THE BEARING OF ACTUAL OSMOTIC EXPERIMENTS UPON THE CONCEPTION OF THE NATURE OF SOLUTIONS.

Dr. Louis Kahlenberg, Professor of Physical Chemistry in the University of Wisconsin, communicated a Paper on "The Bearing of Actual Osmotic Experiments upon the Conception of the Nature of Solutions."

Osmosis was discovered in 1748 by Nollet, and since that date a large number of physiologists, physicists, and chemists have carried on experimental investigations with a view to discover the nature and laws of the osmotic process. In all actual osmotic experiments with which we are here concerned there are present three phases, namely, two liquids and a septum which separates these two liquids from each other. Frequently these liquids have consisted of a solution on the one hand and pure solvent on the other. Experimental studies have been directed to ascertain what substances pass through given septa and at what rate. The influence of temperature upon the process has received consideration, and attempts have been made to determine the maximum pressure which is produced by the tendency of one of the liquids to increase in bulk during the experiments because of the influx of material from the other side of the septum. This pressure so developed has commonly been known as the osmotic pressure.

As a result of all this experimental inquiry it has been conclusively demonstrated that whether osmosis will actually take place or not depends upon the nature of the septum employed and upon the nature of the liquids that bathe it. Furthermore, if osmosis does occur, these factors also determine the direction and extent of the process. Temperature is also a factor in osmosis, but it is of very minor consequence as compared with that of the nature of the septum and the liquids employed. Again, it has developed from these experiments that osmosis always goes on in both directions, and that the rate of flow of material through the septum in the two directions is practically never equal; in other words, there is *always* a major and a minor current present in each experiment. In some special cases it has been found that this minor current is almost insignificant as compared with the major current, so that it *appears* as though the osmotic process were one-sided in these instances. In such cases the septum has been termed semi-permeable, and of late years interest has centred to a considerable extent upon the experimental study of osmosis in cases where such so-called semi-permeable membranes were employed. As a natural consequence "semi-permeable" membranes were much sought for, and in the course of this search the fact clearly developed that there really is no such thing as a semi-permeable membrane in the strict sense of the word. As already indicated, in certain specific cases—and these have been found to be relatively few in number—the major osmotic current so far outweighs the minor that an approximation to a one-sided process is reached. Until recently precipitated membranes, and among these in particular copper ferrocyanide membranes, have been practically the only ones which have been found to be semi-permeable, and

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that only for few substances, amongst which cane sugar is by far the most prominent. Precipitated membranes were first used by Moritz Traube in 1865, and were again prominent in the researches of Pfeffer in 1877. These botanists clearly recognised the importance of the experimental study of the peculiar osmotic properties of these precipitated membranes as bearing upon physiological processes in which frequently membranes with similar strong selective action come into play. Recently I have shown (*Trans. Wis. Acad.*, vol. 15; also *Journ. Phys. Chem.*, March, 1906) that vulcanised caoutchouc, though not a precipitated membrane, is semi-permeable in certain specific cases, among which is that of cane sugar when dissolved in pyridine. In that Paper I have demonstrated experimentally that it is peculiarly strong selective action on the part of the septum which causes it to be approximately semi-permeable in certain instances. All the results of previous investigators also go to support this view, which is consequently incontrovertible. Indeed, from a knowledge of the peculiar selective property of, for instance, vulcanised caoutchouc, I have been able to predict whether a certain substance would pass through that septum or not; in other words, I have been able to foretell whether in given cases the membrane would be practically semi-permeable or not. As a result of this I have actually been able to separate certain crystalloids from each other by dialysis, certain colloids from crystalloids by *having the colloid pass through* the septum and the crystalloid remain behind; and finally, I have just recently even succeeded in separating two colloidal substances from each other by dialysis. A description of the latter case has not yet been published, and I purposely refrain from giving the experimental details here, for it would seem best not to divert attention from the main issue at stake.

Now this peculiar selective action exhibited by the membrane is simply due to solubility or insolubility of the substance or substances in question in that membrane. This I have demonstrated experimentally (*l.c.*), and the work of earlier experimenters all goes to support this claim. Thus, in order that a substance may pass through a given septum it is necessary (1) that the substance be dissolved in, or, as some would choose to put it, that it be taken up or imbibed by the membrane; (2) that the liquid on the other side of the septum have the power to dissolve the substance with such a degree of avidity as to enable it to rob the septum of some of the substance. These same forces which cause a substance to pass through a septum—that is to say, which cause the liquid on one side of the septum to increase—clearly produce the pressure, the so-called osmotic pressure, which is manifested when such increase in bulk is hindered by mechanical contrivances. It is clear, therefore, that the production of osmotic pressure is due to the same forces that cause solution to take place, and that when we have an explanation of the process of solution we also shall have an explanation of the osmotic process and the production of osmotic pressure. Obviously osmosis is a more complicated process than simple solution, for in osmosis three phases are striving to get into equilibrium with one another, and that too against an external pressure when mechanical contrivances are used to prevent the process from going on, as when it is sought to measure osmotic pressures. From this consideration it would follow that we must not look to osmotic experiments to obtain a better conception of the nature of solutions and the process by which they are formed; but we should rather expect a clearer understanding of osmosis to come from a study of the simpler process of solution through other channels.

