# Studies of Solution. II.

A Conception of Osmotic Pressure.

## By

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In the present article, the theory of osmotic pressure will be considered and a new conception of that pressure be presented according to the hypothetical figure of solution attained from the studies of molecular solution volumes of solute and solvent in solution and reported in the preceding article.

The theory of osmotic pressure of solution given by van't Hoff has played a prominent part in the development of physical chemistry, and several conceptions have been proposed concerning the nature of that pressure, but as yet none are satisfactory.

This problem may conveniently be treated separately in two parts, that is:

- 1. The action of a semipermeable membrane;
- 2. The mechanism of the existence of the pressure difference between a solution and the pure solvent.

The osmotic phenomena, however, can not naturally be separated in such a way, and especially for the study of the first part, the experimental results of the second part must be taken into consideration. The study of the second part may be carried on without regard to the first part and independent of the nature of the action of the semipermeable membrane, and indeed, van't Hoff's theory concerns only the second part of the problem. Here also only the second part is taken into consideration with an assumption of the possibility of a perfect semipermeable membrane and without inquiry as to what theory, atomic sieve, solution, absorption,<sup>1</sup> or capillary, may be true as to the nature of the action of a semipermeable membrane.

<sup>&</sup>lt;sup>1</sup> Recently F. Tinker (Proc. R. Soc. London 4, 92. (1916)) studied the structures of semipermeable membranes and supported adsorption theory of osmosis.

In the famous work of van't Hoff<sup>1</sup>, Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen " the following words are found in its beginning :

"Bei einer Untersuchungen, die im wesentlichen Kenntniss der chemischen Gleichgewichtsgesetze in Lösungen bezweckte, hat sich allmählich herausgestellt, dass eine tiefgehende Analogie, ja fast Identität mit den Gasen, speziell auch in physikalischer Beziehung, vorliegt, falls nur bei Lösungen vom sogenanten osmotischen Druck die Rede ist, da wo es sich bei Gasen um den gewöhnlichen Spannkraftdruck handelt." The important conclusion of this paper is: Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert they were gassified at the same temperature without change of volumes; and this is expressed in the simple equation

$$PV = nRT$$

where P denotes osmotic pressure, V total volume of solution, n number of mols of solute, and R the gas constant.

From this paper of van't Hoff, we see, that the simple mathematical relation given above is an experimental fact which, therefore, admits no discussion. But as to the analogy between solution and gaseous state there may be some discussions because, though the state of solution and that of gas were quite different, it is not to be denied that in some cases an accidental coincidence of the mathematical equations of the two states may occur.



In Fig. 1, if A be a pure solvent, say water, B a solution, say aqueous solution of cane sugar, and cd a perfect semipermeable membrane, then a certain quantity of solvent will penetrate into solution

<sup>1</sup> Zs. physik. Chem. 1, 481 (1887).

through the membrane cd, and a hydrostatic pressure will be produced in the solution as shown by ef in the figure. The pressure which is acting on the semipermeable membrane, that is the so called osmotic pressure, is usually determined from this hydrostatic pressure. If the analogy between the gaseous state and the solution were established, the above osmotic pressure should be considered as the effect of the kinetic motion of the solute molecules.

Now, for a comparison, let us consider a gaseous mixture. In Fig. 2. A and B were first equally filled, with pure oxygen under one atmosphere pressure; and then a certain quantity of nitrogen under one atmosphere was added to B. After mixing, to maintain the total pressure of B still at one atmosphere, the volume of B must be enlarged by the volume of nitrogen added. If cd be a hypothetical semipermeable membrane through which oxygen will pass but nitrogen not, since the partial pressure of oxygen in B is lower than in A, a certain amount of oxygen in A will penetrate into B through the membrane cd until the partial pressure of oxygen becomes equal on the both sides of the membrane. Let  $v_1$  and  $v_2$  be the volumes of oxygen and nitrogen in B respectively. If an external pressure be added and  $v_1 + v_2$  be compressed to  $v_1$ , the oxygen in A will be in equiliblium with that of B without any passage of oxygen through the membrane. If the external pressure at first be  $P_1=I$ , then from the gas law, the following relation is obtained:

