[-\log_e(1-x)]$  in the form of a series, we obtain the more convenient form of the equation:—

$$P = \frac{RT}{V_0} (x + \frac{1}{2}x^2 + \frac{1}{3}x^3 + \dots) \quad . \quad . \quad . \quad (5)$$

### Experimental Verification of the Theory.

The theory of "ideal" solutions has here been stated merely as a thermodynamic deduction, of which it is desirable to obtain experimental confirmation. Such confirmation could not be looked for in the case of aqueous solutions, with which practically all direct measurements of osmotic pressure have been carried out, because such solutions, as we shall see more fully later, do not satisfy the definition of "ideality". Verification of the thermodynamic equation must therefore be looked for in other directions.

It has already been said that the osmotic work  $PV$  represents



the energy required to separate isothermally and reversibly a volume  $V$  of solvent from a solution having the osmotic pressure  $P$ , by means of a perfectly semi-permeable membrane. The same volume of solvent can, however, be separated from the solution in other ways, e.g. by evaporation or by freezing; and in these cases the free surface layer of the solution, and the bounding surfaces of the crystalline solvent act, as it were, as the semi-permeable membranes. If these processes are carried out isothermally and reversibly, the work done must be the same as when the separation of solvent is effected mechanically by means of a semi-permeable piston. There must, therefore, be a definite relationship between the osmotic pressure, the vapour pressure and the freezing-point of a solution; so that if we determine the vapour pressure or the freezing-point of a solution relatively to that of the pure solvent, we are enabled to calculate the osmotic pressure of the solution.\* This fact is of the highest importance in connexion with the quantitative study of concentrated solutions; for it must be evident from what was stated previously that the difficulties surrounding the direct determination of osmotic pressures (e.g. difficulty of securing a perfectly semi-permeable membrane, difficulty of preventing distortion of apparatus, etc.) are so great as to preclude all hope of obtaining direct measurements of osmotic pressure sufficiently varied and extended in scope to furnish an experimental basis for a general theory of solutions. By means of freezing-point determinations, however, and of vapour pressure measurements, the quantitative relationships can be ascertained not only for a great variety of solvents but also for a wide range of concentration and of temperature. Such measurements, moreover, can be carried out with greater accuracy than the direct determinations of osmotic pressure; and it is, therefore, to such measurements that we must look for experimental verification of the thermodynamic equations.

The thermodynamic equation connecting the osmotic pressure with the vapour pressure of solutions, has been worked out by several mathematicians, to whom reference will be made later (Chap. VII). For the present the relationship may be written thus:—

\* It must constantly be borne in mind that the term osmotic pressure is employed in the sense of the equilibrium pressure obtainable with a perfectly semi-permeable membrane.

$$P = - \frac{RT}{V_o} \log_e \frac{p}{p_o} \quad (6)$$

where P is the osmotic pressure,  $V_o$  is the molecular volume of the solvent,  $p$  is the vapour pressure of the solution and  $p_o$  the vapour pressure of the solvent. In this simplified expression the compressibility of the solution is neglected, and the assumption has also been made that the vapour follows the gas laws. By means of this equation the fundamental equation (4) can be tested.

To carry out this test it is, of course, necessary to employ solutions which can be regarded as "ideal"; and this requirement is satisfied by a number of mixtures of organic hydrocarbons and halogen compounds. In the case of such solutions the partial vapour pressure of each of the components is proportional to its molar fraction, and obeys therefore the simple law of mixtures.

When, now, equation (6) is applied to such solutions, the vapour pressure law and, consequently, the fundamental equation (4) are found to be verified. This is seen from Table XV, which refers to mixtures of ethylene bromide and propylene bromide. The vapour pressures of these solutions have been determined by v. Zawidzki<sup>66</sup> and the osmotic pressures have been calculated therefrom by Lewis.<sup>63</sup>

In the following table the first column gives the molar fraction of propylene bromide (the "solute"); the second, the partial pressure of ethylene bromide (the "solvent"); and the succeeding columns give the values of the "osmotic pressure," calculated respectively by the equations of van't Hoff, and of Morse, and by the thermodynamic equation (4) for ideal solutions. In the last column are given the values of the osmotic pressure, calculated by the equation (6).

TABLE XV.—PROPYLENE BROMIDE AND ETHYLENE BROMIDE AT 85°.

Molar Fraction of Propylene Bromide.	Partial Vapour Pressure of Ethylene Bromide.	van't Hoff.	Morse.	Equation (4).	Equation (6).
0.0	172.6	—	—	—	—
0.147	145.1	47	55	51	55
0.298	121.1	90	136	113	114
0.526	81.9	150	351	241	240
0.720	48.0	198	820	412	414
0.860	23.5	232	1960	640	649
0.915	13.8	241	3440	806	827

The above table illustrates how closely the thermodynamic equation for ideal solutions agrees with the results of experiment, and serves, at the same time, to illustrate the inadequacy both of the van't Hoff and of the Morse method of calculating osmotic pressures in the case of concentrated solutions. Since the concentration of the solution varies from 0 per cent to about 90 per cent of one component (propylene bromide), the value of the thermodynamic equation as representing a general theory of solutions, as well also as the value of the conception of ideal solutions, are well illustrated. The equation is found to hold equally well in the case of a considerable number of other binary mixtures of normal, completely miscible liquids.<sup>64</sup>

### Temperature Coefficient of Osmotic Pressure.

In deducing the equation for the relationship between the osmotic pressure and the concentration in the case of ideal solutions, the assumption was made, as part of the definition of an ideal solution, that there is no change in the total volume and no heat effect on dilution. In considering the influence of temperature on the osmotic pressure, it is necessary to take the heat of dilution into account.

As the general thermodynamic equation for the diminution of the free energy in an isothermal reversible process, we have the well-known expression,

$$F = Q + T \frac{dF}{dT} \quad . \quad . \quad . \quad . \quad (7)$$

where  $F$  is the diminution of the free energy and  $Q$  the decrease of the total energy at the absolute temperature  $T$ . In the case where 1 gram of solvent passes reversibly and isothermally into a large quantity of solution through a semi-permeable membrane the diminution of the free energy is represented by  $Pv_s$ , where  $P$  is the osmotic pressure and  $v_s$  is the increase of volume produced. If  $Q$  is the heat of dilution at constant temperature, we obtain the expression,<sup>67</sup>

$$Pv_s = Q + T \frac{\partial(Pv_s)}{\partial T} \quad . \quad . \quad . \quad . \quad (8)$$

The value of  $v_s$  is given by the equation,<sup>68</sup>

$$v_s = \frac{1}{\delta} \left( 1 + \frac{s}{\delta} \frac{d\delta}{ds} \right) \quad . \quad . \quad . \quad . \quad (9)$$

where  $\delta$  is the density of the solution and  $s$  is the weight of solute contained in 1 gram of solution.

In order to integrate the differential equation (8), it is necessary to know how  $Q$  varies with the temperature, and this must be determined experimentally. The general effect of heat of dilution on the osmotic pressure can, however, be obtained by making various assumptions with regard to the heat of dilution and its variation with the temperature.

On the assumption that  $Q=0$ , the integral of equation (8) becomes

$$\frac{P_1 V'_s}{T_1} = \frac{P_2 V''_s}{T_2} \quad \dots \quad (10)$$

where  $V_s$  is the increase of volume when 1 mole of solvent is added to the solution. That is to say, the product  $PV_s$  is proportional to the absolute temperature.

From this, then, it will be seen that in order that the van't Hoff-Gay-Lussac law shall be valid, it is necessary that the heat of dilution shall be zero, and at the same time that the volume change on dilution shall be independent of the temperature. Obviously both these conditions will be satisfied in the case of infinitely dilute solutions. In the case of concentrated solutions, however, it is equally obvious that simple proportionality between osmotic pressure and the absolute temperature will not obtain, when the heat of dilution has an appreciable value, unless there are concomitant and compensatory changes in  $V_s$ ; which is scarcely to be regarded as probable, but which can, in any given case, be determined.

If, however, the heat of dilution is not equal to zero, the form of equation giving the variation of osmotic pressure with the temperature will depend on the manner of variation of  $Q$  with the temperature. If, for example,  $Q$  is constant, independently of the temperature, then one obtains, on integrating equation (8),

$$\frac{P_1 V'_s - Q}{T_1} = \frac{P_2 V''_s - Q}{T_2} \quad \dots \quad (11)$$

That is to say,  $PV_s - Q$  is proportional to the absolute temperature; or the osmotic work is proportional to the absolute temperature plus  $Q$ .

When  $Q$  is not independent of the temperature, other, more

complicated, relationships are obtained between the osmotic pressure and the temperature.

It is worthy of special note that when the heat of dilution is appreciable, the osmotic pressure cannot be calculated from the simple relationship  $P = \frac{RT}{V}$ . Where there is a marked evolution

of heat on dilution, the osmotic pressure obtained will be abnormally high (as compared with an ideal solution); and consequently, when molecular weights are calculated from these values, abnormally low results will be obtained. It is necessary, therefore, in such cases to take the heat of dilution into account, as has been emphasized more especially, in recent years, by T. Ewan<sup>67</sup> and by W. D. Bancroft.<sup>67</sup>

The importance of this is seen, for example, in the case of solutions of sulphuric acid in water, where there is a marked positive heat of dilution. As Bancroft has shown, when one calculates the molecular weight of sulphuric acid from the osmotic pressure of its solutions, values ranging from 57.7 in a 5.6 per cent solution, to 11.7 in a 68.5 per cent solution are obtained if the heat of dilution is neglected. If, however, the heat of dilution is taken into account, the molecular weights obtained *increase* with increasing concentration, as one would expect.

Even in the case of what one might justly call dilute solutions, it will not be possible to calculate accurately the osmotic pressure of a solution from the simple formula  $PV = RT$ , if the heat of dilution is large, and, consequently, molecular weights calculated from such osmotic pressure will also be erroneous.

## CHAPTER VI.

### DISCUSSION OF THE OSMOTIC PRESSURE OF AQUEOUS SOLUTIONS OF CANE SUGAR IN THE LIGHT OF THE THEORY OF IDEAL SOLUTIONS.

We have already seen that for ideal solutions the relation between osmotic pressure and concentration can be represented by equation (4), or the identical equation (5). The latter equation can also be written in the form

$$P = \frac{RT}{V_0} \cdot x (1 + \frac{1}{2}x + \frac{1}{3}x^2 \dots) \quad (12)$$

If the concentration of the solution is expressed in terms of  $c$  gram-molecules of solute in 1000 grams of water (as was done by Morse), we can put  $x = \frac{c}{55.5 + c}$ , where 55.5 represents number of gram-molecules in 1000 grams of water, if the association of the latter is neglected. Since the molecular volume of water at 20° is 1001.8/55.5 (neglecting association) we may write:—

$$P = \frac{81.6 \times 293 \times 55.5}{1001.8} \cdot \frac{c}{55.5 + c} \left[ 1 + \frac{1}{2} \left( \frac{c}{55.5 + c} \right) \dots \right] \quad (13)$$

which is the expression for the osmotic pressure of solutions at 20°, if we regard the solution as being "ideal". In Table XVI the osmotic pressure of cane-sugar solutions at 20° has been calculated by means of this equation.\*

From table on next page it will be seen that the values of the osmotic pressure calculated by the method of Morse are practically identical with those calculated according to the thermodynamic equation (13). The reason for this is not far to seek.