By regarding an osmotic membrane simply as a sieve with meshes of definite size, it has at times been hoped by some that the size of molecules

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might be ascertained. However, experiments have conclusively shown that molecules which must be considered to be larger frequently go through a membrane very much more readily than molecules which we are bound to consider as smaller. The sieve theory is consequently untenable. To my mind an experimental study of the simple process of solution leads to the conclusion that it is essentially chemical in character. It is unnecessary to rehearse here the specific reasons for this view, for they have already been expressed in print (compare *Phil. Mag.*, Feb., 1905 ; also *Chemiker Zeitung*, 29, No. 81, 1905). My view, therefore, is that osmosis is due to essentially the same specific attractions that are commonly termed chemical affinity, and that the osmotic pressure is also produced by the same force. Osmotic pressures may consequently be quite variable as different septa and different liquids are employed ; furthermore, such pressures may frequently be very great indeed, and this accords with what has been found experimentally. By thus cognising that the act of solution is chemical in character, and that osmosis and osmotic pressure are caused by the same agency as that which causes changes called chemical by common consent, we have, of course, not explained what chemical affinity itself is, though we have clearly made a definite gain by recognising an important relation which experiment indicates exists. Personally I incline to the opinion that once solutions are again commonly looked upon as chemical combinations between solvent and solute, as at one time they practically always were by those who busied themselves experimentally with solutions in various solvents, we shall by application of our improved experimental means be in a better position to acquire a thorough knowledge of the laws regulating chemical change, even though we may not hope thus to unravel the mystery of what chemical affinity in itself is.

If now we inquire as to the reason why so-called semi-permeable membranes have of recent years been chiefly employed in experimental osmotic work, it appears that this is because of the bearing which such work has upon the theory of solution of Van't Hoff. The latter, using Pfeffer's data of the osmotic pressures developed when aqueous solutions of sugar are separated from water by means of septa of copper ferrocyanide, pointed out that the results are approximately such as may be computed by use of the simple gas equation. Here, then, seemed to be experimental evidence for putting into quantitative form the long-recognised fact that between a substance in the gaseous state and one in solution there is a certain degree of analogy. It was soon promulgated that just as gaseous pressure is caused by the bombardment of the molecules against the sides of the containing vessel, so osmotic pressure is caused by the bombardment of the semi-permeable membrane by the dissolved molecules, a view which, though quite irreconcilable with experimental facts, is yet even at present taught in prominent texts. It has boldly been maintained that as long as the membrane is "semi-permeable" the osmotic pressure is necessarily the same in the case of any septum for a given solution against the pure solvent. This is contrary to experience. Even an inspection of Pfeffer's data secured by separating aqueous sugar solutions from water by means of septa of Prussian blue and calcium phosphate instead of copper ferrocyanide indicate the specific influence of the septum which my own experimental researches further demonstrate conclusively.

By conceiving solvent abstracted from a dilute solution contained in a cylinder fitted with a semi-permeable piston and afterwards returning this solvent to the solution in a reversible Carnot's cycle, relations have been deduced between the latent heat of fusion of the solvent and the freezing-