therefore

$$(v_1 + v_2) P_1 = v_1(P_1 + P_2),$$
  
 $v_2 P_1 = v_1 P_2 = nRT,$   
 $P_2 = \frac{n}{v_1} RT.$ 

 $P_2$  is what is analogous to osmotic pressure in solution. In the case of solution, the external pressure is generally  $P_1=1$ . Thus to establish the equilibrium between the solution and solvent through a semipermeable membrane, an additional external pressure  $P_2$ , must be applied on the side of solution; otherwise, a certain quantity of the solvent would penetrate into the solution, and the equilibrium state is attained and a certain hydrostatic pressure is reached in the solution. From such considerations it seems that there is no contradiction to the analogy between the gaseous state and solution.

Further, let us see how much compression is necessary to establish equilibrium between the solution and the pure solvent through a

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semipermeable membrane. The following data from Morse's<sup>1</sup> experiments on cane sugar solution, may be considered.

# Aqueous Solution of Cane Sugar at 0°C.

Weight normal conc.	Volume of solvent.	Volume of solute.	Sum.	Volume of solution.	Differ- ence.	Contrac- tion. %	Osmotic pressure obs
0• I	1000-13	21.328	1021-458	1020-73	0•728	0.07	(2.462)
0.2	,,	106.640	1106.770	1103.01	3.760	0.37	11.895
I۰O	,,	213.280	1213-410	1206.69	6.720	0.55	24.826

As shown in the table, the contraction accompanying the formation of solution of one weight normal concentration, is only 0.55%; and, if we take into consideration the analogy between the gaseous state and solution, it must be concluded that this solution receives an osmotic pressure of 24.826 atm. by the additional compression from 1206.69 cc. to 1000.13 cc. or of 20.7%. There is no known data concerning the compressibility of cane sugar solution; but it may be supposed to be less than that of water. As to the compressibility of water, there is the well known investigation by Amagat<sup>2</sup>; according to which, for a compression of 2.8% of a volume of water at 0°C., a pressure of 600 atm. was needed. Thus it is impossible to consider that the directly measured osmotic pressure of about 25 atms. could counterbalance the above stated compression of cane sugar solution. This may be explained as follows. In a gaseous state the actual volume of gas molecules is very small in comparison to this apparent volume, while in solid state, such as cane sugar, on the contrary the actual volume of the molecules is equal or very nearly equal to the apparent volume. Taking this difference between gaseous and solid states into consideration, it may be assumed that the dissolution of cane sugar in the solvent would not much increase the free volume for the motion of the solvent molecules, and in that case the osmotic pressure equilibrium would be established by a little compression.

This explanation may perhaps be correct; but, if the consideration that the free volume is very small or does not exist in solid state is admissible, there is no reason to doubt that the same conception might be applied to the state of liquid. The term "b" in van der Waals' equation gives us an idea of actual volume of gaseous and

<sup>1</sup> The Osmotic Pressure of Aqueous Solution, p. 104.

<sup>2</sup> C. R., 116, 41 (1893).

liquid substances. The recent determinations of "b" of water by L. Gay<sup>1</sup> are as follows:

Temperature	Mol. vol.	Ь
(abs.)	in cc.	in cc.
323	18.233	14.577
343	18.424	14.928

According to the theory of van der Waals, "b" is four times the actual volume, but recently T. W. Richards<sup>2</sup> has shown that it is nearly equal to it. If we admit the analogy between the gaseous state and solution, we must yet acknowledge that there is a very small free volume in solution in comparison with its total volume, for the free movement of the solute molecules by their kinetic energy. And this fact always holds, even when the solution is *very dilute*. In other words, we can not neglect the actual volume of the solvent in any dilution in the determination of the condition of the solution.

If, therefore, the analogy between the gaseous state and solution holds, the equation of the state of solution is not van't Hoff's equation:

but 
$$PV = nRT$$
  
 $P(V-b') = nRT^*$ 

where "b'" is not the same as "b" for the pure solvent, but near it and it cannot to be neglected in connection with V. Yet, the van't Hoff's equation holds in dilute solution and then its coincidence with the gas law may be accidental. Thus the analogy, which had been suggested as a plausible explanation by van't Hoff, now becomes questionable.