\* It should be noted that in equation (13) the value of R has been taken as 81.6 (c.c., atm.), instead of the more usual value 82.07, because Morse based his calculations on the standard  $H = 1$ .

TABLE XVI.—OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 20°

Weight Normal Concentration.	Osmotic Pressure Observed.	Osmotic Pressure Calculated according to	
		Morse.	Equation (13).
0.1	2.59	2.39	2.38
0.2	5.06	4.78	4.76
0.3	7.61	7.17	7.14
0.4	10.14	9.56	9.51
0.5	12.75	11.95	11.87
0.6	15.39	14.34	14.24
0.7	18.13	16.73	16.59
0.8	20.91	19.12	18.94
0.9	23.72	21.51	21.29
1.0	26.64	23.90	23.64

Morse, as has already been pointed out, expressed the osmotic pressure as a function of the concentration represented by  $\frac{n}{N}$ , or by the ratio of the number of solute molecules to solvent molecules.

This ratio can also be written in the form  $\frac{x}{1-x}$  where  $x$  is the molar fraction of the solute. The equation of Morse therefore takes the form

$$P = \frac{RT}{V_0} \left( \frac{x}{1-x} \right) = \frac{RT}{V_0} (x + x^2 + x^3 + \dots) \quad (14)$$

It must, however, be remembered that in the equation as used by Morse,  $V_0$  refers to the temperature of 4° and not to that of the experiment.

The further difference between equation (14) and equation (13) for ideal solutions, appears only in the term  $x^2$  (and higher powers of  $x$ ) and will therefore become appreciable only at higher concentrations\* and at higher temperatures (owing to the variation of  $V_0$ ).

\* In view of the fact that the success which attended the application of Morse's method of expressing concentration to the calculation of osmotic pressures, has led other workers (e.g. H. E. Armstrong and his collaborators; cf. Walden, *Zeitschr. physikal. Chem.*, 1907, 58, 500) to adopt that method also in connexion with their investigations of concentrated solutions, the above relationship may be emphasised. The special virtue of the Morse method of calculation, which was previously employed in connexion with concentrated solutions by Cohen (*Zeitschr. physikal. Chem.*, 1897, 23, 442), lies not in its being a modification of the van't Hoff equation on the lines of the van der Waals correction for gases, but in its being an approximation to

A comparison of equation (4) with that of van't Hoff will show very clearly the nature of the simplifying assumptions introduced, and will explain the inadequacy of the van't Hoff equation when applied to concentrated solutions.

Since  $x$  represents the molar fraction, equation (5) can be written in the form

$$P = \frac{RT}{V_0} \left[ \left( \frac{n}{N+n} \right) + \frac{1}{2} \left( \frac{n}{N+n} \right)^2 + \dots \right] \quad (5a)$$

If, now, the assumption is made that the solution is infinitely dilute, then  $\left( \frac{n}{N+n} \right)$  becomes equal to  $\frac{n}{N}$ ,  $n$  being negligible compared with  $N$ . When, however, this is so, it follows that the fraction  $\left( \frac{n}{N+n} \right)$  becomes very small and consequently  $\left( \frac{n}{N+n} \right)^2$  and higher powers of the fraction, become negligible. For very dilute solutions, therefore, the thermodynamic equation reduces to

$$P = \frac{RT}{V_0} \cdot \frac{n}{N} \quad (15)$$

But  $NV_0$  represents the volume of the water in the solution, and this, in the case of very dilute solutions, can be put equal to the volume of the solution itself. For the limiting case of very dilute solution, therefore, we obtain the van't Hoff equation

$$P = \frac{nRT}{V} \quad (16)$$

where  $V$  is the volume of the *solution*.

### Deviations of Aqueous Solutions from the Ideal Condition.

From Table XVI it is seen that although the values of osmotic pressure obtained by means of the thermodynamic equation (13) are in considerably better agreement with the observed values than are those calculated according to the theory of van't Hoff, the two sets of values are by no means in perfect concordance. We must, therefore, conclude that in the case of the solutions under consideration, one or more of the assumptions introduced in the deduction of the thermodynamic equation is

the general thermodynamic equation. Being merely an approximation, it will necessarily have its limitations, which should be borne in mind when making use of it.



no longer valid; that is to say, these solutions do not accord with the definition of ideal solutions which was stated previously. The assumptions made were:—

1. The components of the solution are neither associated nor dissociated.
2. The components of the solution do not interact with each other.
3. The components of the solution mix without change of volume or heat effect.
4. The solvent is incompressible.

With regard to these assumptions, it may be said that Nos. 3 and 4 are open to experimental determination, and the extent of their validity can therefore be defined; in the case of the fourth assumption, it is obvious that this can introduce an appreciable error only at very high pressures. The importance of the heat of dilution has already been pointed out (p. 34). The first and second assumptions, however, are not open, in the same direct manner, to experimental determination; and it is in connexion with these assumptions that hypotheses regarding the nature and constitution of solutions can rightly claim consideration.

So far as the aqueous solutions of cane sugar, which are at present under consideration, are concerned, it is clear that the first property postulated for ideal solutions is not possessed by them; for it may certainly be concluded that water is associated. This fact, then, should be taken into account in applying the thermodynamic equation; that is to say, the molecular volume,\*  $V_o$ , at  $20^\circ$ , will not be equal to  $\frac{1001.8}{55.5}$ , but to  $\frac{1001.8}{55.5 \div a}$ , where  $a$  represents the association factor. Taking, according to van Laar,<sup>69</sup> the value of  $a$  as equal to 1.65 at  $20^\circ$ , we obtain  $V_o = \frac{1001.8}{34}$ ; and if the osmotic pressure of a weight-normal solution be now calculated by means of the general thermodynamic equation, one obtains the value 23.50 in place of the previous value 23.64

\* It may again be recalled that the use of  $V_o$  in the equation for concentrated solutions involves the assumption that there is no change in volume on dilution. This is nearly true in the case of solutions of cane sugar. See, however, Lord Berkeley, E. G. J. Hartley and C. V. Burton, *Phil. Trans.*, 1908, A. 209, 177.

(Table XVI). Up to this concentration, therefore, the influence of association of the solvent is but slight.

Since differences are still found between the experimental values of the osmotic pressure and those calculated by the thermodynamic equation, we are led to the conclusion that the remaining assumption is not justified, and that the further deviations are due to association or dissociation of the solute or to hydration or combination of the solvent and solute. The last mentioned seems the most plausible assumption.

If it be assumed that one molecule of solute combines, on an average, with  $\beta$  molecules of solvent, we must introduce into equation (13) the factor  $\frac{c'}{55.5 + c' - \beta c'}$  (where  $c'$  is the concentration of the hydrated molecules) in place of  $\frac{c}{55.5 + c}$ . Introducing the further assumption that  $\beta = 5$ , and that it remains constant throughout the range of concentration studied, we obtain the values given in the following Table XVII. In the last two columns of this table are given the values of osmotic pressure calculated on the assumptions, respectively, that water is not associated and that it is associated ( $a = 1.65$ ).

TABLE XVII.—OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 20°.

Weight Normal Concentration.	Osmotic Pressure Observed.	Osmotic Pressure calculated according to Equation (13).			
		Assuming no Hydration of Solute and no Association of Solvent.	Assuming no Hydration of Solute but Association of Solvent.	Assuming Hydration = 5H <sub>2</sub> O	
				Solvent not Associated.	Solvent Associated.
0.1	2.59	2.38	2.38	2.41	2.42
0.2	5.06	4.76	4.76	4.85	—
0.3	7.61	7.14	7.13	7.33	7.45
0.4	10.14	9.51	9.49	9.87	—
0.5	12.75	11.87	11.84	12.43	12.78
0.6	15.39	14.24	14.19	15.05	—
0.7	18.13	16.59	16.53	17.71	18.40
0.8	20.91	18.94	18.85	20.42	—
0.9	23.72	21.29	21.19	23.15	24.37
1.0	26.64	23.64	23.50	25.96	27.50

From the above table it is seen that by assuming that cane sugar forms a pentahydrate, but that the water is non-associated, values are obtained for the osmotic pressure which are in good agreement with those observed, although the former are all

somewhat lower than the latter. If it is assumed that the water is associated as well as that the sugar is hydrated, fair agreement between the calculated and observed values is also obtained, but in this case the calculated values become greater than the observed values, in the more concentrated solutions. If it is assumed that the water is not associated but that the cane sugar forms a hexahydrate, the calculated osmotic pressure of a weight normal solution is 26.47 atm., which is in practically exact agreement with the observed value. In making these calculations, no account has been taken of a possible alteration in the association of the water by the presence of the solute. Since, however, there exists at present no independent means of deciding the exact degree of association of water in the aqueous solution, nor the degree of hydration of the solute, it appears to be doubtful whether any more definite conclusion can be drawn than that in aqueous solution at 20°, cane sugar is hydrated to the extent of approximately 5H<sub>2</sub>O. Moreover, this degree of hydration appears to remain nearly constant over the range of concentrations investigated, for Callendar<sup>55</sup> has shown that the osmotic pressures calculated on this assumption (but neglecting association of the water) agree with the values determined at 0° by Lord Berkeley and E. G. J. Hartley, as is seen from Table XVIII. Washburn,<sup>70</sup> by the application of the thermodynamic

TABLE XVIII.—OSMOTIC PRESSURE OF SOLUTIONS OF CANE SUGAR AT 0°

Grams Sugar in 1 Litre of Solution.	Osmotic Pressure in Atmospheres.	
	Calculated, assuming the Formation of a Pentahydrate.	Determined by Lord Berkeley and Hartley.
180.1	14.1	13.95
300.2	26.8	26.77
420.3	43.7	43.97
540.4	67.6	67.51

equation to the freezing point determinations of solutions of cane sugar, has concluded that the latter exists in solution as the hexahydrate. For the case of solutions of lower concentration than weight-normal, it is, however, scarcely possible to decide between the two hydrates.

Callendar similarly has shown that in the case of glucose

solutions, the glucose molecule probably combines with two molecules of water.