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point of the solution, also between the boiling-point of the solution and the latent heat of vaporisation of the solvent. In deducing these relations the usual thermodynamic formulæ have been applied, and the assumption has been made that the gas equation holds for dilute solutions. In thus computing the so-called molecular lowering of the freezing-point and molecular elevation of the boiling-point for various solvents from a knowledge of the freezing-point and latent heat of fusion, and of the boiling-point and latent heat of vaporisation of the solvent, results are obtained which are frequently far from the experimental values found for different solutes in case of one and the same solvent. But by assuming that the solutes are either dissociated or polymerised or united with a certain amount of solvent, or that any two or all three of these processes take place simultaneously, the experimental data are readily explained, and it is fondly imagined that thus we get a better insight into the nature of solutions. To justify such assumptions of dissociation and polymerisation it has been pointed out that this is exactly parallel with what takes place in the case of gases, and reference is made to the classical experimental researches of Saint Claire Deville. As frequently aqueous solutions that conduct electricity yield greater molecular lowerings of the freezing-point and greater molecular elevations of the boiling-point than is required by the formulæ deduced as above stated, it is claimed that the solutes are in such solutions "electrolytically" dissociated. Finally, the attempt is made to explain all the various physical, chemical, and physiological properties on the basis of these various assumptions. In a previous communication to the Faraday Society I have already discussed the weaknesses of such explanations, so that it is unnecessary to dwell upon them at present. I should like to add, however, that it has recently been demonstrated in my laboratory (compare Sammis, *Journ. Phys. Chem.*, Nov., 1906) that lead will replace copper from copper oleate in hydrocarbon solutions, which are the best of insulators. With this discovery it may now be asserted that, as to type, all chemical reactions may be produced in the best of insulators just as they take place in excellent electrolytes. Furthermore, we have shown conclusively by experiment that in such typical cases as sugar inversion, ester catalysis, and solution of metals in acids, the conductivity of the solution may be materially altered by the introduction of such substances as benzene and acetone without causing anything like a proportional change in the speed of the reaction. In fact, it has been shown that the electrical conductivity and the rate of reaction may be varied practically independently of each other. The different molecular lowerings of the freezing-point and elevations of the boiling-point due to the introduction of various substances into one and the same solvent are very simply explained by the assumption that they result from different degrees of affinity or attraction between solvent and solute (compare *Chemiker Zeitung*, l.c.).

From the freezing-points, boiling-points, and vapour-tensions of solutions their so-called osmotic pressures have conversely been computed by using formulæ established with the aid of thermodynamic reasoning. In many cases, too, the so-called osmotic pressure has been directly calculated from the concentration of the solution by simple application of the gas laws, the "degree of electrolytic dissociation" being strenuously considered in the case of an electrolyte. This practice has been termed the "indirect" method of determining osmotic pressures.

Now, all thermodynamic deductions of relations between osmotic pressure on the one hand, and vapour tensions, freezing-points, or boiling-points on the other hand, involve the assumption of a membrane which is semi-permeable, and which at the same time is quite passive; that is to say, which has no selective action.

However, as stated above, *all experimental evidence we have goes to demonstrate (1) that there is no such thing as a semi-permeable membrane in the strict sense of the word, and (2) the more nearly a membrane is semi-permeable in character in practice, the greater is its selective action; in other words, it is the pronounced selective action of the membrane which makes it approximately semi-permeable. It is clear, therefore, that such a membrane as thermodynamic reasoning postulates can never be realised in practice, nor can we hope by experiment to produce even approximately such a membrane; for as we experimentally approximate toward fulfilling the first requirement, semi-permeability, we do this at the sacrifice of the second requirement, passivity.* The semi-permeable membrane of the thermodynamicist is therefore a thing which has no counterpart in actual osmotic experiments, *not even approximately.* Consequently the semi-permeable membrane and the osmotic pressure of the thermodynamicist are quite different things from the actual osmotic septa and osmotic pressures of experimental practice. A clear recognition of this will do much to clear up existing confusion and misunderstanding. Mr. Whetham's recent admission (*Nature*, July 26, 1906) that actual experimental osmotic pressures and so-called thermodynamic osmotic pressures are quite different things goes far toward arriving at an understanding. We need also to grasp clearly the fact that actual membranes as used in osmotic experiments are quite different from the septa postulated in the thermodynamic deductions. The reasons for this have already been given above.

When summed up, then, the situation is as follows: Actual osmotic experiments have suggested that the concentration of a solution might be imagined to be changed reversibly by the application of a hypothetical membrane, which is simultaneously semi-permeable and devoid of specific selective action. By imagining a reversible cyclic process to take place in which the concentration of the solution is altered by the hypothetical means mentioned, relations between the freezing-point and vapour tensions of solutions on the one hand, and the theoretical equilibrium pressure required to be put on the hypothetical semi-permeable piston on the other hand, have been deduced. For this hypothetical equilibrium pressure Mr. Whetham (*l.c.*) proposes the name "thermodynamic osmotic pressure" in contradistinction to the osmotic pressure developed in actual osmotic experiments, which he suggests should be termed "experimental osmotic pressure." I fear, however, that as long as the term "osmotic" is in any way attached to this hypothetical thermodynamic quantity, there will be more or less confusion. It is to be hoped, therefore, that another term will be invented for the so-called thermodynamic osmotic pressure, which does not involve the use of the term "osmotic." Further, the semi-permeable membrane assumed in thermodynamic considerations ought to be called a thermodynamic semi-permeable membrane, so as to distinguish it from actual experimental osmotic membranes which are approximately semi-permeable because of their selective properties. In conclusion, may I be permitted once more to emphasise the fact that *to speak of the experimental osmotic pressure of any solution—the only osmotic pressure which has any counterpart in reality—without mentioning specifically just what septum is used to separate that solution from what other liquid is quite devoid of all meaning.*

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