On the other hand, chemists who treat the problems of solution thermodynamically, have explained the osmotic relations of solution with the difference of activities or free energies between solution and solvent, quite indifferently to the hypothesis of the cause of osmotic

<sup>1</sup> C. R., 157, 711, 1914, and 158, 34 (1914).

<sup>&</sup>lt;sup>2</sup> J. Amer. chem. soc., 36, 2417 (1914).

<sup>\*</sup> Very similar equation for the osmotic pressure has been proposed by O. Sackur (Zs. physik. Chem., **70**, 477. 1910) such as, P(V-b)=RT, where P is the osmotic pressure, V the volume in which 1 mol of solute is dissolved. This equation shows fairly good coincidence with the experimental data even in quite concentrated solutions, but as seen from the definition of V in this equation it is not the same as the above derived equaiton, and moreover the Sackur's equation does not support the analogy of the gaseous state and solution.

pressure. In the recent work of E. W. Washburn<sup>1</sup>: "An Introduction to the Principles of Physical Chemistry" the definition of osmotic pressure is clearly given as follows: "The osmotic pressure of a solution is the pressure difference which must be established upon the solution and pure solvent respectively, in order to make the escaping tendency of the solvent the same from both of them. The osmotic pressure is, therefore, not a real pressure existing within the solution but is a definite physical quantity quite independent of osmosis, semipermeable membrane or molecular theory. It is connected with the other colligative properties of the solution by definite relation which can be deduced by purely thermodynamic reasoning. For dilute solutions the osmotic pressure becomes in the limit equal to CR7where C is the concentration of solute, but as the concentration increases the osmotic pressure approaches infinitely as its upper limit."

In argument such thermodynamical theories, Findlay<sup>2</sup> says as follows: "Valuable as the thermodynamical 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*."

Of course, we can not content ourselves with merely purely thermodynamical deductions for an explanation of the osmotic phenomena, or for a theory of solution, and we need to explain this phenomena from two sides, that is, qualitative and quantitative. Once more let us quote Findlay's words: "For it must be remembered that the problem of solutions consists of two parts, the qualitative and quantitative. On the one hand, insight is desired into the nature and constitution of solution, into the processes involved in the production of a solution whether these depend on chemical affinity, surface tention, or other causes; and, on the other hand, an equal need is felt for a 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 quantitative are, however, but two complementary sides of one problem and while some investigators may attach surpreme importance to the qualitative side-to the construction of pictures or models of the con-

<sup>1</sup> See p. 161.

<sup>&</sup>lt;sup>2</sup> Osmotic Pressure, p. 47.

stitution 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 bebetween the workers on the two sides, that knowing will finally be attained."

Against the osmotic theory of solution of van't Hoff, the criticism has been levelled from the time of its enunciation to the present day, by L. Meyer<sup>1</sup>, Quincke<sup>2</sup>, Kahlenbeg<sup>3</sup> and more recently in the controversy between van Laar and Ehrenfest<sup>4</sup>. In the opinion of Ehrenfest, the osmotic pressure is not caused by the bombardment on a semipermeable membrane of the molecules of the solute, as has just been described, but this is caused by the water which penetrate through the semipermeable membrane, giving rise to a hydrostatic pressure which prevent the further intrussion of the water. Thus, there are many theories opposing the osmotic theory of van't Hoff, yet none are satisfactory on both sides, qualitative and quantitative.

If van't Hoff's theory as to the cause of osmotic pressure is rejected, its place would be taken by that of osmotic suction as proposed by Ehrenfest. The writer has held that opinion from the beginning of this study of solution, but has not published it until now.

In the preceding report, on the investigation, of the change of molecular solution volumes of solute and solvent in solution, a hypothetical picture of solution was attained and according to it the author tried to explain the osmotic pressure qualitatively and quantatively in the following way.

