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Nobel Prize in Chemistry 1968

Lars Onsager

The Nobel Prize in Chemistry 1968 was awarded to Lars Onsager *"for the discovery of the reciprocal relations bearing his name, which are fundamental for the thermodynamics of irreversible processes"*.

RESEARCH INFORMATION:

Professor Lars Onsager has been awarded this year's Nobel Prize for Chemistry for the discovery of the reciprocal relations, named after him, and basic to irreversible thermodynamics. On hearing this motivation for the award one immediately gets a strong impression that Onsager's contribution concerns a difficult theoretical field. A closer study shows this indeed to be the case. Onsager's reciprocal relations can be described as a universal natural law, the scope and importance of which becomes clear only after being put in proper relation to complicated questions in border areas between physics and chemistry. A short historical review emphasizes this.

Onsager presented his fundamental discovery at a Scandinavian scientific meeting in Copenhagen in 1929. It was published in its final form in 1931 in the wellknown journal *Physical Review* in two parts with the title "Reciprocal relations in irreversible processes". The elegant presentation meant that the size of the two papers was no more than 22 and

15 pages respectively. Judged from the number of pages this work is thus one of the smallest ever to be rewarded with a Nobel Prize.

One could have expected that the importance of this work would have been immediately obvious to the scientific community. Instead it turned out that Onsager was far ahead of his time.

The reciprocal relations, which were thus published more than a third of a century ago, attracted for a long time almost no attention whatsoever. It was first after the second world war that they became more widely known. During the last decade they have played a dominant role in the rapid development of irreversible thermodynamics with numerous applications not only in physics and chemistry but also in biology and technology. Here we thus have a case to which a special Rule of the Nobel Foundation is of more than usual applicability. It reads: "Work done in the past may be selected for the award only on the supposition that its significance has until recently not been fully appreciated."

The great importance of irreversible thermodynamics becomes apparent if we realize that almost all common processes are irreversible and cannot by themselves go backwards. As examples can be mentioned conduction of heat from a hot to a cold body and mixing or diffusion. When we dissolve a cold lump of sugar in a cup of hot tea these processes take place simultaneously.

Earlier attempts to treat such processes by means of classical thermodynamics gave little success. Despite its name it was not suited to the treatment of dynamic processes. It is instead a perfect tool for the study of static states and chemical equilibria. This science was developed during the nineteenth and the beginning of this century. In this work many of the most renowned scientists of that time took part. The Three Laws of Thermodynamics gradually emerged and formed the basis of this science. These are among our most generally known laws of nature. The First Law is the Law of Conservation of Energy. The Second and the Third Laws define the important quantity entropy which among other things provides a connection between thermodynamics and statistics. The study of the random motion of molecules by means of statistical methods has been decisive for the

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development of thermodynamics. The American scientist J. Willard Gibbs (1839-1903) who made so many important contributions to statistical thermodynamics, has his name attached to the special professorship which Onsager now holds.

It can be said that Onsager's reciprocal relations represent a further law making possible a thermodynamic study of irreversible processes.

In the previously mentioned case with sugar and tea it is the transport of sugar and heat during the dissolution process which is of interest in this connection. When such processes occur simultaneously they influence each other: a temperature difference will not only cause a flow of heat but also a flow of molecules and so on.

Onsager's great contribution was that he could prove that if the equations governing the flows are written in an appropriate form, then there exist certain simple connections between the coefficients in these equations. These connections - the reciprocal relations - make possible a complete theoretical description of irreversible processes.

The proof of the reciprocal relations was brilliant. Onsager started from a statistical mechanical calculation of the fluctuations in a system, which could be directly based on the simple laws of motion which are symmetrical with regard to time. Furthermore he made the independent assumption that the return of a fluctuation to equilibrium in the mean occurs according to the transport equations mentioned earlier. By means of this combination of macroscopic and microscopic concepts in conjunction with an extremely skilful mathematical analysis he obtained those relationships which are now called Onsager's Reciprocal Relations..

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http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1968/press.html