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Osmotic pressure and chemical equilibrium

*Nobel Lecture, December 13, 1901**

Although the investigations on which I am about to speak were carried out 15 years ago, I am going to begin by describing still earlier studies - those which, in fact, formed the basis of my own. These studies concern the experimental determination of osmotic pressure.

What is osmotic pressure? When a solution, e.g. of sugar in water, is separated from the pure solvent – in this case water – by a membrane which allows water but not sugar to pass through it, then water forces its way through the membrane into the solution. This process naturally results in greater pressure on that side of the membrane to which the water is penetrating, i.e. to the solution side.

This pressure is osmotic pressure.

It is thanks to this osmotic pressure that the sap of the oak-tree rises to the topmost twigs. This pressure was known to exist as long ago as the beginning of the 19th century, but it is only somewhat more than 20 years ago since this phenomenon has been the subject of precise measurements. It was the botanist Pfeffer who first measured this pressure in 1877 by making a membrane which satisfied the following three conditions: It was permeable to water, impermeable to sugar, and it withstood the by no means negligible pressure to which it was subjected.

Osmotic forces are in fact unexpectedly great: with a 1% sugar solution they are equal to no less than 2/3 atm.

Thus, Pfeffer measured osmotic pressure but he was unable to find the relation between the value of this pressure and the concentration of the solution, its temperature, etc. He put this problem to the celebrated physicist Clausius in Bonn, but he, too, failed to discover any regular interrelations. Pfeffer's results therefore remained in a specialized botanical paper, thus escaping the notice of scientists in other fields.

The importance of a solution of this problem becomes clear when one

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remembers the vital role played by osmotic pressure in plant and animal life. The membranes of the cell are in fact permeable to water but not to substances dissolved in the cell fluid. Osmotic pressure can therefore develop in the cells. It was the botanist Hugo de Vries in particular who emphasized its importance to plant life: Such pressure (turgor) must exist in the plant cells, if they are not to wither; in other words it is essential for growth. Thus, plants wither not only when they lose water through evaporation but also when they are surrounded by an aqueous solution of common salt, potassium chloride, magnesium chloride, sugar or other substance, if the solution is of higher osmotic pressure, whereas they do not wilt if the osmotic pressure is lower. The critical point can be very accurately determined with the aid of a microscope, and thus De Vries found a method of establishing how concentrated a solution must be if it is to have the same osmotic pressure as the plant cells, i.e. if it is to be "isotonic" with them.

Donders and Hamburger then discovered that osmotic pressure plays no less important a part in animal than in plant life. The life of the higher animals stands or falls with the erythrocytes. These are cells which in relation to the osmotic pressure of the liquid surrounding them behave in a manner similar to plant cells, i.e. if the external osmotic pressure is too great, then a phenomenon similar to wilting occurs. And at that time it was particularly remarkable that solutions found to be isotonic in this respect were also isotonic for the plant cell.

Lastly, in chemistry osmotic pressure is very important because, among other things, it can be related directly to what is known as chemical affinity. In the binding of water of crystallization, for instance, one can imagine that natural gypsum, the chemical formula of which is $CaSO_4 \cdot 2H_2O$, binds its water of crystallization in almost the same way as the plant cell holds water within itself, and the force with which this takes place can be measured in the same way as De Vries measured the osmotic force of cells. If a piece of transparent selenite is placed successively in aqueous solutions of increasing concentration of any substance, then there finally comes a point at which the gypsum can no longer retain its water but gives it up to the solution of greater osmotic pressure: "it wilts". The force with which gypsum binds its water can therefore be measured directly by osmotic pressure.

So much for the earlier work.

In the subsequent study of processes in this field the law around which the prize-winning work centred was now discovered.

It was found namely that with sufficiently dilute solutions the osmotic pressure was the same as the gas pressure, i.e. the pressure which the dissolved substance would exert as gas. To some extent this is obvious: Just as one imagines the gas pressure P to arise as a result of the movement of molecules and of their collisions with the walls (Fig. 1), so can one imagine the osmotic pressure p to arise as a result of the collisions of the dissolved molecules with the semi-permeable membrane (Fig. 2) surrounded by the solvent (denoted by shading).

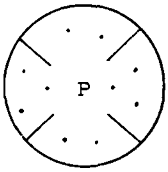

Fig.1.

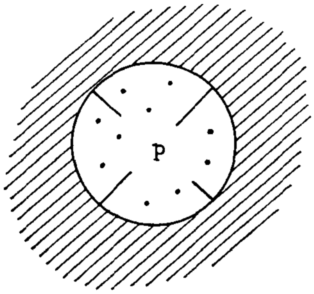

Fig.2.

However, independently of an anyway hypothetical conception on the cause of this pressure, it was found that under the same circumstances, i.e. with the same number of molecules in the same volume and at the same temperature, the pressures also were the same. This can be expressed mathematically by the equation

$$p = P \tag{1}$$

osmotic pressure = gas pressure. From this formula it is possible to calculate theoretically the value found by Pfeffer: $\frac{2}{3}$ atm. for a 1% sugar solution.

