

NOBEL LECTURES

CHEMISTRY

1901 – 1921

World Scientific

NOBEL LECTURES
INCLUDING PRESENTATION SPEECHES
AND LAUREATES' BIOGRAPHIES

CHEMISTRY

1901–1921



World Scientific

Singapore • New Jersey • London • Hong Kong

Published for the Nobel Foundation in 1999 by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 912805

USA office: Suite 1B, 1060 Main Street, River Edge, NJ 07661

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

NOBEL LECTURES IN CHEMISTRY (1901–1921)

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ISBN 981-02-3405-8

Printed in Singapore.

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PHYSICS

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Foreword

Since 1901 the Nobel Foundation has published annually *Les Prix Nobel* with reports from the Nobel award ceremonies in Stockholm and Oslo as well as the biographies and Nobel lectures of the Laureates. In order to make the lectures available to people with special interests in the different prize fields the Foundation gave Elsevier Publishing Company the right to publish in English the lectures for 1901–1970, which were published in 1964–1972 through the following volumes:

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Since the Elsevier series has been out of print for many years the Nobel Foundation has given World Scientific Publishing Company the right to publish these Nobel lectures, biographies and presentation speeches. The Nobel Foundation is very pleased that the intellectual and spiritual message to the world laid down in the laureates' lectures will, thanks to the efforts of World Scientific, reach new readers all over the world.

Bengt Samuelsson
Chairman of the Board

Michael Sohlman
Executive Director

Stockholm, March 1998

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Chemistry 1901

JACOBUS HENRICUS VAN'T HOFF

*«in recognition of the extraordinary services he has rendered by the discovery
of the laws of chemical dynamics and osmotic pressure in solutions»*

Chemistry 1901

*Presentation Speech by the former Rector of the National Archives
Dr. C. T. Odhner, President of the Royal Swedish Academy of Sciences*

Your Royal Highnesses, Ladies and Gentlemen.

The Academy has awarded the Nobel Prize for Chemistry to Jacobus Henricus Van 't Hoff, Professor in the University of Berlin, for his pioneering work on chemical dynamics and osmotic pressure in solutions.

As a result of his investigations in the fields of atomic and molecular theory Van 't Hoff has made the most important discoveries in theoretical chemistry since Dalton's time.

With regard to atomic theory Van 't Hoff, following an idea put forward by Pasteur, advanced the hypothesis that the elementary atoms have attachment points geometrically oriented in space—a hypothesis which in so far as carbon compounds are concerned led to the theory of the asymmetry of carbon atoms and to the founding of stereochemistry.

Still more revolutionary were Van 't Hoff's discoveries in the field of molecular theory. Van 't Hoff's investigations showed that the law, which has been named after the Italian Avogadro, according to which the number of gas molecules in a given volume is the same for all gases at the same pressure and temperature, embraces not only substances in the gaseous phase but also those in solution, provided that their pressure, known as osmotic pressure, is taken into account in the same way as the gas pressure in the case of gases. He proved that gas pressure and osmotic pressure are identical, and thereby that the molecules themselves in the gaseous phase and in solutions are also identical. As a result of this the concept of the molecule in chemistry was found to be definite and universally valid to a degree hitherto undreamed-of. He also discovered how to express the state of chemical equilibrium in reactions and the electromotive force which a reaction can produce; he explained how the transition occurs between the various modifications of the elements, between hydrates of differing water contents, how double salts are formed, etc.

By applying these simple principles, which were originally borrowed from mechanics and thermodynamics, Van 't Hoff became one of the founders of chemical dynamics. His researches have been a substantial factor in bringing about the magnificent advances in physical chemistry, in which

field his discoveries match the great contributions which other investigators, including those in our country, have made in the field of electrochemistry and in the theory of chemical reaction. This has opened up great prospects for scientific research. On the other hand, the investigations on the state of substances in solutions have had and will continue to have the greatest practical consequences—consequences whose benefit to mankind can best be appreciated if we remember that chemical reactions occur predominantly in solutions and that the vital functions of living organisms are maintained by metabolic processes which take place in solutions.

JACOBUS H. VAN 'T HOFF

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 $\frac{2}{3}$ 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

* The speaker is restricted in his choice of subject by the rules of the Nobel Foundation and craves indulgence if he touches upon matters not suited to presentation in popular form.

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 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 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).

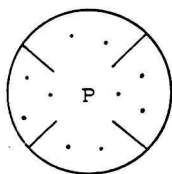


Fig. 1.

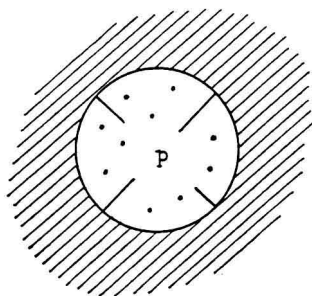


Fig. 2.

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

$$p = P \quad (1)$$

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 time used for these exceptions:

$$p = iP \quad (2)$$

We shall be returning to this point later. In the case of the non-electrolytes this reduces to (1), since $i = 1$. Now let us apply the basic relationship and