SCIENCE

Vol. 86 Friday, July 9, 1937 No. 2219

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SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. McKeen Cattell and published every Friday by

THE SCIENCE PRESS
New York City: Grand Central Terminal
Lancaster, Pa. Garrison, N. Y.

Annual Subscription, $6.00 Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the Association may be secured from the office of the permanent secretary, in the Smithsonian Institution Building, Washington, D. C.

THE INTERIONIC ATTRACTION THEORY OF ELECTROLYTES

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THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH

In 1883 Arrhenius advanced the theory that in solutions of salts, acids and bases the molecules are, partly at least, split up into positively and negatively charged *ions*. Thus, for example, an aqueous solution of sodium chloride was conceived to consist in large part of positively charged sodium ions and negatively charged chloride ions, which may be represented by Na^+ and Cl^-. The theory encountered vigorous opposition, based mostly on the apparently quite reasonable objections that sodium, for instance, which is well known to be a soft inflammable metal, could hardly be present in water, and also, that if positive and negative ions are as close together as they must be in a solution they would certainly be expected to attract each other and recombine. In spite of these objections and others, the theory gained adherents rapidly since it accounted more or less adequately for the main facts about solutions of what we now term electrolytes. The most important facts about such solutions are that, in the first place, they are conductors of electricity and, in addition, that they exhibit abnormal thermodynamic properties, by which we mean that, for example, they produce exceptionally large depressions of the freezing points and vapor pressures of the solvents in which they are dissolved.

The mental picture with which Arrhenius worked was somewhat as shown in Fig. 1. The symbols + and − represent the positive and negative ions, respectively. A part of the ions are considered to be free, and another portion of the ions are in contact with each other, forming neutral molecules. The former were considered to conduct electricity and the latter to have no influence on the conductance of a solution. The positions of the ions and neutral molecules would, of course, be rapidly shifting, due to thermal vibrations. Neutral molecules were thought to be constantly break-

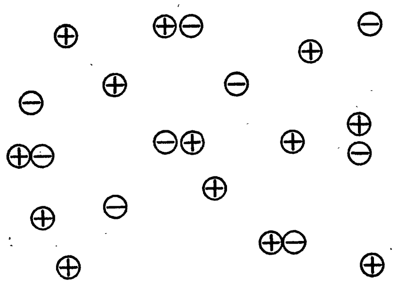

FIG. 1

ing up into ions and the ions, in turn, uniting to form molecules, the proportion of ions, however, increasing as the solution was made more and more dilute.

A large part of Arrhenius's theory can be summed up in the famous formula.

$$\alpha = \frac{\Lambda}{\Lambda_0} \qquad (1)$$

in which α is the "degree of dissociation," that is to say, the fraction of the total electrolyte present as ions. In this formula Λ is the conductance of a gram equivalent of the electrolyte and Λ_0 is the conductance of the same quantity of electrolyte at infinite dilution, under which condition the electrolyte is presumably completely dissociated. As will be discussed in more detail later, this equation involves the tacit assumption that the conducting properties, *i.e.,* the mobilities, of the ions, are the same at every dilution. A similar assumption was made by Arrhenius and later workers in dealing with the thermodynamic properties of the ions, which were also considered to be the same at all dilutions.

Although certain weaknesses were evident almost from the first, Arrhenius's theory held the field for several decades, and its reverberations in chemistry, physics and biology could hardly be traced in a lifetime of reading. In large measure the theory originated the borderland sciences of physical chemistry and biophysics. It is entitled to profound respect as one of the most useful stimulators of research that science has produced.

One of the early objections to the theory, represented by the statement that atoms of metallic sodium, for instance, could hardly remain in aqueous solution, was easily met by pointing out the fact that a charged sodium atom, to which molecules of solvent are probably attached, can be quite different from the metal. The other objection, that positive and negative ions can not remain in close proximity in solution without at least influencing each other, contains the real weakness of the Arrhenius theory. The great advances made recently in the theory of electrolytes, to be outlined in part in this paper, have all been in the direction of an attack on this vulnerable point.

Although Arrhenius's theory accounted quantitatively, with sufficient accuracy, for the behavior of "weak" electrolytes, *i.e.,* solutions of acids and bases which yield relatively poorly conducting solutions, the theory failed seriously when it was applied to highly conducting solutions. Thus computing the degree of dissociation with the aid of equation 1, it was found that for weak electrolytes the law of mass action held, for instance, for the equilibrium

$$HA \rightleftarrows H^+ + A^- \qquad (2)$$

where HA represents a weak acid, such as acetic acid. A large amount of ingenuity was expended in the attempt to explain the failure of strong electrolytes, such as sodium chloride, to fit into the same scheme. This and other related facts were lumped together as the "anomaly of the strong electrolyte," which plagued workers in this field for a full generation.

