SCIENTIFIC BOOKS

Hydrates in Aqueous Solution. Evidence for the existence of hydrates in solution, their approximate composition, and certain spectroscopic investigations bearing upon the hydrate problem. By HARRY C. JONES, with the assistance of F. H. GETMAN, H. P. BASSETT, L. McMASTER and H. S. UHLER. Pp. viii + 264. Publication No. 60 of the Carnegie Institution, Washington, D. C., 1907.

The first part of this monograph, covering 157 pages, presents the detailed results of earlier work and the measurements of Getman and Bassett of freezing-points, electrical conductivity, specific gravity and refractive power of solutions. All the observations were made on aqueous solutions, except a series of determinations made by McMaster, presented on pages 149 to 152, which relate to solutions of lithium chloride, bromide and nitrate in methyl and ethyl alcohol and to calcium nitrate in the latter solvent. In the case of the aqueous solutions, 98 compounds, including acids, salts and bases were studied; and in the course of this work between 1,400 and 1,500 solutions were examined. The purpose of making the specific gravity determinations was merely to permit a computation of the lowering of the freezing-point per 1,000 grams of solvent, the solutions having been prepared by dissolving a certain weight of substance in water and then diluting to a definite volume.

The refractive indexes when charted as ordinates against the concentration of the solutions as abscissas yield curves which are practically straight lines in all cases. They consequently bear no simple relation to either the conductivity or freezing-point curves, and are, indeed, not used later in the argument concerning hydrates in solution.

The electrical conductivities of the solutions were measured for the purpose of ascertaining the so-called degree of electrolytic dissociation of the dissolved substances. When the molecular conductivities are charted as ordinates and the corresponding volumes as abscissas, smooth curves are obtained in all cases. These curves have in general a similar trend, being concave toward the axis of abscissas for the various electrolytes investigated.

The ebullioscopic method was employed in but few of the aqueous solutions; the alcoholic solutions were, of course, investigated by this method. On the other hand, the cryoscopic method was very extensively employed in studying the aqueous solutions, and in order to make comparison possible, the electrical conductivity measurements were made at 0° C. When the molecular lowerings of the freezing-point are charted as ordinates and the molecular concentrations as abscissas, curves are obtained which are in general convex toward the axis of abscissas. In some cases the points of inflexion are quite well defined, in other cases the curves are fairly flat, and in still others they are nearly straight lines. In the few cases where boiling-point curves have been similarly charted, these show the same general behavior, except that the points of inflexion occur at a greater concentration than in the freezing-point curves.

The chief argument presented in the monograph for the existence of hydrates in solution is the occurrence of minima in these freezing-point and boiling-point curves. From the fact that the minima occur at higher concentrations in the boiling-point curves, it is argued that the hydrates are less stable at higher temperatures and hence require greater concentration for their formation than at lower temperatures. To be sure a point is also made of a supposed relation between lowering of the freezing-point and water of crystallization of the dissolved substance, it being claimed that high crystal water content and a large depression of the freezing-point go together. As a matter of fact, however, the behavior of solutions of many salts rich in crystal water speaks strongly against this supposed relation. So for instance, the sulphates in general give relatively small lowerings of the freezing-point, a fact which, moreover, is not new. This behavior of the sulphates it is stated is 'abnormal' and due to polymerization of the salts. However, no independent evidence is adduced to support the assumption that such polymerization occurs, and so the relation which it is claimed exists between lowering of the freezing-point and crystal water content of the solute can not be considered as established. The well-known fact that salts generally separate from hot solutions with less water of crystallization than from cold solutions is also regarded as evidence of the existence of hydrates in solution.

The fact that salts frequently crystallize with water has long been considered as evidence in favor of the assumption that hydrates exist in solution. The reasoning has simply been that whatever separates from a solution at a given temperature has also existed in that solution. So in this respect the paper really presents nothing new. Furthermore, it has long been known that the various physical properties of solutions can not be foretold on the assumption that solutions are merely mechanical mixtures of solvent and solute. The deviations which the properties of solutions have shown from those computed on the assumption that they are merely mechanical mixtures have always been regarded as evidence in favor of the idea that in the process of solution some form of combination between solvent and solute takes place; and so the argument in favor of the existence of hydrates in solution based upon the occurrence of minima in the freezing-point curves also presents nothing new in principle. However, there has been in the past great difficulty in determining definitely just what the composition of the supposed hydrates in solution really is, and as Professor Jones presumes to compute, at least approximately, the composition of these hydrates, the vital interest of the whole monograph really centers upon the results of these computations.

