A SYMPOSIUM ON MOLECULAR CONSTITUTION

AN INTRODUCTION

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The choice of molecular constitution as the subject for this symposium requires little explanation, for it has long been one of the goals of chemistry to devise models to account for the properties of substances in terms of structure. Although interest in molecular constitution was awakened in 1803 by the formulation of Dalton's brilliant but incomplete atomic theory, the first satisfactory contributions were the result of the principle enunciated in 1811 by the physicist, Avogadro. Unfortunately this principle was not fully comprehended by the scientific world until resurrected by Cannizzaro in 1858 in his masterly presentation. Cannizzaro not only gave a clear and illuminating distinction between atoms and molecules, but also established a method of settling for all time the vexed question of the number of atoms in a molecule.

We are all familiar with the rapid and systematic development which chemistry enjoyed in the years following the reading of this famous paper at Karlsruhe. This growth was due in no small measure to the development of a structural chemistry in which the classical concept of valence—the result of the combination of Avogadro's physical principle with the chemical laws of multiple proportions by whole numbers—played the leading rôle.

However, if we except the special contributions of Le Bel and van't Hoff on stereoisomerism, we must admit that the *methods* for attacking the problem of molecular constitution have remained, until comparatively recent times, essentially those

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established in 1858. Certain notable contributions, such as Wislicenus' idea of geometrical isomerism and Werner's coördination number, were made in the intervening years, but the methods which they employed to establish their propositions did not involve the introduction of fundamentally new principles. They made the best of what they had. The later illumination was lacking.

On the other hand, modern physics, which looks upon matter as an assemblage of positive and negative electricity organized in accordance with quantum rules, and the molecular characteristics primarily as a manifestation of the attractive and repulsive forces that arise from these specific distributions of electricity, has given the chemist a new viewpoint. From this he may profitably resurvey the problem of molecular constitution.

At the same time, modern physics has furnished many new tools with which the problem can be attacked afresh. I refer particularly to the x-ray, the spectroscope (in terms of the Bohr-Einstein frequency condition) and the determination of electric moments through refined measurement of the dielectric constant. To keep the symposium within reasonable compass it has seemed advisable to restrict the subject matter to a discussion of results which may be obtained from these three methods of analysis. Limitations of space and time also demand that these sub-topics be further limited in their scope. In this introduction we can only point out some of the salient features of the papers which follow.

In the first paper, Dr. Langmuir extends his well-known work of 1916 on the constitution of liquids and solids as manifested in surface tension and the behavior of surface films, by considering the molecular forces involved from the viewpoint of their electrical origin as developed by Debye in 1920 and in later papers. The effects of these molecular fields may be classified as (1) segregation, (2) orientation, and (3) deformation. Segregation is manifested most conspicuously in electrolytic solutions, but inasmuch as solutions have been the subject of two recent symposia, while orientation and deformation have not been previously discussed, these latter topics will constitute the themes of the more detailed papers by Professors Smyth and Williams.

The x-ray having settled many of the simpler questions of constitution in the solid state, Professor Jaeger now utilizes this instrument to elucidate the more complicated question of the structure of the ultramarines, where we find many puzzling examples of change in color and composition arising from methods of preparation. In his paper, which appears in full in the Transactions of the Faraday Society, he shows that the ultramarines have a structure similar in many respects to the base exchanging zeolites and that the color is associated with the position of the sulfur atom in the mass.

When applied to liquids, the x-ray method yields only diffuse halos on a photographic plate instead of the sharp lines obtained from crystals. Most physicists have let the matter go at that. Professor Stewart now finds that he can partially resolve these halos by using more refined methods, and it is comforting to learn that the lengths and thicknesses which he computes for the hydrocarbons using Bragg's law check up satisfactorily with those deduced earlier by Langmuir and Harkins using surface tension methods. Checks obtained from methods involving such radically different principles as these should foster greater confidence in the conclusions reached.