The most convenient method for measuring the thermodynamic properties of an electrolyte is, when applicable, to use it in a concentration cell. The simplest type of such a cell is shown in Fig. 2. Here vessel A contains the more concentrated of two solutions, of sodium chloride, for example, and vessel B the more dilute. Into these solutions are placed electrodes (in this case silver covered with silver chloride), several being used for comparison. Such a concentration cell can be conveniently represented by the symbols

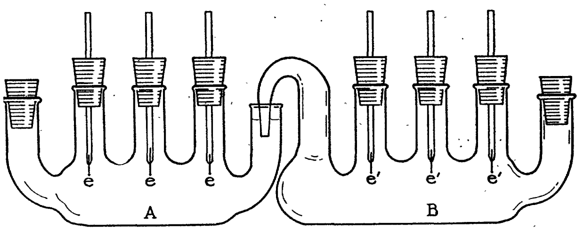

FIG. 2

$$\text{Ag; AgCl, } \underset{(C_A)}{\text{NaCl}} : \underset{(C_B)}{\text{NaCl}}\text{, AgCl; Ag.} \qquad (3)$$

Now if the ions are "thermodynamically ideal" solutes the electromotive force, E, between electrodes in the two solutions should follow the equation

$$E = \frac{2t\,RT}{F} \log \frac{C_A \alpha_A}{C_B \alpha_B} \qquad (4)$$

in which t is the transference number of the positive ion (*i.e.,* the proportion of the total conductance of the solution due to that ion), R is the gas constant, T the absolute temperature, and F the faraday. C_A and C_B are the salt concentrations in vessels and A and B, respectively, of Fig. 2, and the degrees of dissociation α_A and α_B are computed from equation 1. Now it was part of the anomaly of strong electrolytes that this equation is very far from agreement with the actual measurements. A way of sidetracking this difficulty and obtaining workable equations was suggested by G. N. Lewis. In effect he rewrote equation 4 as follows:

$$E = \frac{2t\,RT}{F}\log\frac{C_A f_A}{C_B f_B} \qquad (5)$$

The f values used in this equation are obtained from the data and are called "activity coefficients." For a long time the f values were purely empirical. They were, however, very useful since, if once determined, they could, with suitable precautions, be used in any thermodynamic equation. For moderately concentrated solutions these activity coefficients are less than unity but approach that value as a limit as the solutions become more and more dilute.

The rather remarkable assumption made by Arrhenius and his followers that charged ions could be present in solution without influencing each other's properties, remained almost unchallenged until Milner in 1912 and Debye and Hückel in 1923, in epoch-making papers, showed that the variation of the activity coefficients of ion constituents from unity can be explained by the electrostatic attractions and repulsions of the charges carried by the ions. Positive ions will attract negative ions, and *vice versa.* Due to heat vibrations of the ions themselves and of the solvent molecules, no regular arrangement of the ions persists, although it can be said that if you were taking a ride on one of the positive ions more of your neighbors would be negative ions than positive ones, and this would be more true the greater the concentration. Thus in a salt solution the ions are not quite independent of each other, and their thermodynamic properties would thus be expected to change with the concentration.

Using these simple assumptions and ingenious mathematical-physical reasoning, Debye and Hückel arrived at the formula

$$-\log f_i = \frac{A\sqrt{C}}{1+Ba_i\sqrt{C}} \qquad (6)$$

in which f_i is the ion activity coefficient, A is a constant computable from universal constants, B contains such constants and a_i is the size of the ions, or more precisely speaking, the "distance of closest approach" of the positive and negative ions.

We have, at the Rockefeller Institute, made what we think are the most precise tests yet obtained of the Debye-Hückel theory, which has emerged with flying colors. Drs. A. S. Brown and Theodore Shedlovsky have measured the potentials of cells of the type represented by equation 3, and precision transference numbers have been obtained by Dr. L. G. Longsworth. These transference numbers are not, however, constants as assumed in obtaining equation 4, but are functions of the concentration C, which complicates the computation but not the theory. The actual equation used in the computations is

$$E = \frac{2\,RT}{F}\int_2^1 t\,d\log C f_i \qquad (7)$$

The results are represented in Fig. 3, where the negative of the logarithm of the activity coefficient is plotted against the square root of the concentration. The distance of closest approach, a_i, computed from the data is seen to vary from 5.6 Ångström units for hydrochloric acid to 2.3 Ångström units for silver nitrate. It will be seen from the plot that the agreement of observed and computed values is very close. As a matter of fact the agreement of the observed values of f_i and those computed from equation 6 agree within a few hundredths of a per cent. up to a concentration of about 0.05 normal. It is evident that, for the substances mentioned, the new theory accounts adequately for the experimental results. If, as assumed in Arrhenius's theory, the ions had no influence on each other the activity coefficient, f_i, would be unity. This would correspond to the straight line forming the lower border of the diagram.[1]