As described in the preceding paper, in the solution of *nonvolatile substance*, the molecular solution volume of solute increases with the increase of concentration of solute; and on the contrary the molecular solution volume decreases: this phenomenon makes the supposition plausible that the molecules of solute and solvent will compress each other by their cohesion or physico-chemical affinity in solution. This compressed state may perhaps be comparable to the state of stress and strain, and the effect of pressure does not, therefore, express itself as an external pressure. The order of this pressure can be estimated, as

<sup>&</sup>lt;sup>1</sup> Zs. physik. chem., 5, 23 (1890).

<sup>&</sup>lt;sup>2</sup> Ann. Physik, (iv) 7, 681 (1902).

<sup>&</sup>lt;sup>3</sup> J. Phys. chem., 10, 141 (1906).

<sup>4</sup> Nature, 97. 68 (1916).

described in the preceding paper, in comparision with the external pressure which would be needed to compress the solvent only.

It is not the only possible supposition that there exists a parallelism between the change of "molecular solution volumes" of solute and solvent and that of their molecular volumes in solution. The phenomenon of the change of molecular solution volumes may, however, be explained in another way. In solution, some molecules of solute and solvent will perhaps not be homogeneously disintegrated but in polymerised state or in some states of aggregation and only those which are disintegrated approach one another and are compressed in their volumes by the mutual affinity or they build up some kinds of solvate. Admitting such a state of solution, the observed phenomenon of the change of molecular solution volumes may be explained by the change of the degree of disintegration of molecular solution, the observed of solution.

In any supposition whatever, the mean molecular volumes of solute and solvent in solution will be smaller than those in pure state.

Now, admitting the state of solution to be of such a nature, let a pure solvent be brought into contact with a solution by a semipermeable membrane, then it will penetrate into the solution to lower the compression of the solvent molecules in solution : on the contrary, if the pure solute be brought in contact with solution it will dissolve until it saturates the solution, to decrease the compression of the solute molecules in solution. The relation of the molecular solution volume of solute in the saturated solution and its solubility have already been considered in the preceding paper. In solution, solute and solvent are only relative term; and from this point of view, *the osmotic pressure can be explained as the solutional pressure of the water into solution*.

According to this, the osmotic pressure is the pressure which comes into play against the penetration of the solvent into the solution; and the cause of hydrostatic pressure thus produced in solution is the penetration of a quantity of solvent into the solution. Then inner pressure of compression of the solvent in solution is, therefore, the first cause of the osmotic pressure.

In concentrated solution, its inner pressure would not be equal to the osmotic pressure or hydrostatic pressure produced in solution, but in dilute solution, these pressures would be equal. The numerical value of inner pressure in dilute solution can not be determined exactly, but it seems to be of the order of the osmotic pressure as described in the preceding paper. This is the author's theory of the osmotic pressure in the qualitative side; and it is something new in its explanation why hydrostatic pressure would be produced in the side of the solution which is in contact with the pure solute. Further, as to the quantitative side of this theory of osmotic pressure, reference must be made to Porter's very comprehensive theory of compressible solutions of any degree of concentration<sup>1</sup>. Porter's attention was at first directed to the success of the direct determination of the osmotic pressure by Earl of Berkeley and E. G. Hartley<sup>2</sup>. Their method of measurement was to determine the equilibrium pressure, that is the pressure which must be supplied to the solution to bring about a state of equilibrium between it and the solvent so that no solute, i.e. water, passes in another direction as a whole when the solution and solvent are separated by a semipermeable membrane, Porter studied the relation between osmotic and vapour pressure purely thermodynamically and derived the following equation:

$$\int_{A+\pi_{a\pi}}^{A+p} s \, dp = \int_{\pi_{a\pi}}^{\pi_{a0}} v \, dp + \int_{A+\pi_{a0}}^{A+p} u \, dp.$$

In this equation s denotes the diminution in volume when I gram of solvent escapes from a practically infinite volume of solution, vis the specific volume of the vapour, and u is the specific volume of solvent; A is the atmospheric pressure;  $\pi_{a0}$  is the vapour pressure of the solvent in air when it is under a total pressure of  $A + \pi_{a0}$ ; and  $\pi_{a\pi}$  is the vapour pressure of the solution in air when it is under a total pressure of  $A + \pi_{a\pi}$ .

