SCIENTIFIC BOOKS.

The Theory of Electrolytic Dissociation and some of its Applications. By HARRY C. JONES, Associate in Physical Chemistry in Johns Hopkins University. New York, The Macmillan Company. 1900. Pp. xii + 289. Price, $1.60.

For several decades the dominant field in chemistry has been the study of organic compounds, and it is only within the last ten years or so that the tide has given evidence of turning in other directions. Chemical theory has been developed very largely in its application to organic chemistry and it is partly at least because these theories have proved inadequate in their wider and more general application that attention is being turned more strongly to inorganic chemistry and physical chemistry. There has always been a limited number of chemists who have confined themselves largely to inorganic chemistry, but the great impetus in this direction has come from Mendeleef's generalization of the periodic law, and the consequent necessity of studying closely the relations which subsist between the different elements. So, too, physical chemistry, that is, the study of the physical properties of chemical substances, has always attracted a few investigators. Perhaps the most notable workers have been Kopp, who determined and compared large numbers of physical constants of organic substances, and the founders of thermo-chemistry, Berthelot and Julius Thomsen. But with the work of van't Hoff and Arrhenius was called into being a new physical chemistry, one of the most important fundamental doctrines of which is the theory of electrolytic dissociation, and whose most influential teacher has been Ostwald. The *Zeitschrift für anorganische Chemie* and the *Zeitschrift für physikalische Chemie*, as well as the *Journal of Physical Chemistry* in this country, testify to the activity of the workers in these two newer fields.

The demands of teachers have also occasioned the production in physical chemistry of a very considerable text-book and reference book of literature, much of it far from satisfactory, as is naturally to be expected in a department of science young as yet, and hence in a very immature state. Some of these books attempt a survey of the whole field of the older and the newer physical chemistry, some dwell on the new almost exclusively. The book before us is less ambitious, aiming only to treat of a single, though the most important theory of physical chemistry of to-day. In doing this, however, a view of the relation of this theory to the whole field, and of the newer to the earlier physical chemistry is given. Dr. Jones is to be congratulated upon having written a book which, while brief, is clear and is readable.

The book is divided into four chapters: Chapter I. The earlier physical chemistry, 70 pages; Chapter II. The origin of the theory, 33 pages; Chapter III. Evidence bearing upon the theory, 67 pages; Chapter IV. Some applications of the theory, 112 pages; as far as space goes an excellent balance. In the preface the author states that these chapters seek to answer respectively the questions: "What was physical chemistry before the theory of electrolytic dissociation arose? How did the theory arise? Is it true? What is its scientific use?"

Chapter I. takes up first the work done upon the relations between properties and composition, and properties and constitution. A few pages then outline the development of thermo-chemistry. The next topic is development of electro-chemical theory; the later theories of electrolysis, Hittorf's work on the migration velocity of the ions and Kohlrausch's work on the conductivity of solutions, complete the connection between the older and newer physical chemistry, indeed, these last rather belong to the new. This chapter is completed by the development of chemical dynamics and chemical statics, including the law of mass action, and the work of Willard Gibbs. The treatment of these topics is necessarily brief, but it suffices well to lead up to the main topic of the book.

Chapter II. It is a curious fact that the origin of some of the great ideas of chemistry must be credited to those who were not chemists. The atomic theory, Avogadro's theory, the discovery of the inert gases are examples; so also the theory of electrolytic dissociation owes its origin to the osmotic investigations of a botanist, W. Pfeffer, working in the field of vegetable physiology. Pfeffer in 1877 published a series of quantitative studies of osmotic pressure, using the copper ferrocyanid cell, which was destined to be much used at a later period. At not far from the same time, ideas on the arrangement of atoms in space began to germinate in the mind of van't Hoff. "From this he (van't Hoff) was led to study reaction velocity, and from this the conditions of equilibrium. But closely connected with the problem of equilibrium was that of affinity. He took up, as an example of affinity, the attraction of salts for their water of crystallization, and sought to measure this more directly than had been done." It was at this point that his attention was called to the work of Pfeffer, and after studying concentrated solutions he turned to dilute. In 1887 just ten years after Pfeffer's work, van't Hoff published a paper entitled 'The Rôle of Osmotic Pressure in the Analogy between Solutions and Gases,' and in this shows the application of Boyle's law to dilute solutions. The next step was to show that Gay-Lussac's law also applied to dilute solutions, and finally that these could only be true on the assumption that the law of Avogadro was equally true, that is "that solutions which at the same temperature have the same osmotic pressure, contain in a given volume the same number of dissolved particles."

It soon however became clear that "the osmotic pressures of large classes of chemical substances do not conform to these laws. The exceptions include all the acids, all the bases and all the salts," that is electrolytes, and in all these the osmotic pressure is greater than would be expected. Thus far van't Hoff. The next step is taken by Arrhenius who reasoned that as the anomalous vapor density of ammonium chlorid, etc., was due to the dissociation of the compound into simpler molecules, so in dilute solution the salt is dissociated and this dissociation is into its ions, thus going back to Clausius' theory of electrolysis. In this way came into existence the theory of electrolytic dissociation as advanced by Arrhenius, which is briefly, that all electrolytes when in aqueous solution are dissociated to a greater or less extent into their ions, which are the positive and negative portion of the molecule laden with a charge of electricity.