Tentative as the above calculations may be, it is of importance to observe that by assuming association of solvent and hydration of the solute molecules, it is possible to take into account simply and without undue straining of probabilities, the deviations from "ideality" in the case of concentrated aqueous solutions. Moreover, it is of importance to note that by determining the deviations of solutions from "ideality," a means is given of obtaining a truer insight into the constitution of solutions than when one applies, as some investigators have done, to concentrated solutions an equation, such as that of van't Hoff, which is valid only for very dilute solutions.

In connexion with the assumption that cane sugar is hydrated in aqueous solution, it is of interest to note that, as emphasised by Callendar, agreement between the calculated and experimental values of the osmotic pressure is obtained on the supposition that the degree of hydration is constant; that is to say, on the supposition that a definite hydrate, e.g.  $C_{12}H_{22}O_{11} \cdot 5H_2O$ , is formed which persists throughout a range of concentration. This fact, which leads to the view that definite stable hydrates are formed, is contrary to that sometimes expressed<sup>71</sup> that unstable hydrates are formed, the composition of which continuously undergoes change with the concentration, but is in harmony with the older hydrate theory of solutions as put forward, for example, by Mendeléeef.

### Variation of Osmotic Pressure with the Temperature.

It has already been pointed out (p. 34) that the temperature coefficient of osmotic pressure depends on the heat of dilution and its manner of variation with the temperature. In view of the fact that the heat of dilution is very small in the case of solutions of cane sugar, it is to be expected that the osmotic pressure will be nearly proportional to the absolute temperature.\* As has already been pointed out (p. 26), the experiments of Morse

\*G. N. Lewis (*J. Amer. Chem. Soc.*, 1908, 30, 668) has pointed out that, using the heats of dilution as determined by Ewan and von Stackelberg, the osmotic pressure of a weight-normal solution of cane sugar at 15° would change about 0.27 per cent per degree, while an ideal solution would change about 0.35 per cent per degree.

and his co-workers are in harmony with this view when the range of temperature is not very great ( $0^{\circ}$  to  $25^{\circ}$ ).

The value of  $Q$ , however, although small is not zero, and in order to ascertain the temperature coefficient of osmotic pressure over a large range of temperature, it is necessary to know the temperature coefficient of  $Q$ . This has been given by Ewan<sup>67</sup> in the form

$$\frac{dQ}{dT} = c_w - c_s - (1 + m) \frac{dc_s}{dm} \quad . \quad .$$

where  $c_w$  and  $c_s$  are the specific heats of water and of the solution respectively. The experimental determinations are not free from doubt, but it would appear that  $\frac{dQ}{dT}$  is either zero or has a small negative value. Throughout a considerable range of temperature, therefore, we may expect that the osmotic pressure will be nearly proportional to the absolute temperature; and it may also be expected that at higher temperatures the osmotic pressure will be less than that calculated according to direct proportionality, if it be the case that  $\frac{dQ}{dT}$  is negative.

On consulting Table XII., p. 25, it is seen that the ratio of osmotic pressure to gas pressure is approximately constant for all concentrations up to  $25^{\circ}$ , but that above that temperature the ratio becomes less, especially in the more dilute solutions. At the temperature of  $80^{\circ}$  the ratio has become equal to unity even in the most concentrated solutions. It follows therefore that the osmotic pressure at  $80^{\circ}$  is less than it would be if calculated from the osmotic pressure, say at  $20^{\circ}$ , by the law of direct proportionality. The value so calculated would be 32.10 atm., the value found is 28.00 atm., for a weight normal solution.

One ought, however, to beware of attributing this difference solely to the influence of heat of dilution. When it is recalled that the osmotic pressure is dependent on the factor  $\frac{n}{N+n}$ , and when it is remembered not only that the solvent is associated but that hydrate formation probably also occurs, it is clear that the change of osmotic pressure with temperature will also depend on any changes which may occur either in the degree of association of the solvent, or in the composition of the hydrate or hydrates, the existence of which has been assumed.

As regards the association factor of the solvent, it is known that this diminishes with rise of temperature, the complex water molecules dissociating into the simpler monad molecules; and it is also to be expected that elevation of temperature will bring about a dissociation of the solute hydrate. Both these effects will result in a higher value for  $(N + n)$ , and consequently in a lower value of the osmotic pressure. Without, therefore, taking into consideration at all the influence of the heat of dilution on the osmotic pressure, it must be expected that in the case of concentrated aqueous solutions, more especially but not only when hydrates are formed, the osmotic pressure will increase with the temperature less rapidly than corresponds with the van't Hoff-Gay-Lussac law.

A simple calculation will illustrate this. We have already seen that using the equation

$$P = \frac{81.6 \times 293 \times 34}{1002} \cdot \frac{c}{34 + c} \left[ 1 + \frac{1}{2} \left( \frac{c}{34 + c} \right) \right]$$

the value 23.50 atm., was calculated for the osmotic pressure of a weight normal solution at 20° (Table XVII). If we carry out a similar calculation for the osmotic pressure of a weight-normal solution at 80°, again assuming no hydration of the solute, but remembering that the molecular volume of the solvent is now \*  $\frac{1032}{38.0}$ , we obtain the value of 27.56 atm., for the osmotic pressure, which is in very fair agreement with the value 28.00 atm., determined by Morse, and his collaborators.<sup>72</sup> Even when no association of the solvent is assumed, a similar value, 28.16 atm., is calculated. From this, then, it appears that, without assuming the formation of a hydrate of cane sugar, the calculated value of the osmotic pressure is in agreement with the experimentally determined value; a fact which indicates that at a temperature of 80° the hydrate, the existence of which was assumed (and with which assumption the results of experiment were in harmony) is completely dissociated.

It should, however, be mentioned that according to Callendar's calculations<sup>55</sup> based on the determinations by Kahlenberg<sup>73</sup> of the boiling point of cane sugar solutions, the pentahydrate still

\* At 80°, the association factor of water is, according to van Laar (*Zeitschr. physikal. Chem.*, 1899, 31, 1), 1.46.

exists at that temperature in the case of the more dilute solutions, but dissociates with formation of a lower hydrate as the concentration increases.

It will, however, be realized that the preceding calculations, interesting as they are, are of a somewhat tentative character; and although Callendar has shown that by the assumption of hydrate formation the actual behaviour of aqueous solutions of a number of different solutes can be explained, a larger number of accurate determinations of the osmotic pressure and a more complete investigation of the different factors which enter into the problem, are much to be desired. That the study of osmotic pressures may possess an importance beyond that of yielding a basis for a quantitative theory of solutions and may be brought into relation with the problem of saturation and supersaturation in solutions, has recently been shown by the Earl of Berkeley.<sup>133</sup>

### Summary.

It may perhaps be well, at the close of this chapter to refer to some of the criticisms which, even recently, have been expressed regarding the osmotic theory of solutions and the thermodynamic treatment of the problem.

In the first place, recent critics have pointed out that van't Hoff's theory cannot be a correct theory of solutions because it is no longer valid when applied to concentrated solutions. But as has already been stated van't Hoff's theory never claimed to be valid except for very dilute solutions, and for these the theory is perfectly valid. The adverse criticism is therefore really levelled not against the theory of van't Hoff itself, but against the abuse of the theory and its unjustifiable extension to regions of concentration to which van't Hoff never intended that it should be applied. The theory itself, when properly applied, does not thereby lose its validity.

But another ground on which adverse criticism has been levelled against the osmotic theory of solutions from the time of its enunciation to the present day (e.g. by L. Meyer,<sup>74</sup> Quincke,<sup>75</sup> Kahlenberg<sup>38</sup>) is that osmotic pressure is not due to the bombardment of the semi-permeable membrane by the solute molecules (as had indeed been suggested as a plausible explanation by van't Hoff), but is due to the entrance of solvent into the solution through the semi-permeable membrane. But this criticism rests

on a misunderstanding. The employment of the conception of osmotic pressure in the thermodynamic deduction of the laws of solutions is quite independent of any view which may be held regarding its nature; and this was pointed out by van't Hoff himself.<sup>76</sup> In his thermodynamic treatment of solutions, van't Hoff employed the conception of osmotic pressure as an experimentally determinable quantity which could be introduced into the thermodynamic treatment, and about the nature of which there was no need to trouble oneself. Thus he wrote<sup>77</sup>: "Once again we have the essentially futile question, what then exerts the osmotic pressure? Really, as already emphasized, I am concerned only with its magnitude; and since it has been found to be equal to the gas pressure, one is inclined to think that the mechanism of its production is similar to that found in the case of gas pressure. Let him, however, who is led astray by this view, simply leave the question of mechanism alone altogether."

Another objection has been raised, by Kahlenberg, against the thermodynamic deduction of the quantitative laws of solutions on the two-fold ground that no truly semi-permeable membrane is known, and that, even if one is found to exist, it is not a passive membrane but is selective in its action. The question of the existence of semi-permeable membranes has already been discussed (p. 4), and as regards the passivity of the membrane, the above criticism likewise rests on a misunderstanding. That the property of semi-permeability is a specific and not a universal one, in the case of any membrane, was recognized even by M. Traube, but this does not render the semi-permeable membrane necessarily "active" from the thermodynamic point of view. From this point of view, a passive membrane is merely one with which the processes involved are completely reversible, and if this requirement is satisfied, the mode of action of the membrane is a matter of no importance.

However, important as it no doubt once appeared to be to make sure that a semi-permeable membrane is indeed realisable in practice, because the van't Hoff theory of solutions was developed by the aid of the conception, it is more important, at the present day, to recognize that the quantitative theory of solutions is quite independent of the conceptions either of semi-permeable membranes or of osmotic pressure itself. The one fundamental fact to be recognized, as has been emphasized by



van Laar,<sup>59</sup> Jahn<sup>78</sup> and others, is that there is a difference between the free energy of the solvent in the solution and in the pure state ; and that what is called the osmotic pressure of the solution is, like the diminution of the vapour pressure, merely one manner in which this energy difference is rendered manifest. That this is so is clearly seen from the fact that the thermodynamic equation for ideal solutions has been established by van der Waals, for example, on a kinetic basis ; by van Laar,<sup>59</sup> by the use of the function, introduced by Willard Gibbs, known as the thermodynamic potential ; and, more recently, by G. N. Lewis<sup>79</sup> by means of another thermodynamic function known as the "fugacity". The quantitative laws of solutions, deduced thermodynamically, are therefore quite independent of the phenomena of osmosis altogether ; and the reason why osmotic pressure has played such a prominent rôle in connexion with the problem of solutions is to be found, no doubt, in the fact that it is a property, the meaning of which can be readily grasped, whereas the thermodynamic potential, for example, appears as an abstract conception which is not open to direct experimental demonstration. For this reason the conception of osmotic pressure will, in the future as in the past, indubitably be preferred by many, the more so as the thermodynamic equation for solutions can, of course, be deduced equally well on the basis of this conception as on the basis of the thermodynamic potential, or of other thermodynamic functions.