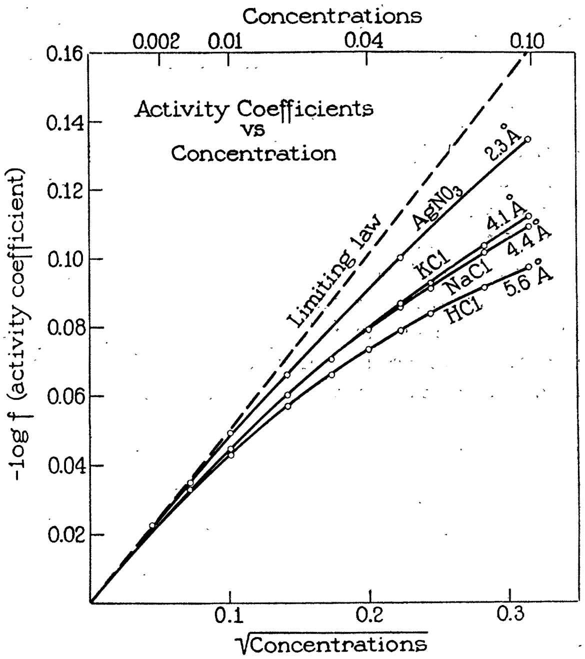

FIG. 3

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[1] Fig. 3 also contains the straight line representing the "limiting law"

$$-\log f = A\sqrt{C}$$

which holds for exceedingly dilute solutions. It is not valid, as might be expected, for substances with very small distances of closest approach, since under those conditions the effects of certain approximations made in deriving equation 6 affect the computations. This matter has been investigated by Gronwall, LaMer and Sandved, *Physik. Z.*, 29: 358, 1928.

However, in obtaining equation 6 a very important simplifying assumption was made. Instead of postulating, as Arrhenius did, that the dissolved electrolyte is partly present as ions and partly as undissociated electrolyte it was found, for strong electrolytes at least, that agreement between theory and observation could be more readily obtained if it were assumed that the electrolyte is *all* present as ions. It was, somewhat unfortunately, this aspect of the theory that attracted most attention when it first appeared. It will be shown later in this paper that for "weak" electrolytes it is necessary to introduce a degree of dissociation into the discussion, and also that in interpreting the experimental data for these substances the interionic attraction theory is as essential as it is for "strong" electrolytes.

The success of the interionic attraction theory in the thermodynamic field has been accompanied by conquests in the region of the kinetic properties of solutions, particularly the conductivity. It will be recalled that the equivalent conductance, Λ, of a strong electrolyte, such as sodium chloride, decreases as the concentration is increased. Arrhenius and his followers considered, as has already been mentioned, this decrease of equivalent conductance to be due to a falling off in the number of carriers of electricity. A portion of the oppositely charged ions were supposed, in increasing degree as the concentration is raised, to stick together, as indicated in Fig. 1, and thus take no part in the conductance. We have already seen that the present notion is that a solution of a strong electrolyte consists entirely of ions. There must, obviously, be some other explanation of the observed decrease in conductance. Debye and Hückel, and Onsager, have, as a matter of fact, shown that there are two "effects" or mechanisms tending to bring about decreases in the equivalent conductance of an electrolyte with increase of concentration. Both of these arise from the attractions and repulsions of the charged ions. These are (a) the *electrophoretic effect* and (b) the time of *relaxation effect.* One of the consequences of the interionic attraction theory is that each ion carries around with it a so-called "ion atmosphere" due to considerations that have already been discussed. If a positive ion has, on the average, more negative than positive ions near it the result will be the same as if a charge of negative electricity were spread out symmetrically in all directions in the solvent, most of it lying near the chosen ion but spreading out more and more thinly as the distance from the ion increases. Although in the mathematical discussions of this potential it is treated as a reality, it is actually the result of a time average of a distribution of the ions, each ion serving both as a center of an ionic atmosphere and as a part of the ionic atmosphere of other ions. Now if a potential gradient is impressed on the solution, as in an electrolysis or a measurement of conductance, the charges of the ionic atmosphere will tend to move, carrying solvent with them, in a direction opposite to that of the chosen ion. This counter-current of solvent will impose a drag on the ion, tending to decrease its velocity. This is known as the "electrophoretic effect."

