
CURRENT SCIENCE—50 YEARS AGO

ELECTRICITY IN CHEMISTRY*†

ALMOST the first application of electricity to chemistry was the experiment of Nicholson and Carlisle in which water was decomposed into its elements by a current from the voltaic pile, which had just then been discovered. This was in 1800. In the immediately following decades, the new tool of electricity held the fascination of the leading chemists. In particular, the classical work of Faraday and the laws enunciated by him have remained to this time fundamental in all considerations dealing with the relationships between electricity and chemistry.

Studies on these relationships increased rapidly, and when Arrhenius promulgated his hypothesis of ionization equilibria in solutions, a definite big impetus was given to the whole subject. The thermodynamic study of energy in chemical systems had just then been initiated and was in the full vigour of its youth. It was soon realized that the electrical energy connected with galvanic cells was of a reversible type and that rigorous methods of thermodynamics could be applied to many of the chemical changes involved in the galvanic cells. The relationships between chemical and electrical energies, particularly in liquid systems, have since been developed by systematic work into a subject in itself, under the caption of 'Electro-chemistry'. This term 'electro-chemistry' can at the present day however comprehend a much wider range of topics, for, much of the recent investigations on the electrical nature of matter and of the chemical reactions between them, the investigations mostly carried out by physicists on the electrical conductivity in solids and gases, and several other aspects of molecular physics could all be included under this head. Indeed it will be difficult to draw any sharp line between 'electro-chemistry' and other branches of physics and chemistry.

Still the old and somewhat arbitrarily defined

'electro-chemistry', which includes mostly studies of chemical reactions brought about by electrical energy and of chemical reactions giving rise to electrical energy, is itself a wide and steadily growing subject. Considerable progress has been made in this field after Debye and Huckel indicated how the then troublesome deviations of strong electrolytes from ideal behaviour in solutions, could be accounted for quantitatively by taking into consideration the interionic attractions and repulsions. As is well known the basic idea in this theory is that each ion is surrounded on the average by an oppositely charged 'ionic atmosphere' distributed with radial symmetry around the ion as centre. This concept besides its success in thermodynamics and potentiometry, has won laurels also in the field of conductometry. The ionic atmosphere gives rise to a retarding effect on the mobility of the ion, and this along with another effect pointed out by Onsager, as due to a finite time of relaxation between the ion and its atmosphere, is able to successfully account for the observed equivalent conductance of solutions of strong electrolytes at least over the range of low and moderate concentrations. Other consequences of the Debye and Huckel theory such as the Wien effect at high field strengths, and the dispersion effect at high frequencies have been predicted and verified. All these new ideas and theories have brought in their wake, considerable improvements in the technique of electrical measurement on solutions.

As regards practical applications, the principles of electro-chemistry have been utilized from the earliest days in the arts of electro-plating, electro-metallurgy, etc., while indirectly they have been of even greater use in the control of industrial processes, through conductivity, pH and EMF determinations. On the fundamental side, electro-chemistry has provided some powerful tools in investigations relating to chemical reactions involving strong electrolytes, the nature of molecular complexes, hydrolysis and solubility of substances from conductometric measurements, studies on the course of reactions from potentiometric and conductometric titrations, the analysis of proteins from electrophoretic studies as developed by A. Tiselius, etc.

**The Principles of Electrochemistry*. By Duncan A. MacInnes, (Reinhold Publishing Corporation, New York, Chapman & Hall, Ltd., London), 1939, pp. 478 with 148 illustrations, Price \$ 6.00.

†Published in *Curr. Sci.*, 1939, Vol. 8, p. 330.

Among the leading contributors to this renaissance in electro-chemistry, Dr MacInnes is a prominent figure. The work of MacInnes and his associates is characterized throughout by systematic attempts to improve the accuracy of experimental data, and they have achieved many significant successes in verifying the predictions of the interionic attraction theory with respect to activity coefficients, conductivity, etc. The book itself which Dr MacInnes is now presenting to the scientific world can rightly be described as another and fundamental contribution to the science of electro-chemistry. It breathes of precision throughout: the experimental portions described deal with the modern refinements of technique while the theories are clearly and succinctly recounted by leading up from first principles wherever possible. Ample references to the original literature, most of them of recent dates, have been provided to help the reader further on. In many ways a marked and very welcome feature of the book, is the careful, painstaking and critical evaluation of the available experimental data, and of the derived physical constants. The result is, that for

the field covered the book takes a front rank with other critical compilations of data on physical constants. There is, besides, a logical development of ideas, the scope of the book being extended in the last five chapters to the use of conductance measurements in various physico-chemical investigations, the effect of structure and substitution on the ionization constants of organic acids and bases, the dielectric constants of liquids and the dipole moments of molecules, electrokinetic phenomena, passivity and overvoltage.

There is but little to offer by way of helpful criticism, as it is patent that the book has been brought out with much painstaking care and with clearly defined objectives. However, a few illustrative problems either as an appendix at the end of the book, or at the end of the relevant chapters would have added to the usefulness of this book. As a work of reference to all, it is almost a necessity.

M. A. G. RAU

NEWS

METALLIC HYDROGEN (?)

Important scientific discoveries are, for some reason, first announced in the news media and only later in scientific journals! Now comes the news that at the Geophysical Laboratory, Carnegie Institution, Washington, DC, H. K. Mao, the high-pressure scientist (renowned for his remarkable work with the 'diamond anvil apparatus', which he perfected) and his collaborator Russel J. Hemley have obtained 'positive signs of hydrogen gas transforming itself into a metal'. Scientists had predicted that hydrogen

may become a metal, and for almost five decades there has been a continual search for metallic hydrogen. Mao and Hemley state: 'Hydrogen was subjected to unprecedented pressures between anvils of diamond. It went through a series of transformations, and finally ended up as a black mass. This raises hopes of gaining new insights into the fundamental properties of atomic bonds.' We await the publication of the results in a scientific journal with all the experimental proofs.