It was found, however, that a relatively small group of solutions - all of them aqueous - of acids, bases and salts, which are known as electrolytes, e.g. solutions of sodium chloride or potassium chloride (i.e. mostly those which were investigated first), constituted an exception. In the case of these the law did not apply. The osmotic pressure was *i times* greater than the theoretical value, and consequently the following formula was for a tune used for these exceptions:

$$p = iP \tag{2}$$

We shall be returning to this point later. In the case of the non-electrolytes this reduces to (I), since i = 1. Now let us apply the basic relationship and consider the so-called chemical equilibrium. A distinction must be made between complete and incomplete reactions, according to the final state in which a chemical reaction results. After dynamite has been exploded not the slightest trace of the original substance is found. The reaction is complete. In other cases, however, the reaction ceases before complete transformation- for instance, where methanol and formic acid are converted into water and methyl formate according to the equation:

$$CH_4O + CH_2O_2 = H_2O + C_2H_4O_2$$

A similar formula might also be drawn up for the dynamite explosion. In the reaction which has just been formulated, however, only $\frac{2}{3}$ of the possible quantity of the products on the right side are formed. The reason for this is that not only are methyl formate and water produced from methanol and formic acid, but that conversely methanol and formic acid are produced again from methyl formate and water. This can be illustrated in the formula by introducing the sign for a reversible reaction instead of the sign of equality:

$$CH_4O + CH_2O_2 \rightleftarrows H_2O + C_2H_4O_2$$

Such transformations, then, take place in either direction: the final state being known as *chemical equilibrium.*

The laws governing this chemical equilibrium in the case of dissolved substances can now be deduced by using the basic relationship for osmotic pressure.

The first of these,

for non-electrolytes : $\Sigma n \log p = K$ (3a)
for electrolytes : $\Sigma ni \log p = K$ (3b)

determines the quantity of the product which will form in a given volume from given quantities with substances reacting with one another, provided that a single so-called equilibrium constant, K, is known.

Since the value i enters into this formula in the case of electrolytes, we see that it plays an important part in the relevant laws of equilibrium.

In the second law

$$\frac{dK}{dt} = \frac{W}{2T^2} \tag{4}$$

we find yet another factor affecting the equilibrium, namely the temperature T (so-called absolute temperature). W is the quantity of heat evolved during the reaction.

Finally, in the last formula

$$K = -\frac{A}{2T} \tag{5}$$

allowance is also made for the quantity of work done during a chemical reaction, e.g. a dynamite explosion, the quantity being linked with the equilibrium constants.

Following this brief mathematical excursion we will now turn to some of the results which were subsequently obtained by means of these formulae.

I. The molecular weight of dissolved substances is now easy to determine. Fifteen years ago it was possible to assess the molecular weight of gaseous substances only. By means of osmotic pressure it is now also possible to determine the molecular weight of dissolved substances. But it is not only liquids which have come into the range of molecular weight determination. In addition, homogeneous mixtures, e.g. isomorphic mixtures of solid substances are comparable to solutions, and the laws of osmosis can therefore be extended to solid substances. Consequently, it is now possible to determine molecular weight not only in the gaseous, but also in the liquid and in the solid state of aggregation. The problem of molecular weight determination has thus to a certain extent been solved.

The results are very interesting. It has often been thought that during the transition from the gaseous to the liquid phase several gas molecules unite to form a liquid molecule, and that the molecules in the solid state of aggregation consist of still larger complexes. In reality, however, the situation is very simple. It is in fact only in exceptional cases that in a liquid or solid state of aggregation, molecules consisting of two gas molecules of the substance have been found, whereas nothing like a substance which forms aggregates of three gas molecules has yet been found for certain.

II. Equation (2) was at first the critical point in the theory. I should not have had the pleasure of giving this lecture if Professor Arrhenius had not succeeded in demonstrating the cause of these exceptions and therefore in reducing Equation (2) to (1).

III. We need go no further into Equation (3a). It coincides essentially with the law of mass action formulated by the two Norwegians Guldberg and

Waage, except with regard to *i* and *n* (number of molecules participating in the reaction).

IV. Equation (4) links the chemical equilibrium constant *K* with the heat *W* evolved by the reaction. It can of course be tested experimentally, and has indeed been confirmed experimentally.

A corollary to this law shows how the chemical equilibrium varies with temperature – namely how, as the temperature increases, more of the one compound is formed at the expense of the other, or vice versa. This corollary can be stated as follows: At low temperature the greater yield is always of that product whose formation is accompanied by evolution of heat.

In most cases, in fact, the equilibrium at ordinary temperature has shifted so far in favour of those products which are situated on one side of the arrows in the chemical formula that no trace of the products on the other side can be detected. An example of this is the formation of water from a mixture of oxygen and hydrogen, the so-called oxyhydrogen gas. At ordinary temperature the equilibrium is so much on the side of the water that the oxyhydrogen gas cannot be detected at all. At higher temperatures there is a shift towards the gas; a measurable equilibrium between water, oxygen, and hydrogen is established. The above-mentioned formula thus embraces the dissociation processes which were studied by Deville and Deprez.

V. It is only very recently that it has been possible to test Equation (5) experimentally. Bredig and Knüpfer have determined *K* from the equilibrium and have also determined by chemical methods the work done during the reaction.

In conclusion a timely remark. Whereas application of the laws of osmosis has proved very fruitful in the field of chemistry, what De Vries and Donders emphasized 15 years ago, namely that osmotic pressure plays a fundamental role in plant and animal life, has since been fully confirmed as well. The determination of osmotic pressure and of the associated lowering of the freezing-point of solutions is already frequently of great importance in physiology and medicine, e.g. in the study of disease. However, the peculiar discovery made very recently by Loeb is the most important one of all. This scientist has been studying the problem of fertilization, which is bound up so closely with the problem of life, and he has found that the eggs of sea urchins will develop as a result of the temporary action of a specific osmotic pressure brought about by solutions of potassium chloride, magnesium chloride, sugar, etc.