One of the most important conclusions from this equation is that when a solution is in osmotic equilibrium with the pure solvent, the vapour pressure of the solution is equal to the vapour pressure of the pure solvent, each measured for the actual hydrostatic pressure of the fluid to which it refers.

Now, returning to the author's consideration of osmotic pressure, the solution, which is in osmotic equilibrium with pure solvent through a semipermeable membrane, would have a hydrostatic pressure caused by the penetration of the pure solvent and this hydrostatic pressure is acting to prevent the further penetration of the solvent. In the opinion of the writer, this cause of the penetration of solvent into solution is the compression of the solvent molecules in the solution. And compression or inner pressure in solution would be directly compared to

<sup>&</sup>lt;sup>1</sup> Proc. R. Soc., London, **76** A, 519. (1907) and **80** A, 457. (1908) Porter's theory is fully quoted in the recent work W. C. McC. Lewis: A system of Physical Chemistry (1916) p. 224.

<sup>&</sup>lt;sup>2</sup> Phil. Trans, A, 206, 486. (1906).

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the hydrostatic pressure produced in solution or the external pressure added on the solution to establish the osmotic equilibrium with the pure solvent as Berkley and Hartly<sup>1</sup> did. From this point of view the osmotic pressure is replaced by an external pressure added on the solution, and the relation of osmotic pressure to other properties of solution, such as vapour pressure, may easily be drawn.

The relation of the vapour pressure of a liquid and its external pressure is represented by the well known relation of Poynting :

$$\left(\frac{\partial p}{\partial P}\right)_T = \frac{V}{v},\tag{1}$$

where P and p are the external pressure on a liquid and its vapour pressure respectively, V and v are molecular volumes in liquid and vapour states respectively.

According to the Porter's theory, the solution, which is in osmotic equilibrium with the pure solvent, has the same vapour pressure as that of the pure solvent and when the external pressure added on the solution is removed, its vapour pressure will be lowered, and its lowering may be estimated from Poynting's equation applying it directly on solution where P, the external pressure added on the solution, denotes the osmotic pressure of the solution. But, upon the older view of osmotic pressure, the osmotic pressure is considered to exist even when the solution stands alone without any contact with the pure solvent. To represent such osmotic pressure or inner pressure of the author, P in the above equation must change its sign, then the equation becomes as follows:

$$\left(\frac{\partial p}{\partial F}\right)_{T} = -\frac{V}{v},\tag{2}$$

where P denotes the osmotic pressure or the author's inner pressure.

"It is a weil known experimental fact that if we add, say an inert gas, to a vessel containing a liquid and its saturated vapour, that increases in pressure in the vessel due to the inert gas, causes an increase in the actual pressure (partial pressure) of the saturated vapour. From the molecular stand point one might regard the phenomenon as to the closer packing of the molecules of liquid under the increased pressure, and therefore the possibility exists of more molecules per unit surface area capable of forming vapour, i.e. the vapour pressure rises."<sup>2</sup> This relation is mathematically shown in Poynting's equation. In the author's view, the molecules of the solvent in solution are compressed by the inner pressure, yet the vapour pressure of the solvent is depressed, apparently in contradiction to

<sup>1</sup> Loc. cit.

<sup>2</sup> From W. C. McC. Lewis: A System of Physical Chemistry, Vol. II, p. 224.

the above reasoning. But this may be easily explained in the following way. When the volume change accompanying the formation of the solution is neglected, the number of molecules of the solvent on unit surface of a solution are not increased by compression of the solvent or increase of the inner pressure, and on the contrary, the contact surface of the solvent molecules with the vapour phase decreases by the insertion of the solute molecules; thus the vapour pressure of a solution would be depressed. As to the mathematical relation of this lowering, it is expressed by the above eq. (2) which is of the same form as Poynting's equation.

