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Nobel Prize in Chemistry 1936

Petrus (Peter) Josephus Wilhelmus Debye

The Nobel Prize in Chemistry 1936 was awarded to Peter Debye *"for his contributions to our knowledge of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases"*.

RESEARCH INFORMATION:

Chemists have for long been expressing their conceptions of the construction of compounds of substances by stereochemical formulae which are meant to represent the reciprocal position of the atoms in molecules. For many decades collected chemical experience has been concentrated in these formulae. They have enabled us to survey the enormous diversity of chemical compounds and have given us an insight into their possibilities of reaction, as a result of which it has been possible to harvest the experience gained in practice. The structural formulae are a certain guide in all works for the manufacture of new dyes, medicinal preparations, explosives and other useful substances of the most varied nature. This year's winner of the Nobel Prize for Chemistry has stated that they reflect the chemical behaviour of the substances in such a wonderful way that even the physicist cannot doubt that they do in fact represent the essential features of the real structural principles of the atomic aggregates. These formulae do not, however, represent actual models of molecules, but only indicate the grouping of the atoms.

It is only recently that these images which the chemists have made of the structure of the molecules could be accurately checked and the orientation ascertained of the atoms in compounds of substances in their details. For this purpose chemical research has made use of the services of X-rays. When such rays penetrate into a substance in which the atoms are in any way regularly arranged, the diffracted radiation, as a result of interference, is weakened in certain directions and strengthened in others. This is the same phenomenon which causes ordinary light to be dispersed in a spectrum if the light is diffracted through a series of closely drawn equidistant lines on a glass or metal plate, i.e. through a grating. Von Laue and the two research scientists, Bragg father-and-son, showed how these interference phenomena could be utilized to determine the regular arrangement of the atoms in the crystals, and were therefore awarded the Nobel Prizes for Physics in 1914 and 1915. Debye has taken an effective share in the investigation of the phenomena which have arisen in the resultant field of research and has contributed by his important initiative to the development of the X-ray crystallographic methods of investigation.

In the course of this work he soon found that even the relatively simple arrangement pattern resulting from the fact that the molecules of a gas have the same structure, can suffice to produce a detectable interference effect when X-rays penetrate a gas. As is the case with the reciprocal action of X-rays with crystals, the diffracted rays have an intensity which changes regularly with the angle of diffraction. Debye later worked out a complete theory for this phenomenon and as a result he has succeeded in creating a valuable method for the determination of the structure of molecules. A narrow sheaf of X-rays of known wavelength penetrates into a gas; the diffracted radiation is recorded, usually by photography. With the aid of Debye's theory a test is made to find whether a conceivable molecular model is in agreement with the distribution of intensity of the diffracted radiation; if such an arrangement of the atoms is confirmed, their dimensions can be ascertained and hence important information is obtained on molecular structure.

The cathode rays, which consist of high-speed negative particles of electricity - electrons - and which can therefore be called electron rays, have a wave nature, as was discovered by L. de Broglie, and so can be utilized to investigate the structure of the molecule. Consequently, Debye's theory on the interference of X-rays can readily be applied. There is, however, one difference, which is that the electron rays are diffracted mainly through the nuclei of the atoms, whereas the X-rays are scattered on the electron clouds which surround the atomic nuclei. As a result of this, the electron interferences give information on the position of the atomic nuclei in the molecule, whilst the X-ray interferences reveal where the centres of gravity of the electron clouds lie. In general, however, at least in practice, the particle systems so determined fall together. What is ascertained in both cases, then, is the position of the centres of the atoms.

The fact that matter is built up of electrically charged constituents is utilized by Debye to elaborate another very important method for investigating the structure of the molecule. According to Debye, if a substance is placed between the charged plates of a condenser, the effect of the electric field upon its molecules can be doubled. Inside every atom the positive nucleus is somewhat displaced in relation to the surrounding electron cloud, which is in consequence also deformed; furthermore the reciprocal position of the atoms in the molecule is disturbed. In addition to this deformation effect, a direction effect must also occur in certain cases. If indeed the distribution of the charge with the molecule is asymmetrical, the field endeavours to orientate this in a certain manner. Such a molecule possesses a so-called dipole moment. With regard to the electrical effects it possesses two equally large charges, one positive and one negative, which are concentrated at a certain distance from one another. The product from this distance and the charge gives the dipole moment of the molecule. To know this size is significant, for important conclusions can be drawn from it with relation to the structure of the molecule.

Debye has elaborated a theory of the effect of electric fields on molecules and has worked out methods for the determination of their dipole moments. These can be determined by measurements of the variation of the insulating power and of the density

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with the temperature. Debye's theory applies strictly only for diluted gases, in which there is no need to reckon with a reciprocal effect between the molecules. It is difficult, however, to prepare the experimental material for the gases necessary for the calculation of the dipole moments. It is therefore of value that the theory, as has been established experimentally, can also be applied without noteworthy errors to diluted solutions of substances in non-polar solvents.

A large quantity of important information has been collected on the structure of both inorganic and organic molecules by investigations according to these new methods, which complement each other in an outstanding manner. At least one hundred gaseous substances have already been studied now with the help of X-ray and electron interferences, whilst the molecular structure of thousands of substances has been elucidated by dipole moment measurements. Investigations of the charge symmetry of molecules have been of very great value especially to organic chemistry. It has been shown that certain bonds between atoms in organic compounds are characterized by specific electric moments. But characteristic moments can also be ascribed to groups of atoms or radicals. These bond or radical moments can in general be concentrated with a suffcient degree of accuracy to a resultant total moment, somewhat like the forces acting upon a body can be replaced by a resultant. A structural formula can therefore be checked by calculating its dipole moment and by comparing the result obtained with the dipole moment found by experiment

The measurements of the dipole moments, as well as those of the X-ray and electron-ray interferences in gases, are being utilized more and more, together with other investigations on molecular structure, as an essential aid to constitutional determination. The form of the molecules, the distance between their atoms, and also the greater or lesser degree of movement of certain groups entering into the molecules can now be exactly measured. This is obviously important in such cases where we have to deal with chemical compounds of identical composition but of different structure, i.e. where isomerism is present. During the last decade no means of research has been made available to organic chemistry which has been, even approximately, so effective in its importance.

For more details please visit:

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1936/press.html