Valuable as the thermodynamic theory of solutions has proved to be in correlating quantitatively the properties of solutions, it throws but little light on the mechanism of osmosis or on the intimate structure and constitution of solutions. Nor has it ever claimed to do so.\* Thermodynamics gives us a theory of *solutions* ; it gives us no theory of *solution*. For it must be remembered that the problem of solutions consists of two parts, the qualitative and the quantitative. On the one hand, insight is desired into the nature and constitution of a solution, into the processes involved in the production of a solution, whether these depend on chemical affinity, surface tension, or other causes ; and, on the other hand, an equal need is felt for some quantitative expression by means of which the relationships between the concentration of solutions and their physical properties can be studied quantitatively and computed. The qualitative and the

quantitative are, however, but two complementary sides of the one problem ; and while some investigators may attach supreme importance to the qualitative side—to the construction of pictures or models of the constitution of solutions—others will make more use of the quantitative relationships by means of which the efficiency of these models can be tested. It is, however, by mutual understanding and co-operation between the workers on the two sides, that knowledge will finally be attained.

Into a discussion of the constitution of solutions we cannot enter here ; the subject will be dealt with in another monograph in this series. The views which have been held regarding the constitution of solutions have been very varied, and since thermodynamics is too general in its method of treatment to yield a complete answer to the problem, hypothesis, guided and tested by experiment, must enter. Although the previous discussion may indicate that the view that solution is produced by the chemical combination of the components does not, in some cases, run counter to the requirements of thermodynamics, it must be borne in mind that there are also cases where no such combination appears to occur.

Considering how long a period has already passed since the mathematical theory of ideal solutions was first established, it must seem somewhat remarkable that to so many chemists the theory still appears to be so little known, and that even at the present day discussions are seriously carried on regarding the validity of the van't Hoff theory as a general theory of solutions. From what has been said in the previous pages, it will now surely commend itself to chemists to adopt as the basis for the discussion of the properties of concentrated solutions, not the simple van't Hoff equation, which admittedly cannot be correct in the case of such solutions, but the theory of ideal concentrated solutions which was outlined in the previous chapter and applied in the preceding pages to the case of aqueous solutions of cane sugar.

## CHAPTER VII.

### INDIRECT DETERMINATION OF THE OSMOTIC PRESSURE.

AS has already been stated, the manipulative difficulties and, more especially, the difficulty of obtaining truly semi-permeable membranes preclude the possibility of carrying out the direct determination of osmotic pressure over any large range of temperature and concentration in the case of any considerable number of solvents and solutes. It has, however, been pointed out that the osmotic pressure of a solution is merely a measure of the diminution of the free energy of a solvent by the addition of a solute, or a measure of the work done in separating the solvent from the solution, and since these can be determined experimentally by other methods which do not involve ordinary membranes, it becomes possible to determine indirectly the value of what is called the osmotic pressure of a solution. Of the indirect methods of determining the osmotic pressure, those depending on determinations of the vapour pressure, the freezing point and the boiling point of solutions, are the most important. The analogy between such determinations and those carried out directly with precipitation membranes depends on the fact that the surface layer of the solution in contact either with the vapour or with the solid solvent, acts as a semi-permeable membrane, since it allows the passage of the solvent but not of the (non-volatile) solute molecules.

#### **Diminution of the Vapour Pressure.**

The application of the vapour pressure method to concentrated solutions of cane sugar has, in recent years, been studied by Lord Berkeley and E. G. J. Hartley,<sup>80</sup> for the purpose of comparing the values of osmotic pressure determined in this way with those obtained directly with a copper ferrocyanide membrane (p. 20). These investigators have also determined by the same method the osmotic pressure of concentrated aqueous solutions of calcium ferrocyanide.<sup>44</sup> Similar determinations with aqueous

solutions of sodium chloride, potassium chloride, and cane sugar have been made by Krauskopf,<sup>81</sup> and by E. P. Perman and T. W. Price<sup>82</sup> with solutions of carbamide, cane sugar, glycerol, raffinose, potassium chloride and calcium chloride. These investigators have, however, not yet applied their measurements to the determination of the osmotic pressure of the solutions.

The method employed for the determination of the vapour pressure was a dynamical one; first suggested by Ostwald and investigated experimentally by J. Walker.<sup>83</sup> It depends on the principle that when an indifferent gas is bubbled through a liquid, the amount of the latter taken up by the gas is proportional to the vapour pressure. If, then, a stream of air is passed through a solution and then through the pure solvent, the amount of vapour taken up from the latter will be proportional to the difference between the vapour pressure of the solvent and the solution.

In carrying out their determinations, Lord Berkeley and E. G. J. Hartley introduced the modification that instead of causing the air to bubble *through* the liquids, they caused it to pass *over* the surface of the liquids, which were contained in a train of glass tubes placed on a rocking table in a thermostat. By rocking the table, the liquid was caused to flow from end to end of the tubes, thereby keeping the solution stirred and also facilitating the saturation of the air by the vapour.

The values of the osmotic pressure were then calculated from the diminution of the vapour pressure by means of the equation

$$P = \frac{A \cdot s}{\sigma} \cdot \log_e \frac{p_0}{p} \quad \dots \quad (17)$$

where  $p_0$  and  $p$  are the vapour pressures of the water and solution respectively,  $s$  is the density of the water at the temperature of the experiment, and  $\sigma$  is the vapour density of water vapour under the standard atmosphere  $A$ . The following table contains

TABLE XIX.

Grams of Sucrose per Litre.	Osmotic Pressure at 0°, in Atmospheres	
	Deduced from the Vapour Pressure.	Determined Directly.
540	69.4	67.51
660	101.9	100.78
750	136.0	133.74

the values of the osmotic pressure so calculated, together with the values obtained directly by the method already described (p. 18). The values refer to solutions of cane sugar at 0° C.

The accuracy aimed at was 5 per cent, and it will be observed that the deviations between the two sets of values are well within that error.

### Relationship between Osmotic Pressure and Vapour Pressure.

The method formerly employed for deducing the relationship between vapour pressure and osmotic pressure of a solution was to consider the equilibrium between a column of solution separated at the lower end from the pure solvent by means of a semi-permeable membrane, the whole system being enclosed in a vessel containing only the vapour of the solvent. The vapour pressure of the solution at the top of the column would then be equal to the vapour pressure at the surface of the solvent minus the pressure of a column of vapour equal in height to the column of solution, the hydrostatic pressure of which balances the osmotic pressure. In this way Arrhenius<sup>84</sup> obtained an expression which can be written in the form

$$P = \frac{A\varrho}{\sigma} \cdot \log_e \frac{p_0}{p} \quad (18)$$

for the relationship between the osmotic pressure and the vapour pressure. In this expression  $\varrho$  is the density of the solution.

When the osmotic pressure was calculated by means of this equation, Lord Berkeley and E. G. J. Hartley found that values were obtained which differed considerably (up to 30 per cent) from the values obtained by direct measurement. The reason for this Lord Berkeley and Hartley perceived to lie in the variation of density and concentration from top to bottom of the column of solution.\*

Another factor also must be borne in mind. As pointed out by Lord Berkeley and E. G. J. Hartley direct measurement gives the osmotic pressure corresponding to the concentration at the top of the column whereas the value of the osmotic pressure calculated

\* Callendar (*Proc. Roy. Soc.*, 1908, A. 80, p. 474) gives a table showing the variation of concentration in a vertical column of solutions of cane sugar at 0°. From this it appears that in a solution containing 180 grams of cane sugar per litre, the variation amounts to about 7 per cent.

by the equation of Arrhenius gives the osmotic pressure at the bottom of the column. It is therefore necessary to obtain an equation connecting the vapour pressure with the osmotic pressure at the top of the column; and this equation Lord Berkeley and E. G. J. Hartley deduced by a modification of the column method. In this way they obtained equation (17) which, as will be seen, differs from the equation of Arrhenius, equation (18), only in the substitution of  $s$ , the density of the solvent, for  $\rho$ , the density of the solution. In deducing equation (17), the compressibility of the solvent (water) was neglected, and also the pressure of the column of vapour equal to the height of the column of solution.

Another, more exact, expression connecting the osmotic pressure with the vapour pressure of a solution was deduced by W. Spens<sup>85</sup> by the isothermal cycle method, which yields, by neglecting small quantities and assuming that Boyle's law is valid for water vapour,\* the approximate equation

$$Pv_s = sp \log_e \frac{p_o}{p} \quad (19)$$

where  $v_s$  is the *increment in volume* of a large mass of solution when unit mass of solvent is added and  $s$  is the specific volume of the vapour. The equation of Lord Berkeley and Hartley when written in the same form is  $Pu = sp \log_e \frac{p_o}{p}$ , where  $u$  is the

specific volume of the solvent. These two equations will be identical only when the increment produced by the addition of the solvent is equal to the volume of the solvent added; that is, when the contraction on dilution is negligible. Such, indeed, appears to be very nearly the case with solutions of cane sugar, but with other solutions marked differences are sometimes found.

The same problem—the relationship between vapour pressure and osmotic pressure—has also been investigated mathematically by A. W. Porter,<sup>86</sup> who has deduced the general equations applicable to solutions of any compressibility, and, by H. L. Callendar,<sup>55</sup> the method employed in both cases being that of the isothermal cycle.† Both these physicists have emphasised,

\* For higher values of the pressure, this assumption will, of course, introduce a slight error.

† Other deductions of the connection between osmotic pressure and vapour pressure have been made, using the “thermodynamic potential” of

more especially, the important influence of hydrostatic pressure on the osmotic pressure and vapour pressure of a solution; \* for although this factor had been taken into account by Spens, it had been neglected by Lord Berkeley and Hartley. Increase of the hydrostatic pressure increases in general the osmotic pressure and the vapour pressure; and only when the increment of volume produced by the addition of unit mass of solvent to a large mass of the solution is equal to the specific volume of the solvent, is the osmotic pressure at constant temperature independent of the hydrostatic pressure and dependent only on the concentration.

When a solution is in osmotic equilibrium with the pure solvent, the vapour pressure of the solution under the hydrostatic pressure imposed on it in order to maintain osmotic equilibrium, is equal to the vapour pressure of the solvent under the hydrostatic pressure to which it is subjected (the pressure of its own vapour). In defining osmotic pressure, therefore, it is necessary to distinguish between the value corresponding to the solvent under its own vapour alone, and that corresponding to the solution under its own vapour alone. The values obtained by the usual direct methods are for the solvent under atmospheric pressure, which is approximately the same as for the solvent under its own vapour pressure. On the other hand Porter<sup>86</sup> recommends

Gibbs. For these, less readily understood by the non-mathematical reader, reference may be made to Trevor, *Journ. Physical Chem.*, 1906, 10, 392, 1908, 12, 141; or to van Laar, *Sechs Vorträge über das thermodynamische Potential*. See also G. N. Lewis, *Journ. Amer. Chem. Soc.*, 1908, 30, 668, E. W. Washburn, *ibid.* 1910, 32, 653.