Having got eq. (2), relating to the osmotic pressure, we can easily get the relations of the colligative properties of solution and the osmotic pressure as E. W. Washburn has comprehensively described in "A Simple System of Thermodynamic Chemistry based upon a Modification of the Method of Carnot."<sup>1</sup>

Now, the derivation of the van't Hoff's osmotic equation from eq. (2) may be described as follows. If  $V_0$  be the molecular volume of a pure solvent under one atmosphere pressure, then V, the molecular volume of the solvent under the external pressure of one atmosphere plus inner pressure P, is

$$V = V_0(\mathbf{I} - aP),$$

where a is compressibility of the solvent. Assuming that the vapour of this solvent obeys the gas law, or that pv = RT holds for it, and putting these relations in eq. (2), we obtain the following expression :

$$RTd\ln p = -V_0(\mathbf{I}-aP)dP,$$

Integrating this equation, we have

$$RT \ln p = -V_0 (P - \frac{1}{2} \alpha P^2) + RT \ln p_0,$$
  
$$P - \frac{1}{2} \alpha P^2 = -\frac{RT}{V_0} \ln \frac{p}{p_0},$$
 (3)

or

where  $p_0$  is the vapour pressure of the pure solvent under one atmosphere pressure. Neglecting the second term  $\frac{1}{2}\alpha P^2$  against *P*, by the reason of the very small value of  $\alpha$ , and expanding eq. (3), we have

$$P = \frac{RT}{V_0} \left[ \left( \frac{p_0 - p}{p_0} \right) + \frac{1}{2} \left( \frac{p_0 - p}{p_0} \right)^2 + \frac{1}{3} \left( \frac{p_0 - p}{p_0} \right)^3 \dots \right].$$
(4)

In dilute solutions, we may take the first term only, that is

$$P = \frac{RT}{V_0} \frac{p_0 - p}{p}.$$
 (5)

<sup>1</sup> J. Amer. Chem. Soc., 32, 653. (1910).

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This expression is nothing but the van't Hoff's equation. But to get the equation PV=nRT, we must combine eq. (5) with Raoult's equation

$$\frac{p_0 - p}{p} = \frac{n}{N+n}.$$
(6)

Purely thermodynamically, without using the idea of osmotic pressure, we can not deduce Raoult's equation directly. Thermodynamics gives us only Duhem-Margules's differential equation about the relations of vapour pressures of a solution, such as

$$x \frac{\partial \ln p_1}{\partial x} + (1 - x) \frac{\partial \ln p_2}{\partial x} = 0,$$
 (7)

where  $x = \frac{N_1}{N_1 + N_2}$ ,  $1 - x = \frac{N_2}{N_1 + N_2}$  and  $N_1$ ,  $N_2$  and  $p_1$ ,  $p_2$  are the numbers of mols and partial pressures of components of a solution respectively. As a special solution of this equation, Dolezalek<sup>1</sup> proposed the following equations :

$$p_1 = p_{0,1} \frac{N_1}{N_1 + N_2}, \quad p_2 = p_{0,2} \frac{N_2}{N_1 + N_2},$$

where  $p_{0,1}$  and  $p_{0,2}$  are the vapour pressures of components in pure state. Raoult's equation is a special case of Dolezalek's solution where the solution is dilute and one component is nonvolatile.

Now, recognizing Raoult's equation we can easily get from eq. (5) the following relation,

$$P = \frac{RT}{V_0} \frac{n}{N+n},$$
  

$$PV = nRT.$$
(8)

or

One must notice that on the derivation of this equation the gas constant R comes from the solvent part not from the solute part as in the case of the van't Hoff's equation.

In conclusion, to sum up briefly the contents of this treatise. The analogy of the gaseous state and solution is questionable, and the coincidence of the equations of these states may perhaps be accidental. If one assume the above analogy, it does not lead to the van't Hoff's equation, as the equation of the state of solution, but another. The

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<sup>&</sup>lt;sup>1</sup> Zs. physik. Chem., 64, 727, (1908).

author holds the same view as Ehrenfest with respect to osmotic pressure, and has further explained the cause of the penetration of the pure solvent into the solution to cause the osmotic pressure. From his view of the explanation of osmotic pressure, the mathematical expression of the state of solution can easily be derived.

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