

## Introduction to the Symposium

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## Symposium on the Structure of Molecules and Aggregates of Molecules\*

### Introduction to the Symposium

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IN the previous symposia in the field of physical chemistry held by the Division of Physical and Inorganic Chemistry, molecular structure, intermolecular forces, and the kinetics of chemical reactions have been the topics of discussion. In the present symposium we return to the problem of structure. We shall be concerned in part with the structure of individual molecules and in part with the structure of interacting groups of molecules, as manifested in the liquid and solid states.

Classical physical chemistry was built upon thermodynamics. The equilibrium theory of thermodynamics was employed to correlate and interpret the physical and chemical properties of substances, without reference to their specific structure. While thermodynamics remains a frame of reference for all physico-chemical phenomena, the experimental verification of its laws is so well established, and the important

task of systematizing physico-chemical data so far advanced, that its further exploitation and development now lies in the field of applied chemistry.

Modern physical chemistry is primarily concerned with problems of structure as related both to the properties of systems in equilibrium and to the mechanism of the physical and chemical processes traversed in the attainment of equilibrium. The task which it has set itself is that of relating the properties of physico-chemical systems to the structure and interactions of the molecules of which they are composed. The structure of individual molecules and the nature of intermolecular forces has been studied from the theoretical side by the methods of quantum mechanics and from the experimental side by the techniques of spectroscopy and electron diffraction. The theoretical study of the relation between molecular structure and the physico-chemical properties of systems composed of many molecules has been undertaken by the methods of statistical mechanics. The problem has been attacked from the experimental side by the techniques of x-ray crystallography, in the case of crystals, and of x-ray scattering, in the case of amorphous solids and

\*The Symposium on the Structure of Molecules and Aggregates of Molecules was held, as the Fifth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, at Columbia University, New York, on December 30, 1940 to January 1, 1941. The arrangements for the symposium were made by a committee consisting of J. G. Kirkwood, Chairman, H. Eyring, L. S. Kassel, G. B. Kistiakowsky, L. Pauling, G. Scatchard, H. C. Urey, and J. W. Williams.

liquids. In addition much accurate experimental work has been carried out in the measurement of thermodynamic properties of particular significance to the structural theories.

The structural calculation of the thermodynamic functions of gases in the limit of zero pressure has advanced to such a stage as to be more accurate than available experimental data in many cases. In liquids and solids, the problems are much more complex, and only partial and approximate solutions can be presented for many of them at the present time. However,

considerable progress has been made in the statistical mechanical study of liquids, liquid solutions, and crystalline solids, and in the interpretation of phase transitions, such as condensation, and polymorphic transformations in condensed systems.

It is the purpose of this symposium to present for discussion reports from a number of investigators, actively engaged in theoretical and experimental work on the behavior of physico-chemical systems in relation to the structure and interactions of their component molecules.

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## Molecular Distribution\*

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Various functions, by means of which the distribution of molecules in a system may be described, are defined, and the relations between them are derived. Equations, by means of which these functions may be calculated from a knowledge of the mutual potential energy between pairs of molecules, are also derived. The equations applicable to gaseous systems, which are derived by a development previously used in the theory of condensing systems, enable the calculation of the distribution functions by means of a power series in either the fugacity or the inverse volume. The coefficients of these power series are direct integrals involving the pair potentials between molecules. In condensed systems an alternative procedure is required. The equations then appear in the form of integral equations involving the unknown functions under

the integral signs. These equations are not readily solved, due primarily to the difficulties of performing multiple coordinate integrations. By the use of functions involving the probabilities of population of virtual cells, the cell equation frequently used for the calculation of the thermodynamic properties of liquids is derived as a consequence of the method used here. The direct connection between the equations derived in the theory of condensing systems, and in the usual cell approximations, is thus established. The equations derived here, however, permit consistent use of the cell method to arrive at higher approximations. This development may possibly be of value in making numerical evaluations of the thermodynamic functions of liquids.

### I. INTRODUCTION

FOR the sake of simplicity the discussion will be, at the outset, limited to particularly simple types of systems, although the extension to more complicated types would not involve impracticable difficulties.

Systems will be considered consisting of  $N$

identical monatomic molecules in a volume  $V$ , with volume per molecule  $v = V/N$ , the configurational position of the  $i$ th molecule being uniquely determined by the value of its three Cartesian coordinates,  $x_i, y_i, z_i$ , for which the symbol (i) will be used. The volume element in the three-dimensional configuration space of the  $i$ th molecule will be indicated by  $d\tau_i$ .

It will be assumed that the potential energy,  $U\{\mathbf{N}\}$ , of the system may be written as the sum of the mutual potentials of the  $N(N-1)$  pairs:

$$U\{\mathbf{N}\} = \sum_{N \geq i > j \geq 1} u(i, j), \quad (1)$$

and that the equations of classical statistical

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\*\* At present Sterling Fellow at Yale University.