From studies of reactivity, the organic chemist has known for a long time that certain groups like the methyl group, although non-ionogenic, can be classified as more or less positive in an electric sense, whereas others, like the nitro group, can be considered more or less negative without being construed as electrolytes. Again, the positions of these groups when substituted in the benzene ring have a marked bearing upon the physical properties of the molecules formed. Another important step in advance is explained in the papers by Smyth and Williams on electric moments. They regard radicals like CHO, COOH, NH_2, CH_3, OH, NO_2 and the halogens, as having the properties of an electric vector which is directed into space rather than in a plane, and are able to assign to this vector characteristic positive or negative values. Such values are quantitative measures of the polarity of each radical. When we bear in mind that heretofore only qualitative measures of polarity were available, this step from qualitative to quantitative interpretation speaks for itself.

In the main all of the papers discussed thus far may be said to have confirmed, and rendered more precise in detail those pictures of molecular structure which have been generally accepted on classical grounds for a number of years.

Ever since 1913, when Bohr gave his famous formula for connecting the energy levels of atoms with the frequencies of absorbed or emitted light, which furnished the key that unlocked the wonderland of spectroscopy to the chemist and physicist, it has been clearly evident that the most searching analysis of chemical structure would ultimately be furnished by the spectroscope. Such a vast number of problems within this field immediately presented themselves to physicists that they had to spend most of their time unravelling the complexities of the line spectra of the atoms. They have had to postpone until very recently the interpretation of the highly complex band spectra; a subject of more pressing interest to chemists, because band spectra are produced by atoms linked together in molecules. It opens the way to a far broader field of inquiry and to more practical enlightenment.

Briefly stated, we may say that modern theory, as exemplified in the wave mechanics, enables one to describe the atom and its behavior in terms of integers, called quantum numbers. In his paper Professor Mulliken shows how these numbers change when simple atoms are brought together to form molecules. In this process there is a change in energy. If it decreases we have a stable molecule; otherwise it will be unstable. The energy values associated with the combinations of the lines in the bands enable one to follow these changes in detail and to calculate their respective probabilities, and also the number and strengths of the valence bands involved.

Perhaps the most remarkable result is that we can calculate the heats of dissociation of diatomic molecules like H_2 and I_2 far more accurately than we can measure them by the most refined thermochemical methods at our disposal. Nor is this all. Band spectrum analysis has predicted that if oxygen has isotopes of mass 17 and 18, certain lines should be observed. The predicted lines have since been observed by Giauque and Johnston in intensities corresponding to roughly 0.1 per cent and 0.01 per cent of these isotopes in ordinary oxygen.

Still more striking was the prediction of Heisenberg that two allotropic modifications of hydrogen molecules should exist. This prediction was based upon the calculated energy differences which result from combining hydrogen atoms with parallel and antiparallel magnetic moments resulting from the spins of their protons. Shortly thereafter, Dennison on this assumption was able to account satisfactorily for the anomalous specific heat curves of hydrogen, and experimentalists at once began to investigate if hydrogen, which we have always called a pure substance, really is a mixture of two isolable types. Within a year Bonhoeffer and Harteck, and Eucken, as well as others, were able to produce in almost any desired quantity samples of hydrogen which showed different vapor pressures, melting points, and thermal conductivities.

Surely such tangible results mean important things in chemistry. They make us more ready to accept the statement that molecules like CH, NH, OH and even He_2, which appear to break every classical rule of valency, exist in flames, arcs and discharge tubes, and that some of the molecules of sodium vapor are diatomic.

In interpreting optical rotation comparatively simple geometrical concepts have sufficed, but the problems with which modern chemistry has to deal are far more complicated. It is not surprising that it is necessary to approach the subject of molecular spectra armed with a far more advanced mathematical and physical background than was necessary to grasp stereoisomerism. Those who have mastered the intricacies of band spectra say that the primary difficulty in presenting the subject arises more from the reader's unfamiliarity with the methods and the notation which are necessary to represent the phenomena than from any real difficulty in comprehending the principles involved.

This extensive shift in chemical habits of thought from qualitative to quantitative concepts is accompanied by mathematical processes with which many chemists have not made themselves familiar. The processes have therefore the shock of unfamiliarity. But I verily believe that the difficulties presented by these newer methods are really not serious and that they will soon become so widely mastered as to become common knowledge among chemists. The mental digestion of anything new is usually a painful process; but the pains as well as the difficulties disappear when the novelty wears off and the "stunt" becomes common practice.