\* For the relation between hydrostatic pressure and vapour pressure, Callendar deduced the expression,

$$RT \log_e \frac{p}{p_0} = (c - b) (p - p_0) + V_0 (P - P_0) - \frac{1}{2} a V_0 (P^2 - P_0^2),$$

where  $V$  and  $v$  are the specific volumes of liquid and vapour at the pressures  $P$  and  $p$  respectively;  $P_0$ ,  $p_0$ , are corresponding limits of the pressure at which the specific volumes of liquid and vapour are  $V_0$  and  $v_0$ ;  $(c - b)$  represents the defect of volume of the vapour from the ideal volume (i.e. the deviation from the gas laws); and  $a$  is the coefficient of compressibility of the liquid, which is *assumed* to be constant. According to this equation, Callendar points out, it would require a pressure of about 2000 atms. only, to increase the vapour pressure of water fourfold at 27° C. The term  $(c - b) (p - p_0)$  is negligible at ordinary temperatures (and was neglected by Porter and by Spens), on account of the small value of  $p$ , but it amounts to about 17 per cent at 200°, if  $p/p_0 = 4$ .

the reduction of the osmotic pressure to the value corresponding to the solution under its own vapour pressure; in which case the equilibrium pressure for the solvent would be negative; that is, the solvent would require to be under a tension.

In order to study more fully the relation between osmotic pressure and vapour pressure, Lord Berkeley, E. G. J. Hartley and C. V. Burton<sup>87</sup> supplemented their former determinations of the pressures of sucrose solutions (which they regarded more as preliminary experiments) by measurements of the vapour pressure and of the equilibrium osmotic pressure of aqueous solutions of calcium ferrocyanide. With this salt, solutions of high concentration can be prepared, and for such solutions, moreover, the copper ferrocyanide membrane is truly semi-permeable. To allow of a more exact comparison of equilibrium osmotic pressures and vapour pressures, the compressibility of the solutions was also determined.

From his mathematical investigation of the relation between the osmotic and the vapour pressure of a solution Porter<sup>86</sup> had obtained a general expression for liquids of any degree of compressibility. In the derivation of his equation, Porter assumed the solution and solvent to be under the pressures of their vapour alone, whereas Lord Berkeley and his co-workers carried out their measurements in air. They therefore gave to the equation of Porter the form

$$\int_{A + \pi_{a\pi}}^{A + p} s dp = \int_{\pi_{a\pi}}^{\pi_{ao}} v dp + \int_{A + \pi_{ao}}^{A + p_0} u dp . . . . . (20)$$

in which the limits of integration of Porter's equation have been suitably altered. In this equation  $s$  denotes the diminution in volume when 1 gram of solvent escapes from a practically infinite volume of solution;  $v$  is the specific volume of the vapour, and  $u$  is the specific volume of the solvent;  $A$  is the atmospheric pressure;  $\pi_{ao}$  is the vapour pressure of the solvent in air when it is under a total pressure of  $A + \pi_{ao}$ ; and  $\pi_{a\pi}$  is the vapour pressure of the solution in air when it is under a total pressure of  $A + \pi_{a\pi}$ .

The integrals of this equation have been evaluated by Lord Berkeley, Hartley and Burton for the solutions investigated by them, and they obtain as the equation connecting osmotic and vapour pressure the expression



$$\bar{s}P = \frac{\pi_{ao}}{760\varrho_{ao}} \log_e \frac{\pi_{ao}}{\varrho_{ao}} = \frac{\pi_{ao}}{760\varrho_{ao}} \log_e \frac{l_o}{l_1} \quad (21)$$

Where  $\bar{s}$  represents the mean value of  $s$ , in equation (20), between the limits of pressure concerned,  $\varrho_{ao}$  is the vapour density of water vapour in the air when the water is under the pressure of  $A + \pi_{ao}$ ,  $l_o$  is the observed loss of weight of the solution and water vessels, and  $l_1$  is the observed loss of weight of the solution alone. By means of this equation, the osmotic pressure  $P$  was calculated from the vapour pressures of solvent and solution, and compared with the equilibrium values determined directly. The values are given in Table XX.

TABLE XX.

Grams of Anhydrous Salt to 100 Grams of Water.	Osmotic Pressure at 0° C. in Atmospheres.	
	Deduced from the Vapour Pressure.	Determined Directly.
49.966	131.45	130.66 *
47.219	112.96	112.84
42.889	86.61	87.09
39.503	70.61	70.84
31.388	41.24	41.22

The numbers calculated by means of the thermodynamic theory appear therefore to be in close agreement with those determined experimentally.

### Relation between Vapour Pressure and Concentration.

It was shown, many years ago, by Raoult that in dilute solutions the relative lowering of the vapour pressure is equal to the ratio of the number of solute molecules ( $n$ ) to the number of solvent molecules ( $N$ ) in the solution. In order to explain the diminution of the vapour pressure, Poynting<sup>88</sup> put forward the hypothesis that combination occurs between the solute molecules and the solvent molecules whereby a certain number of the latter are rendered "inactive". Poynting also assumed that the ratio of the vapour pressures of solution and pure solvent is equal to the number of molecules of free solvent to the whole number of molecules of solvent in the solution. If, therefore, each molecule combines with  $\alpha$  molecules of solvent, one obtains the equations:—

\* This value may be 0.5 atm. too low.

$$\frac{p}{p_0} = \frac{N - an}{N} \text{ or } \frac{p_0 - p}{p_0} = \frac{an}{N} \quad (22)$$

where  $p_0$  and  $p$  are the vapour pressure of the solvent and of solution respectively.

According to Raoult, however,  $\frac{p_0 - p}{p_0} = \frac{n}{N}$ , and therefore in order to harmonize the hypothesis of Poynting with the empirical law it is necessary to assume that for all substances which in dilute solution give a normal osmotic pressure,  $\alpha = 1$ . Apart from the fact that the above assumption does not agree with the results of experimental determinations in the case of concentrated solutions (it was suggested only for dilute solutions) it does not appear probable that all non-electrolytes should form monohydrates in solution.

Views similar to the above have also been expressed by I. Traube<sup>90</sup>; and T. M. Lowry<sup>91</sup> has suggested that the lowering of the vapour pressure may be ascribed to a blocking action of the solute molecules, but this view has not led to any satisfactory general result.

It has, however, been pointed out by Callendar<sup>55</sup> that a more natural assumption to make than that made by Poynting, with regard to the dependence of vapour pressure on the number of molecules in the solution, is that the ratio of vapour pressures  $\frac{p}{p_0}$ , is equal to the ratio of the number of free molecules of solvent to the whole number of molecules in the solution. That is to say, if  $n$  and  $N$  are the number of moles of solute and solvent in the solution, and if each solute molecule combines with  $\alpha$  solvent molecules, then we obtain:—

$$\frac{p}{p_0} = \frac{N - an}{N - an + n} \text{ or } \frac{p_0 - p}{p_0} = \frac{n}{N - an + n} \quad (23)$$

The above assumption made by Callendar corresponds exactly with that which was previously made (p. 41) in order to account for the deviation of the osmotic pressure of aqueous solutions of cane sugar from the law for ideal solutions.

In the case of a perfect or ideal solution of two components, it has been shown by Willard Gibbs,<sup>60</sup> van Laar,<sup>59</sup> and others, that if it is assumed that the vapours of the components follow Boyle's

law, the vapour pressure of each constituent is, at constant temperature, and external pressure, proportional to the molar fraction of that constituent. That is to say, if  $p$  and  $p'$  are the partial vapour pressures of the two constituents in the case of the mixture, and if  $p_0$  and  $p'_0$  are the vapour pressures of the pure constituents, and if  $\frac{n_0}{n_0 + n}$  and  $\frac{n}{n + n_0}$  are the molar fractions of the

two constituents respectively, then  $p_0 = p \frac{n_0}{n_0 + n}$  and  $p' = p'_0 \frac{n}{n + n_0}$ .

It has already been pointed out (p. 33) that this relationship holds over the whole range of concentrations in the case of two completely miscible constituents which form an ideal solution with each other. In the case of a solution in which one of the constituents is non-volatile, we obtain the expression  $\frac{p_0 - p}{p_0} = \frac{n}{N + n}$

where  $p_0$  and  $p$  are the vapour pressures of the pure solvent and of the solution respectively. When hydration is assumed, this equation passes into the form proposed by Callendar, where  $n$  now represents the number of moles of hydrated solute and  $a$  the number of moles of solvent with which one mole of solute combines. This relationship has also been employed by Dolezalek,<sup>92</sup> and by Möller.<sup>93</sup>

Combining equation (23) with equation (19) Callendar has calculated the change of osmotic pressure with concentration, and has shown that the calculated values of the osmotic pressure agree with the experimental values when, in the case of cane-sugar solutions, one assumes the value  $a = 5$ ; and in the case of dextrose solutions,  $a = 2$  (See Table XVIII). As has, however, already been pointed out, no account was taken of association of the solvent nor of any change in the association which might be produced by the solute.

Callendar<sup>94</sup> also holds that his theory is borne out by the determinations of Perman and T. W. Price.<sup>82</sup>

### Lowering of the Freezing Point.

That there is an intimate connexion between the value of the osmotic pressure of a solution and its freezing point was pointed out by van't Hoff in his classical paper on the analogy between dissolved substances and gases; and he deduced an expression for this relationship in the case of dilute solutions. More re-

cently, equations, valid also for more or less concentrated solutions, have been deduced by T. Ewan,<sup>67</sup> van Laar,<sup>59</sup> Trevor,<sup>67</sup> Callendar,<sup>55</sup> G. N. Lewis,<sup>63</sup> Washburn,<sup>64</sup> and others.<sup>133</sup> In deriving the osmotic pressure from the lowering of the freezing point of the solvent, it has to be borne in mind that since the freezing point alters with concentration, the calculated osmotic pressures refer not to the same temperature but to different temperatures. In order therefore that the variation of osmotic pressure with concentration alone may be calculated, it is necessary to know the variation of osmotic pressure with temperature. As we have seen (p. 34) this involves a knowledge of the heat of dilution of the solution.

The relationship between osmotic pressure and the freezing point can be obtained most simply by way of the vapour pressure. Since, as is obvious, the solution at the freezing point is in equilibrium with ice (in the case of aqueous solutions), it follows that the vapour pressure of the solution at the temperature of the freezing point must be equal to the vapour pressure of ice at that temperature. This value can then be inserted in the vapour pressure formula on page 53. In order to obtain the value of the vapour pressure, however, it is necessary to know the variation of the vapour pressure of ice and water below 0°, and for this it is necessary to take account of the difference of the specific heats of ice and water, which corresponds to the variation of the latent heat of fusion with temperature.

