

upon our concept of the structure of ribonucleic acid, by W. E. Cohn. This is a rather heterogeneous collection of titles; though they could each deal with the subject of the symposium from a different point of view, the authors do not really appear to have this in mind. However, each of these five papers is a very clear exposition written by distinguished people about their own researches. The lectures published here were originally delivered at Harvard in February and March 1952. Clearly, seminars on original researches lose much if published two and a half years later.

The second part of the book consists of four papers by C. D. Coryell, J. Schubert, G. Schwartenbach and G. Scatchard (with W. L. Hughes, F. R. N. Gurd and P. E. Wilcox) which present a unified story. Before the Second World War the main interest of the Department of Physical Chemistry at Harvard University Medical School was in the ionizing groups of amino-acids, peptides and proteins and the properties of these compounds which are a consequence of their ionic side-chains. After the War such knowledge was applied in a number of laboratories to the study of the interaction of amino-acids and proteins with metals and other ions. The results of such studies can give information about the reactive groups on the surface of protein molecules, they can define the catalytic sites of enzymes and they can give information about the specific role of certain metals in some enzyme catalysis mechanisms. Furthermore, E. J. Cohn and his colleagues have made great use of specific metal-protein interactions for the purification of certain proteins.

The four papers of the second half of the book deal with the fundamental aspects of the interaction of metals with small molecules and proteins from a theoretical point of view, and give a good review of the available experimental results. Such a good account of the work in this field, which is going on at Harvard and in several other laboratories, is very welcome. It is a pity that some of the space of this volume has not been devoted to quantitative data for van der Waals forces in specific protein-protein enzyme-substrate and antigen-antibody interactions.

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## ION-SOLVENT INTERACTION IN SOLUTIONS

### Ionic Processes in Solution

By Dr. Ronald W. Gurney. (International Chemical Series.) Pp. ix+275. (London: McGraw-Hill Publishing Co., Ltd., 1953.) 46s. 6d.

THE properties of an electrolyte solution are influenced by long-range Coulomb forces, by the effect of each ion on the solvent molecules in its neighbourhood, and by the nature of the close-range forces when ions approach one another and their zones of modified solvent interact. Since the acceptance of the Debye-Hückel theory, the centre of interest in electrolyte solutions has been in the shorter-range forces between ion and solvent or between ion and ion; but though data have continued to be accumulated, their interpretation has been dependent on advances in our understanding of the nature of liquids.

In this book by the late Dr. R. W. Gurney attention is focused on the solvent molecule, and his novel treat-

ment leads him to some very interesting and suggestive conclusions. Picture a group of water molecules arranged in the open liquid structure. The central molecule will have four nearest neighbours tetrahedrally arranged, two with protons directed towards negative regions of the central molecule and two with the opposite orientation. Outer molecules of the group will contribute to the stability of this arrangement. If now the central molecule is replaced by an atom of nearly equal size on which we imagine an electrical charge of gradually increasing magnitude to accumulate, the state of lowest potential energy will eventually be one in which the four water molecules in contact with the ion each has a proton pointing towards it, if the charge is negative, and vice versa if it is positive. But before the ionic charge has become large enough to impose this arrangement, it must have passed through a critical value for which there is no preferred direction of the adjacent molecules. Gurney considers that this critical value is only a little less than the electronic charge itself, so that rather large univalent ions, like the caesium and bromide ions, will produce disorder in the solvent surrounding them, whereas small or multiply-charged ions will be able to set up around themselves a new arrangement of local order more stable than that existing in pure water.

As a primary criterion of the order-disorder situation, Gurney uses the viscosity coefficients of the ions. Wolfenden and his collaborators pointed out many years ago a correlation between these viscosity coefficients and the temperature coefficients of the ionic mobilities; for example, at ordinary temperatures the caesium ion, which has a relatively high mobility and low temperature coefficient, reduces the viscosity of water, and all these effects can be attributed to a loosening of the water structure. Gurney takes this further, and shows a striking relation between the viscosity coefficients and the entropies of solution, and, finally, a correlation between the activity coefficients of uni-univalent electrolytes and the order-producing or order-destroying characteristics of their constituent ions.

Dr. Gurney does not give a discussion of ion-pair formation, but here, too, his methods are suggestive. The experimental dissociation constants derived by semi-empirical methods for such electrolytes as caesium chloride have for long been regarded as 'impossible' by many physical chemists because (a) quantum-mechanical forces will be absent, and (b) Bjerrum's electrostatic treatment predicts no association between such large ions in water. The reply to this argument has been that an electrostatic theory using the normal dielectric constant of water cannot give quantitative results for ions at their minimum distance of separation; and this is given substance by Gurney's picture of conditions in the co-sphere of solvent surrounding each ion. As these overlap, the resulting free energy change is equivalent to a substantial short-range force of attraction (or repulsion) between the ions, in terms of which the ion-pair may be more sharply defined.

These comments by no means exhaust the topics to which this book supplies a fresh approach. Everyone interested in the dissociation constants of weak acids should read the treatment of acid-base equilibria, in which again the importance of the entropies in water of the anions is emphasized; and readers, whether they agree with everything said or not, will find the whole book stimulating and provocative.

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