Now an inspection of the method adopted by the author for determining the approximate composition of the hydrates in solutions shows that it consists of assuming the approximate validity of the simple gas laws for all solutions, concentrated as well as dilute; and that in the case of electrolytes the solutes are electrolytically dissociated, the so-called degree of electrolytic dissociation being calculable according to the well-known formula of Arrhenius even in concentrated solutions, at least approximately. On the basis of these assumptions it is computed what the molecular lowering of the freezing-point ought to be; and from this value and that actually found in practise, it is calculated how much water is combined with the solute. In other words, the method simply consists of assuming just so much of solvent as combined with the dissolved substance in any given case as is necessary to make the simple gas laws hold even for concentrated solutions. That the gas laws do not hold for concentrated solutions, even approximately, is a well-recognized fact; and consequently the numerous computations of the approximate composition of the supposed hydrates in the solutions studied and the curves representing the variations of the composition of these hydrates with change of concentration need not be further considered here, for they are quite valueless. The republication of the results of the calculations of the composition of these supposed hydrates in this monograph is all the more inexcusable because Van Laar[1] had already called attention to the gross error of Jones and Getman when a part of the work appeared in the *Zeitschrift für physikalische Chemie*, 49, 385, 1904.

While then the monograph has failed in what must be regarded as its main objective, namely, the computation of the approximate composition of hydrates in solution, the large bulk of experimental evidence presented, though also in part not new, undoubtedly goes to show that solutions are not merely mechanical mixtures, but that combination of a specific nature does take place between solvent and solute. The experimental data recorded will no doubt prove useful in the future.

Part II. of the paper, pages 161 to 259, presents the results of H. S. Uhler of the study of the absorption spectra of aqueous solutions of cobalt chloride, copper chloride and copper bromide and of these solutions mixed in different proportions with calcium chloride, calcium bromide or aluminum bromide. The absorption spectra of cobalt chloride, copper

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[1] *Chemisch Weekblad*, 2, 6–8, 1905. Abstract in *Chem. Centralblatt*, 76, 491, 1905. Also reprinted in 'Vorträge über thermodynamisches Potential,' pp. 6–8; published by Vieweg u. Sohn, Braunschweig, 1906.

chloride and copper bromide in methyl and ethyl alcohol and in acetone are also studied. Photographic records showing the absorption bands in the different solutions are presented, These photographs show admirably how the absorption bands gradually change as the various dehydrating agents mentioned are added to the solutions. In the discussion of the results the difficulties met in interpreting spectroscopic observations of this kind are clearly set forth. In fact the second part of the monograph is more carefully and judiciously written than the first part, the latter containing practically no reference to the experimental work of others, whereas in the second part the work and opinions of other investigators receive due consideration. Attempts to deduce the approximate quantitative composition of the hydrates in solution from the study of the absorption spectra are, of course, not made, for such observations do not lend themselves for that purpose. It is simply claimed that the results bear out Jones's ideas of hydrates in solution in a satisfactory manner.

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Electrons or the Nature and Properties of Negative Electricity. By Sir Oliver Lodge. London, George Bell and Sons. 1906. Pp. xvi + 230.

Up to the time of the publication of Maxwell's 'Treatise on Electricity and Magnetism' in 1873, in which the ideas of Faraday were subjected to mathematical analysis, and greatly extended, the preponderating rôle which the luminiferous ether plays in electrodynamic phenomena had been almost entirely overlooked by theoretical physicists. Attention had been concentrated upon electrical charges and currents, and the influence of the medium which transmits electric and magnetic forces was quite neglected. The steady progress of Maxwell's theory, its evident superiority to its older rivals, and its final triumphant verification by Hertz, naturally caused the pendulum to swing to the other extreme; so that in the early nineties students of physics learned much of tubes of force and ethereal displacement, but had little to do with electric charge, except as a rather old-fashioned idea still useful for certain purposes, but really only a short name for a certain mathematical function of the ethereal displacement.

Time, however, has wrought its revenges. When Maxwell's theory was applied to the finer details of the electrical and optical behavior of matter, especially of moving matter, it was found necessary to reintroduce the definite conception of electric charge in very concrete form; its atomic structure was recognized, and the name 'electron' was given to the atom of electric charge. These theoretical conclusions of Lorentz and Larmor have been strikingly confirmed by a great number of experimental results in widely different fields of investigation. The discovery of the Zeeman effect, the investigation of the nature of cathode rays and of the ionization of gases by J. J. Thomson and his followers, the phenomena of radioactivity and many other facts new and old find their natural explanation in terms of the electron theory. Indeed we have some ground for anticipating a much wider extension of the theory; it is not impossible that we may come to believe that all matter is made up of electrons, which will thus form the raw material out of which the material universe is constructed.

In the book under review, Sir Oliver Lodge has given a simple and lucid account of this theory, of its triumphs and difficulties, and the possibilities of its future development. He tells us that the book "is intended for the student of general physics, and in places for specialists, but most of it may be taken as an exposition of a subject of inevitable interest to all educated men." It is in fact not quite a 'popular' exposition of science in the ordinary sense, and one will look in vain for the exaggerations and over-statements which are too often characteristic of such works. It appeals rather to the discriminating *amateur* of scientific knowledge who has some knowledge of electricity and who will not be hopelessly frightened or repelled by an occasional simple algebraic or trigonometrical expression.