The general expression representing this variation of the vapour pressure with temperature, has been given by Callendar, and can be expressed in the form (see also J. B. Goebel<sup>95</sup>):—

$$\frac{R}{m} \cdot \log_e \frac{p_0}{p'} = \frac{L \cdot \Delta t}{T \cdot T_0} + \frac{1}{T} \int_{T_0}^T (s' - s) dT - \int_{T_0}^T (s' - s) \frac{dT}{T}$$

In this equation  $R$  is the gas constant (in calories) and  $m$  is the molecular weight of the substance in vapour form;  $p_0$  and  $p'$  are the vapour pressures of the liquid and solid phases respectively;  $L$  is the latent heat of fusion per gram at 0° C.,  $T$  and  $T_0$  are the absolute temperatures, and  $\Delta t$  is the difference  $T_0 - T$ ;  $s$  and  $s'$  are the specific heats of ice and water respectively. In the above equation also, the variation of the heat of fusion of the solid has been expressed in terms of the difference of specific heats of the liquid and solid.

To evaluate the integrals, the variation of the specific heat with temperature must be known. This cannot be determined by experiment, but different assumptions as to the variation can be made, and corresponding formulæ obtained. It would seem probable that the difference ( $s' - s$ ) increases with fall of temperature, and it can therefore be assumed that the difference is inversely proportional to the absolute temperature, or  $\frac{(s' - s)}{s_0} = \frac{T_0}{T}$  where  $s_0$  is the difference at  $T_0 = 273^\circ\text{A}$ . By inserting the values  $L = 79.5$ ,  $\frac{R}{m} = 0.1103$ ,  $T_0 = 273$ ,  $s_0 = 0.52$ , Callendar obtained the expression

$$\log_e \frac{p_0}{p'} = \frac{2.64 \cdot \Delta t}{T} + 4.71 \left( \frac{\Delta t}{T} + \frac{T_0}{T} \log_e \frac{T}{T_0} \right)$$

On account of its simplicity, and on account of the uncertainty of our knowledge of the variation of the specific heats, Callendar adopts for practical purposes another formula, namely

$$\log_e \frac{p_0}{p'} = 2.64 \frac{\Delta t}{T_0}$$

The calculated values of  $\frac{p_0}{p'}$  for different temperatures are given in Table XXI.

TABLE XXI.

Temp.	$\frac{p_0}{p'}$	Temp.	$\frac{p_0}{p'}$
— 2°	1.01953	— 20°	1.21340
— 5°	1.04955	— 30°	1.33660
— 7°	1.07004	— 40°	1.47231
— 10°	1.10154	— 50°	1.62181
— 13°	1.13397	— 60°	1.78649
— 15°	1.15611		

Since, as has been pointed out, the vapour pressure of a solution in equilibrium with ice, i.e. at its freezing point, is equal to the vapour pressure of ice (or  $p' = p$ ) the expression  $\log_e \frac{p_0}{p'}$  can be inserted in equation (19) in order to calculate the osmotic pressure. The values of the osmotic pressure so obtained will not, however, be strictly comparable, since they refer to different temperatures, namely the freezing points of the solution. In order therefore to obtain values of the osmotic pressure depend-

ing merely on the concentration, one must reduce all the values to one temperature, say  $0^{\circ}\text{C}.$ ; and to do this one must know the temperature coefficient of osmotic pressure. As already explained (p. 34) this depends on the heat of dilution and also on the compressibility of the solution.

Since the data for the direct comparison of the osmotic pressures calculated from the depression of the freezing point with values directly determined are not available, another method can be employed for carrying out the comparison with the results of experiment.

We have already seen (p. 58) that if it is assumed that the vapour of the solvent obeys the gas laws, the vapour pressure of the solvent in a solution is, at constant temperature and external pressure, proportional to its molar fraction. If we represent the vapour pressure of a solution (of a non-volatile solute) by  $p$  and the vapour pressure of the pure solvent by  $p_0$ , then  $p = p_0 \cdot x$ , where  $x$  is the molar fraction of the solvent in the solution. If, then, the solution is composed of  $n$  moles of solute and  $N$  moles of solvent, the molar fraction of the solvent will be represented by  $\frac{N}{N+n}$  in the case of an ideal or perfect solution (p. 30). Therefore we shall have,

$$\frac{p}{p_0} = \frac{N}{N+n} \quad \text{or} \quad \frac{p_0 - p}{p_0} = \frac{n}{N+n}$$

From Table XXI the values of  $\frac{p_0}{p}$  for different temperatures, calculated by Callendar, are given, consequently the value of the molar fraction  $\frac{n}{N+n}$  at different temperatures is given by the expression  $1 - \frac{1}{p_0/p}$ . By plotting the values of  $\frac{n}{N+n}$  against the corresponding temperatures, the freezing point curve for the ideal solution is obtained; and this curve can then be compared with the experimental curve.

Employing the values of  $\frac{p_0}{p}$  given in Table XXI one obtains the following numbers:—

TABLE XXII.

$\frac{p_0}{p'}$	$\frac{n}{N+n}$	Number of Moles ( $n$ ) of Solute per 100 Moles ( $N = 100$ ) of Solvent.	Number of Moles of Pentahydrate to 100 Moles of Solvent.	Freezing Point of Ideal Solution (Calculated).
1.01953	0.01913	1.95	1.78	- 2.0° C.
1.04955	0.04726	4.96	3.97	- 5.0°
1.07004	0.06546	7.00	5.19	- 7.0°
1.10154	0.09646	10.20	6.96	- 10.0°
1.13397	0.11814	13.40	8.02	- 13.0°

On plotting the above values of  $\frac{n}{100+n}$  against the temperature, the freezing point curve for an ideal solution is obtained. On comparing this curve with values obtained by Jones and Getman<sup>96</sup> for the freezing points of aqueous solutions of cane sugar, it is found that the calculated are lower than the experimental values, and the difference between the two increases with increase of concentration. If, however, it is again assumed that hydration of the sugar molecules occurs with formation of a pentahydrate, and if instead of the expression  $\frac{p_0 - p}{p_0} = \frac{n}{100+n}$  we employ the equation  $\frac{p_0 - p}{p_0} = \frac{n'}{100 - 5n + n'}$ , where  $n'$  is the number of hydrated sugar molecules to 100 molecules of water, we obtain the numbers given in the second last column of Table XXII. On plotting these numbers against the temperature a curve is obtained which agrees excellently with the experimental values of the freezing point, obtained by Jones and Getman, which are given in the following Table XXIII. (Compare T. Ewan<sup>67</sup>.)

TABLE XXIII.—FREEZING POINTS OF SOLUTIONS OF SUCROSE.

Moles of Sucrose per Litre.	Moles of Solute per 100 Moles of Water.	Freezing Point.
0.2	0.377	- 0.404°
0.4	0.789	- 0.848°
0.6	1.243	- 1.345°
0.8	1.742	- 1.950°
1.0	2.306	- 2.662°
1.2	2.930	- 3.550°
1.4	3.628	- 4.612°
1.6	4.445	- 5.800°
1.8	5.369	- 7.230°
2.0	6.283	- 9.130°

It is clear from the above discussion that when tested by the results of freezing point determinations, the experimental and calculated values are again in excellent agreement when the assumption is made that the cane sugar combines with water to form a hydrate. When the association of the solvent is neglected we see that the assumption of the formation of a pentahydrate suffices to explain the results obtained; but what has already been stated (p. 41) with regard to association of solvent and hydration must be borne in mind, as well as the influence of heat of dilution. If the heat of dilution were entirely, as it no doubt is mainly, due to changes in the association of the water and to hydration, the employment of the formula

$$\frac{p_0 - p}{p_0} = \frac{n'}{N + n' - an'}$$

would give the correct relationship between lowering of the vapour pressure (and the related quantities, osmotic pressure, depression of the freezing point, etc.). But as it will probably not be possible to obtain sufficiently accurate and independent determinations of the change in association and hydration of solute, the above method of investigating the problem constitutes a valuable step in the direction of obtaining an approximate knowledge of the constitution of solutions; and the method has been applied by Callendar to a number of solutes, both electrolytes and non-electrolytes.

That the employment of the simple van't Hoff law leads to too small values of the osmotic pressure, has already been pointed out. Similarly, it leads to too great depressions of the freezing point. The employment of this relationship therefore for the calculation of the degree of hydration of a solute must not be employed in the case of concentrated solutions, as has been done by H. C. Jones and his co-workers.\*

#### Elevation of the Boiling Point.

For the investigation of the constitution of solutions one can also employ determinations of the boiling point. The connexion between elevation of the boiling point and osmotic pressure, or vapour pressure, can be deduced in a similar manner to that for

\* For a discussion of this, see also Washburn, *Jahrbuch der Radioaktivität u. Elektronik*, 1908; "Hydrates in Solution," *Technological Quarterly* (Massachusetts Inst. of Technology, 1908).



the depression of the freezing point.<sup>55, 63, 64.</sup> Few data of sufficient accuracy are available for testing satisfactorily the relationship, but Callendar, using the data of Kahlenberg, has shown that the application of the assumptions made previously with regard to the hydration of the solute, leads to values which are in harmony with those determined experimentally.

## CHAPTER VIII.

### VIEWS REGARDING THE CAUSE OF OSMOSIS AND THE ACTION OF THE SEMI-PERMEABLE MEMBRANE.

STATED in its most general terms, the cause of osmosis is the difference which exists between the free energy or activity\* of the solvent in the pure state and in the solution, a difference rendered manifest by the difference in the vapour pressures of the solvent and the solution. If, therefore, we have a solution in direct contact with the pure solvent, equilibrium cannot exist on account of this difference of free energy, or difference in activity or in chemical potential, as it is also called. Diffusion of the solvent therefore takes place from the region of the pure solvent, where the free energy or activity is greater, to the solution, where the activity (of the solvent) is less. Similarly, diffusion of the solute takes place from the solution to the pure solvent, and the process continues until complete uniformity of composition is established. If, however, instead of having the solvent and solution in direct contact with each other a semi-permeable membrane is inserted between them, the "driving force of diffusion," which, as we have seen, depends on the difference between the activity of the constituents in the solvent and in the solution, is not altered. Moreover, since the membrane is permeable to the solvent, diffusion, so far as it is concerned, can take place just as before. We have then the phenomenon of *osmosis*. Since, however, the solute is prevented by the membrane from diffusing into the solvent, the production of uniform concentration throughout the system is impossible, and equilibrium can be established only by the free energy or activity of the solvent in the solution acquiring the same value as in the pure state. Since this can be brought about by increasing the pressure on the solution, the diffusion of the solvent into the solution will continue until the requisite pressure is established; and this pressure is the *osmotic pressure*. Such pressure, as we have seen in the preceding pages,

\* This term is due to G. N. Lewis.

is a function not of the concentration, expressed in grams or gram-molecules per litre, but a function of the molar fraction. Only in infinitely dilute solutions does the former become identical with the latter.