Such is an outline of the development of the theory as traced in this chapter, much of it in the language of Pfeffer, van't Hoff and Arrhenius, and all of it lucid and logical.

Chapter III. is devoted to a presentation of the evidence for the theory. It is first shown that the physical properties of completely dissociated solutions should be additive, as is the case with dilute solutions of strong salts. Then the evidence from the heat of neutralization is given. The next section is perhaps the most important in the chapter, considering the relations between osmotic pressure, lowering of freezing point, rise in boiling point and electrical conductivity; it is just here that to the older chemists who have not been raised on this theory, the evidence for it appears most convincing, indeed it is the phenomena connected with these points which it is most difficult to account for on any other theory than that of electrolytic dissociation. Experiments to show the presence of free ions, effect of an excess of one of the ions and the relation between dissociation and chemical activity are the next subjects considered and the chapter ends with the effect of water on chemical activity. Numerous examples are given, taken largely from the work of H. Brereton Baker, showing the necessity of the presence of at least a trace of water in many chemical reactions.

For instance, dry chlorin will not act on metallic sodium; dry hydrochloric acid will not act on carbonates; dry hydrochloric acid and ammonia will not unite and dry sodium will not decompose concentrated sulfuric acid. Since the publication of the book, Baker has succeeded in distilling phosphorous in an atmosphere of dry oxygen. The question is now asked, "Why is water essential" and an answer is found "in that water has a very high dissociating power, breaking down the molecules into ions which then react. These facts are just what would be predicted if the theory of electrolytic dissociation is true."

Chapter IV. discusses first the application of the theory of electrolytic dissociation to solutions, and here are brought up a large number of the problems most interesting the physical chemists of to-day. This portion is particularly vivid, so much of it is descriptive of the author's own work. Here also is given Thomson's theory of the cause of electrolytic dissociation which while offering a simple explanation of the phenomena, has not as yet been fairly tested experimentally. The next section treats of the application of the theory to a physical problem, that of the seat of electromotive force in primary cells, and closely connected with this is a review of Ostwald's work on 'Chemische Fernewirkung.' Then follows the closing section on the application of the theory to biological problems with especial reference to the toxic action of ions.

Such is an outline of the book, whose perusal will well repay anyone who desires to become familiar with the most important phase of modern physical chemistry. It seems ungracious to offer any criticism of a book which limits itself to a definite field and so well carries out its aim, but after reaching the end of the book, one can hardly help feeling that he would like to hear the other side. The author's position is practically that of an advocate, and he makes the best of his case. It is true that he speaks of difficulties, but he does not discuss them or even allude to many of them. He says, indeed, "It has already been mentioned, and stress should be laid upon it, that there are facts to which the theory, as we now conceive it, does not seem to apply. But the evidence in favor of the theory is so overwhelming, in comparison with the few apparent exceptions, that we should examine the latter very closely before concluding finally that they are real exceptions. Without for a moment ignoring the facts for which the theory does not seem to entirely account, the writer believes that the evidence in favor of a great generalization being expressed by the theory of electrolytic dissociation is as strong as in the case of many of our so-called laws of nature. For how many of these apply under all conditions, and are entirely free from exceptions." But we wish the author had added a short chapter on these apparent exceptions, for if one reads his book to gain a knowledge of the theory, one desires to hear at least something of objections raised to it. As far as concerns aqueous solutions the theory seems to present an important and very useful generalization and yet it is not even here free from difficulties. It is also limited in its field in that it does not account for the fact of solubility, nor answer the questions why this salt is soluble, that insoluble; and in that it applies only to electrolytes. Again, as soon as we leave the field of aqueous solutions we realize that the present statement of the theory is too narrow. The work of Franklin on liquid ammonia as a solvent presents many phenomena wholly inexplicable on the theory of electrolytic dissociation, and work with other solvents raises other difficulties.

That such advances have been made along the line of this theory, as yet hardly in its teens, is a source of wonder; but much more remains to be done. The greatest proportion of this work has been confined to aqueous solutions, but it is only by extending it to all manner of solvents that any comprehensive theory of solutions will be reached. This no one realizes more than Dr. Jones, who is applying his work to the alcohols and other solvents, and the same is true of other American chemists. Perhaps after all Dr. Jones' book is the more attractive, and even more useful, because its author has posed less as judge than as advocate.

The typography of the book and its general make-up are excellent, the proof has been very carefully read. One excellent innovation has been partially adopted, that of giving the year in addition to the volume in the references to periodical literature. This, while entailing little additional work upon the author, not only lightens materially the labor of one who is looking up the original literature, but it gives the reader a much more definite chronological idea of the subject-matter. The custom should be uniformly adopted in scientific literature.

The book is provided with a satisfactory index.

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An Introduction to Physical Chemistry. By JAMES WALKER, D.Sc., Ph.D. London, Macmillan & Co., Limited; New York, The Macmillan Co. 1900. Pp. x + 355. Price, $2.50.

The author states in the preface that his main object in writing this new work on physical chemistry is to emphasize the important bear-