DISCUSSION

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In opening the discussion on Professor Mulliken's paper, I wish to sketch very briefly the change which the study of band spectra is bringing to certain branches of the field of chemistry.

The unit of quantity which has been used by chemistry in the past is the gram molecule or the gram atom; the entire range of quantities used in chemical operations from the most precise quantitative determinations to the largest scale manufacturing processes is not more than a few orders either way from this fundamental unit. As you know, this unit contains some 6.06×10^{23} molecules or atoms and thus, in all classical chemical studies, the number of individual atoms and molecules is very great and only *average* properties are observed.

The characteristic theory of this chemistry has been *thermodynamics,* which is especially suited to the study of systems whose detailed structure is unknown. It gives us the equilibrium conditions of these systems. It is unable to say anything about the velocity with which this equilibrium condition is reached.

The study of atoms and molecules using spectroscopic methods has changed the fundamental unit from the gram atom or molecule to the individual atom or molecule, even though in nearly all spectroscopic experiments we are working with very large numbers of these elementary systems. The spectral line observed visually or on a photographic plate is the result of large numbers of quanta, and so in a sense is the statistical result of these many elementary processes. The line gives us information, however, in regard to one single elementary atomic or molecular process and permits us to build up a more detailed knowledge of the atom or molecule, and this enables us to deduce the macroscopic properties of matter in bulk.

This more detailed knowledge of atoms and molecules permits us to use *statistical mechanics* for our theoretical guidance. Statistical mechanics demands a more detailed knowledge of the elementary units of the macroscopic system, and in turn promises to give us a more powerful attack on problems to which thermodynamics is unsuited. An example of a classical chemical problem solved by this new method is the equilibrium between atomic and molecular iodine (1). The equilibrium for this reaction has been calculated from data of the atomic and molecular spectra alone. It is doubtful if much more complicated examples can be handled in this way, but it is gratifying to know that the fundamental underlying principles and behavior of such a simple equilibrium are understood so well.

In the field of kinetics, where thermodynamics cannot guide us, this spectroscopic information promises to give us a more thorough understanding of the fundamentals. Thus in continuous spectra we see the processes of photochemical dissociation, and in "predissociation," discovered by Victor Henri, we observe a process which enables us to observe indirectly molecules in the process of dissociation.

In these brief remarks, I only wish to emphasize the applications of data of the type presented by Professor Mulliken to ordinary chemical processes. The data are interesting in themselves and illuminate other fields of science which are not so close to classical chemistry.

REFERENCE

(1) Gibson and Heitler: Z. Physik **49**, 465 (1928).