The essential function, then, of a semi-permeable membrane is to allow a solution under pressure to be brought into contact, so far as the solvent is concerned, with the pure solvent not under pressure; or, in other words, the semi-permeable membrane allows of a pressure being exerted on a solution in contact with the solvent, without exerting a pressure on the latter.

But to what is this property of semi-permeability due? To this, various answers have been offered. The first is that due to M. Traube<sup>5</sup> who considered that semi-permeable membranes acted as "atomic sieves," which allowed molecules of certain dimensions to pass through, but prevented the passage of larger molecules. Supposed confirmation of this view was found by Traube in the fact that the permeability of membranes was diminished by clogging the "pores" with other substances. Thus when the gelatine-tannic acid precipitate was clogged with barium sulphate, it became impermeable to ammonium sulphate and to barium nitrate, and a membrane of copper ferrocyanide when clogged with silver chloride became impermeable to potassium chloride.

This view regarding the mode of action of the semi-permeable membranes remained for a considerable time the one generally accepted. Influenced by this explanation and on the basis of osmotic experiments carried out with solutions of propyl alcohol in water, S. U. Pickering<sup>97</sup> concluded that the alcohol formed hydrates in solution which were too large to pass through the assumed pores of the septum. The experimental basis on which this conclusion rested was afterwards shown by Findlay and Short<sup>98</sup> and by Barlow<sup>23</sup> to be unsound. The experiments of Kahlenberg<sup>38</sup> also yielded results which are at variance with the sieve theory of the semi-permeable membrane.

Although, even in comparatively recent years, others, among whom may be mentioned W. Sutherland,<sup>99</sup> have adhered to the above explanation of the nature of semi-permeable membranes, it may be said to have passed almost entirely out of favour. It has been pointed out by Perrin,<sup>100</sup> however, that the explanation of the semi-permeable membrane as forming a sieve or mesh-

work may be found acceptable to account for the impermeability of colloidal membranes to colloids (cf. M. Traube<sup>5</sup>).

According to another view, which will be discussed more fully at a later point, the membrane is regarded as consisting of fine capillary tubes; and quite recently attention has again been directed to this explanation by Bigelow,<sup>101</sup> who showed that water passes through collodion, gold-beater's skin, parchment paper and unglazed porcelain plates, at rates conforming to Poiseuille's equation for the flow of water through capillary tubes; and the same law was shown by Bartell<sup>102</sup> to hold also in the case of membranes of copper ferrocyanide. It was also shown by Bigelow and Bartell<sup>103</sup> and later by Bartell<sup>104</sup> that distinct osmotic effects were obtained with pore diameters of the order 0.5 micron, which is much larger than the probable molecular dimensions. No quantitative measurements of the pressure, however, were made.

To H. E. Armstrong is due what may be called a chemical explanation of permeability of membranes. To quote his own words:<sup>105</sup> "The compounds which penetrate the membrane . . . are all substances which attract water presumably only to a minor extent and which exist to some extent in solution in an unhydrated condition; those which cannot penetrate it, on the other hand, probably all form hydrates of considerable stability in solution.

"I picture surfaces generally, colloid surfaces in particular, as not merely wetted by water but as more or less hydronated and hydrolated" (see p. 74); "that is to say, they are not merely wetted by water complexes but associated with hydrone, the simple fundamental molecule of which water is composed. The intra-molecular passages in a colloid membrane, if thus hydrolated, would be guarded by the attracted hydrone molecules; molecules in a solution bathing the membrane which attempted to effect an entry through such passages if hydrolated, would be seized upon and held back in virtue of the attraction which the two hydrolated surfaces—that of the membrane and that of the solute—would exercise upon one another. The hydrolated passages, however, would be indifferent to molecules which were not hydrolated—consequently such a substance as acetic acid, of which probably only a small proportion is present in solution in the hydrolated state, would gradually pass through them.

"It is obvious that the argument now put forward may be applied to the discussion of a great number of more or less obscure physiological phenomena. . . . The argument affords an explanation of the well-known efficacy, e.g., of mercury salts, of iodine and of alkaloids as drugs. It should point the way to the production of medicaments adjusted to their purpose according as it is desired that they should penetrate this or that membrane."

The explanation of semi-permeability of membranes which is probably most widely accepted at the present day, is that of selective or preferential solubility. The membrane is permeable to those substances which dissolve in it, and is impermeable to those substances which are insoluble in it.

This explanation of the permeability of membranes was first suggested by L'Hermite,<sup>106</sup> who illustrated the action by the following experiment. Chloroform, water and ether were introduced into a cylinder so as to form three layers. The ether, being soluble in water and also in chloroform, gradually passed through the aqueous layer and dissolved in the chloroform; this substance, however, not being soluble in water, did not pass through the aqueous layer. The volume of the chloroform layer therefore increased, or, if the movement of the aqueous layer was prevented by suitable means, a pressure (osmotic pressure) was produced.

Liebig<sup>107</sup> also explained the action of the membrane as being due to the difference in its "absorptive power" for different substances; and in recent years this explanation has come to be very widely accepted. In support of this explanation experiments have been described by Nernst,<sup>108</sup> Kahlenberg,<sup>38</sup> Flusin<sup>109</sup> and others, the large number of qualitative experiments carried out by Kahlenberg being especially worthy of mention. The "solution theory" of the membrane has also been adopted by Overton<sup>110</sup> to explain narcosis by the passage of substances through the walls of animal cells; but this application of the theory has been strongly opposed by I. Traube.<sup>111</sup>

In connexion with the views just stated regarding the nature of the semi-permeable membrane, it may be mentioned that I. Traube and also Bigelow suggest a reconciliation between the solution and the capillary theories on the basis of a view put forward by L'Hermite, that solution is itself capillary in nature,

and that the process of solution depends on the difference of surface tension between solvent and solute.

Corresponding with the different views regarding the nature of semi-permeable membranes, equally divergent views, so far, at least, as the manner of their expression is concerned, have been put forward in connexion with the process of osmosis and the nature of osmotic pressure. These views fall, however, into two classes. On the one hand, there is the kinetic interpretation of osmotic pressure, according to which the pressure is due to the bombardment of the semi-permeable membrane by the solute molecules, in a manner analogous to the kinetic explanation of gaseous pressure: and on the other hand there is the view that osmotic pressure is a hydrostatic pressure produced by the entrance of solvent into the solution.

The origin of the first view is well known. When van't Hoff discovered through his mathematical deduction of the laws of osmotic pressure that in dilute solutions the osmotic pressure was equal to the gaseous pressure which the solute would exercise if in the form of vapour and occupying a volume equal to the volume of the solution, he suggested as a *plausible* explanation of osmotic pressure that it was a bombardment pressure.\* Van't Hoff, however, was chiefly interested in the quantitative relationships and laid no stress on the interpretation, kinetic or otherwise, to be given to the pressure produced with the aid of a semi-permeable membrane.<sup>76</sup> There can be no doubt, however, that the bombardment explanation was accepted by a number of chemists, and may even yet find favour with some. Thus, when solutions of moderate and even of considerable concentration came to be investigated and when considerable deviations from the simple "gas laws" thereby came to light, attempts were made, as we have already seen, to retain the bombardment or gas pressure theory, and to give an explanation of the deviations from the simple law of van't Hoff similar to that of van der Waals for the deviations of gases from Boyle's law. This method of accounting for the deviations from the simple van't Hoff law, is, as Callendar has said, not satisfactory, "because so many different types of equation are possible and the empirical constants cannot

\* It was, however, quite clear to van't Hoff that the production of a pressure was due to the entrance of water into the solution (*Zeitschr. physikal. Chem.*, 1887, 1, 482).

be interpreted or predicted from the properties of the substances concerned".

The explanation was, in itself, attractive by reason of its simplicity, and for this reason it is still largely employed in the elementary exposition of osmotic pressure. To this fact the tenacious life of the bombardment theory is doubtless in great measure due. Moreover, the experiments carried out by Ramsay<sup>112</sup> in which he determined the "osmotic pressure" of a gaseous solution of hydrogen using a semi-permeable septum of palladium, as well as the analogous experiments of Villard,<sup>113</sup> were regarded as furnishing a rather convincing analogy to the osmotic pressure of liquid solutions. The bombardment or gas pressure theory has, however, been subjected to vigorous attack<sup>114</sup> almost from the commencement, and as it has not shown itself capable of explaining the osmotic pressures of concentrated solutions, it has been generally abandoned. The probability of its revival does not, however, appear to be excluded.

We have already seen that the thermodynamic equation for the relationship between osmotic work and concentration involves not the volume of the solution but the volume of the solvent or rather the *increase of volume* when solvent is added to the solution. Further, if hydration occurs, the volume in which the molecules of solute would move would not be either the volume of the solution nor the volume of the solvent in the solution, but the volume occupied by the solvent remaining uncombined with solute. As Callendar has said, however, "it would be straining the analogy unduly to regard the pressure which the molecules would exert in an imaginary volume if they were gaseous as being the primary cause of the phenomenon of osmotic pressure. In reality the equilibrium depends primarily on equality of vapour pressure."

Even when the view is adopted that osmotic pressure is a hydrostatic pressure, very different views have been expressed as to the way in which this hydrostatic pressure is produced.

One of the earliest theories put forward to account for osmosis and osmotic pressure is due to Jäger,<sup>115</sup> who sought to bring osmotic phenomena into relation with the surface tension of the liquids. According to Jäger, the osmotic pressure is proportional to the difference between the surface tensions of the solution and pure solvent. A similar view was put forward also by B. Moore,<sup>116</sup> who regarded the semi-permeable membrane as

being composed of fine capillary tubes which established a connexion between the solvent and the solution. In such a case there will be a movement of liquid from the side of the liquid of lower surface tension to that of higher surface tension. No permanent pressure, however, will be produced unless the radius of the capillary tubes is so small that the whole body of the liquid is subject to capillary forces. In the case of semi-permeable membranes Moore considered that this is the case; and on calculating the radius of capillary necessary according to his theory to give to the osmotic pressures of solutions the values which they possess, by means of capillary action, he found that it lies well within the radius of capillary attraction. The whole section of liquid in the capillary would thus be urged by difference of surface tension in the direction of the liquid of greater surface tension, that is, from the solvent to the solution, in those cases where the solution has a higher surface tension than the solvent. On the basis of this theory, Moore drew the conclusions: (1) The surface tension of all solutions obeying the solution laws should be higher than those of the solvents. (2) For solutions of the same substance in the same solvent, the surface tension should increase directly as the concentration within the same limits as osmotic pressure obeys the gas laws. (3) For solutions of different substances in the same solvent, the differences in the surface tension between solution and solvent should be the same for equi-molecular solutions of these different substances. (4) For equi-molecular solutions, even of different solutes in different solvents, the differences between the surface tensions of solution and solvent must be equal.

As experimental confirmation of his conclusions, Moore quotes the work of Quincke,<sup>117</sup> Volkmann,<sup>118</sup> and others, but it can scarcely be said that the confirmation is sufficiently strong to establish the theory, certainly not as a general theory, of solutions.

With regard to the views expressed by Jäger and by Moore, it was pointed out by Monti<sup>89</sup> that a solution of salicin, although it has a surface tension less than that of water, has nevertheless a positive osmotic pressure (contrary to the first conclusion drawn by Moore); and, moreover, when an aqueous solution of ethyl alcohol is separated from water by an animal membrane, osmosis takes place from the water to the alcohol, that is to say, from the liquid



of higher to that of lower surface tension; a behaviour which is contrary to the view expressed by Moore.

Moore had himself recognized this discrepancy. He had, however, put forward his theory only for solutions which have a lower vapour pressure than the pure solvent, and as aqueous solutions of alcohol have a higher (total) vapour pressure than water, Moore considered that they stood outside the sphere of application of his theory.

The surface tension explanation of osmosis has also been accepted and advocated very vigorously by I. Traube<sup>119</sup> who however, claims a somewhat less wide scope for the theory. According to Traube the difference of surface tensions determines only the direction and velocity of the osmosis. "Osmotic velocity and surface tension run parallel. . . . Hence the difference of the surface tensions is the motive force in osmotic phenomena; it is to this difference that osmotic pressure is due. . . . It must, however, be emphasized that the difference between the surface tensions cannot be considered as equal to the osmotic pressure, for this new pressure is quite different for isosmotic solutions; it is, in the first instance, only the measure of the velocity with which the osmotic pressure rises, and this osmotic pressure is only a counterforce."

That the views of Traube are capable of universal application appears doubtful, and, indeed, cases have been cited by Barlow<sup>120</sup> which are not in harmony with them.

For the purpose of reconciling the surface tension explanation of osmosis with experimental results, Battelli and Stefanini<sup>121</sup> modified the theory of I. Traube and expressed the view that osmosis must in every case occur in such a way as to equalize the surface tensions of the liquids on either side of the membrane. Consequently, in the case of solutions of salicin, for example, if the membrane is truly semi-permeable (although they considered that no absolutely semi-permeable membrane exists), water must pass into solution in order to equalize the surface tension; and this process will continue until a certain pressure is established. When the membrane is not semi-permeable, osmosis takes place in both directions, until equality of surface tension is established; and the major current will take place in such direction as most rapidly to procure this result.

In the case of dilute solutions, also, Battelli and Stefanini

claim to have proved that such solutions as have equal surface tensions have also the same osmotic pressures and vapour pressures, even when they are not equi-molecular. That this cannot hold generally has been pointed out by A. Findlay;<sup>122</sup> for in the case of solutions, say, of salicin and salt, the vapour pressure is diminished in each case, but the surface tension is diminished and increased respectively. The theoretical deduction of the relationship given by Battelli and Stefanini, has also been adversely criticized by Sella.<sup>123</sup> It may, of course, be that in the region of dilute solutions such as were examined by Battelli and Stefanini, the surface tension and vapour pressure do vary proportionally, within the limits of error obtained; but the conclusions drawn by these workers cannot be extended to solutions generally.

With regard to the connexion between permeability of membranes and surface tension, I. Traube had expressed the view that a membrane which is not permeable to a substance in solution when the latter has a greater surface tension than water, becomes permeable when another substance is added which lowers the surface tension of the solution. This view, however, was shown by Battelli and Stefanini to be erroneous.

Although the surface tension theory has, perhaps, always been a favourite one with physicists, it has not shown itself adequate to account quantitatively for the laws of osmotic pressure, in the thermodynamic sense of the term; and no exact connexion has yet been established between surface tension and osmotic pressure or the diminution of the vapour pressure of a solvent by a solute, of such a kind that the latter can be calculated from the former. Indeed, I. Traube, who is at the present day one of the chief advocates of the surface tension theory of osmosis, expressly states that the theory does not afford a basis for the quantitative laws of osmotic pressure. The surface tension theory is advocated by him as a theory of osmosis rather than of osmotic pressure and chiefly for its importance in physiology. Subject to this restriction the theory has shown itself to be of great value.<sup>124</sup>

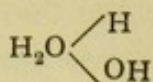
Perhaps the earliest theory of the cause of osmosis was that there exists an attraction between solvent and solute molecules, and as we have already seen (p. 3), M. Traube regarded the osmotic pressure as being a measure of this attraction.<sup>125</sup> Such an explanation is, however, merely a restatement of the

phenomenon ; but it was later rendered more precise by frankly identifying the "attraction between the molecules" with "chemical attraction" and the production of compounds (hydrates). This explanation is based on the view both very old and widely accepted by chemists,<sup>126</sup> that the process of solution is due to the action of chemical affinity between the solvent and solute molecules. In recent years the view has thus been re-stated by I. Traube<sup>119</sup> : "the attraction pressure is the intensity factor of the solution energy ; . . . in aqueous solutions it is the water attractive power . . . consequently we conclude that hydrates exist in solution". Kahlenberg<sup>38</sup> expresses himself in similar language.

To this chemical explanation of the solution process as constituting the origin of osmotic effects, an appearance of greater definiteness has been given by H. E. Armstrong,<sup>127</sup> by giving to the hydrates, the formation of which is assumed, definite structural formulæ. Briefly, we may state his views as applied to aqueous solutions, as follows :—

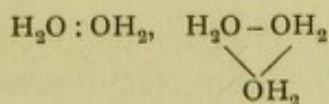
In water there exist probably both simple and polymerized molecules in equilibrium, represented thus :  $(\text{H}_2\text{O})_n \rightleftharpoons n\text{H}_2\text{O}$ . By the addition of a non-electrolyte this equilibrium is disturbed\* in the direction  $(\text{H}_2\text{O})_n \rightarrow n\text{H}_2\text{O}$ , and these monads are regarded as exerting an attraction for similar molecules in the region of pure solvent or of a more dilute solution. There will accordingly be a transfer of solvent across the membrane so as to re-establish the equilibrium, the osmotic attraction, in the case of a non-electrolyte, being due wholly to the influence of the dissociated water complexes.

Still more definitely has Armstrong expressed his views. Water, he regards, as consisting of a mixture of active and inactive molecules. The active molecules are either simple monad hydrone,  $\text{H}_2\text{O}$ , or hydronol

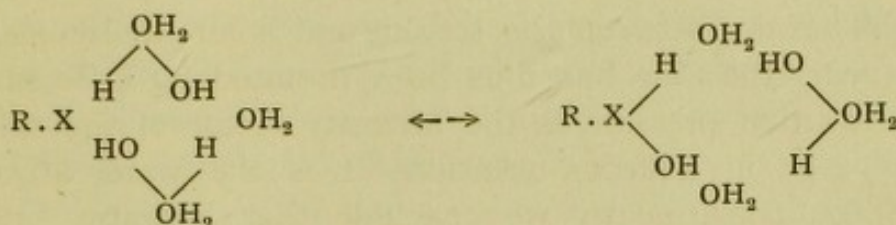


the inactive molecules are associated molecules to which the formulæ

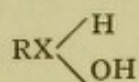
\* A similar view regarding the disturbance of an equilibrium between water-molecules by a solute, has been expressed by W. Sutherland (*Phil. Mag.*, 1900 [6], 1, 460 ; 1906 [6] 12, 1, *Trans. Faraday Soc.*, 1910, 6, 105) who has also adduced a considerable amount of evidence in its support. Compare van Laar, *Zeitschr. physikal. Chem.*, 1899, 31, 1.



etc., are given. When a non-electrolyte R . X is dissolved in water, it reacts with the hydrol and hydrone molecules, thus :—



giving rise to the active (hydrolated) complex



as well as to the inactive (hydronated) complex  $\text{RX} : \text{OH}_2$ , and polymerides of the type  $\text{RX} : \text{XR}$ . In the case of electrolytic solutions, the formation of still more complex molecules is assumed.

The hydrate theory of solution appears, at the present day, to be widely accepted ; but although it is a very plausible theory and is, in many cases, supported by a large mass of experimental evidence, it seems to be an error to explain the solution process as being due in every case to the formation of compounds between solvent and solute. As has already been pointed out (p. 33) not a few cases of solution are known (ideal solutions) where the assumption of solvation (or combination of solvent and solute) is both unnecessary and unsupported by experimental evidence.

Even, however, in those cases where the assumption of hydration furnishes the most satisfactory explanation of the solution process in aqueous solutions, two somewhat opposing views can be and have been held. On the one hand, the view is held, e.g. by H. C. Jones<sup>128</sup> and his co-workers, that the composition of the hydrate formed by any given substance is purely a function of the concentration of the solution. There may therefore be formed in a solution quite a number of very unstable hydrates. On the other hand, there is the view that definite stable hydrates are formed which persist throughout a considerable range of concentration and of temperature. This is the view which was put forward by Mendeléeef, and as we have already seen (p. 43)

this assumption suffices to bring the behaviour of aqueous solutions into harmony with the requirements of thermodynamic theory.

It has already been mentioned that the fundamental cause of osmosis is to be found in the difference which exists between the activity of the solvent in the pure state and in the solution. In harmony with this, Callendar<sup>55</sup> has proposed a vapour pressure theory of osmotic pressure. The semi-permeable membrane according to this theory consists of fine capillaries which are not wetted by the liquids but which admit of the passage of vapour, or in other words the membrane is a vapour sieve. Since the pure solvent at one end of the capillaries has a higher vapour pressure than in the solution at the other end, distillation will take place from the solvent, and the vapour on passing through the capillary will condense on the surface of the solution; and this process will continue till the hydrostatic pressure produced by the addition of solvent to the solution, so effected, is sufficient to raise the vapour pressure of the solution to a value equal to that of the pure solvent. This theory makes no assumption as to the nature of solutions and is sufficiently general and indefinite to include the surface tension and the hydrate theories.

That the semi-permeable membrane is constituted by "vapour cells" and that transfer of solvent takes place in the form of vapour is a view which has also been advocated by Battelli and Stefanini,<sup>121</sup> Garver<sup>129</sup> and others.

Of other theories of osmotic pressure which have been put forward, it will suffice if we mention here the theory of Hulett,<sup>130</sup> according to which the osmotic pressure can be regarded as a negative pressure on the solvent (the vapour pressure of which is thereby lowered); and the electrostatic theory of Perrin<sup>131</sup> and of Girard,<sup>132</sup> according to which the mechanism of osmosis is, if not exclusively at least essentially electrostatic. This theory, which is chiefly of importance in relation to the process of osmosis rather than to the quantitative value of osmotic pressure, may be placed alongside of the surface tension theory.

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