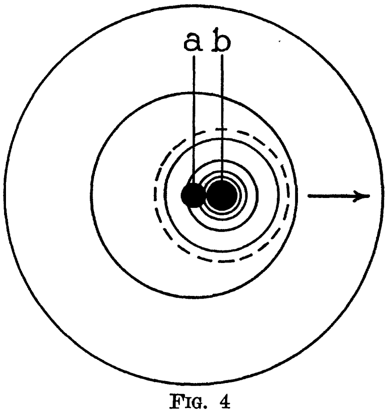

FIG. 4

The second effect is possibly more difficult to visualize, but an attempt is made in Fig. 4. If we move an ion, represented by the black circle, suddenly from position *a* to position *b* its "ionic atmosphere" will go along also in the same direction. However, it takes some time for a message that something has happened at the point where the ion is located to get to the outlying regions of the ion atmosphere. These un-notified regions (outside the dotted circle in the figure) are unsymmetrically spaced around the ion and thus exert a pull on the notified regions. This gives rise to an extra drag on the central ion. This picture gives a rough idea of the "time of relaxation effect."

The mathematical physics involved in the quantitative treatment of the electrophoretic and time of relaxation effects is formidable, but the final result, for binary electrolytes, such as potassium chloride or hydrochloric acid, is quite simple. The equation obtained by Onsager is

$$\Lambda = \Lambda_0 - (\gamma \Lambda_0 + \beta)\sqrt{C} \qquad (8)$$

in which Λ and Λ_0 are respectively the measured and limiting conductances and γ and β are theoretical constants. Due to the complexity of the phenomena and of the mathematics this formula is valid only for very dilute solutions. A test of the equation has been furnished by the careful measurements made in the Rockefeller Institute laboratory by Dr. Shedlovsky. Some typical results are given in Fig. 5, in which equivalent conductance, Λ, values for sodium and potassium chlorides are plotted against the square root of the concentration. For comparison plots of the theoretical equation, 8, are represented as dotted lines. It will be seen

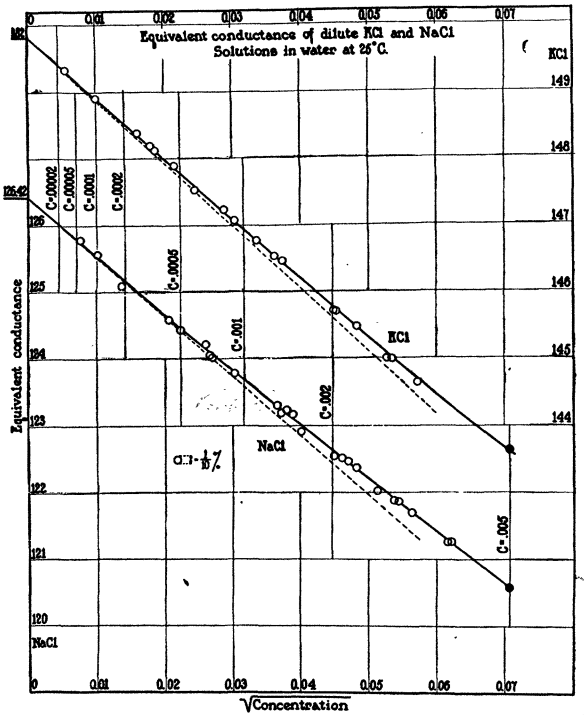

FIG. 5

that the equation represents the experimental results up to a concentration, C, of about 0.001, after which there are deviations which increase as the concentration increases. These deviations appear, however, to be such as would arise from the necessary simplifications used in obtaining the equation. Here again the assumption has been made that salts, such as sodium chloride, are entirely present as ions, *i.e.*, that they are completely dissociated.

There is an additional, and very sensitive, test that can be made of the newer conceptions. According to the theory of Arrhenius, the ions, being quite independent of each other, have the same mobilities at all concentrations, and, therefore, their transference numbers, which are the ratios of the mobility of one ion in a binary electrolyte to the sum of the mobilities of both ions, should remain constant. Modern developments in the Rockefeller Institute laboratory of the "method of moving boundaries" have made it possible to obtain transference numbers with about the same accuracy with which conductance can be measured. The transference number of, for instance, hydrogen ion in hydrochloric acid, t_{H^+}, is given by the relation

$$t_{H^+} = \frac{\lambda_{H^+}}{\lambda_{H^+} + \lambda_{Cl^-}} \qquad (9)$$

in which λ_{H^+} and λ_{Cl^-} are the mobilities of the hydrogen and chloride ions, respectively. If the Arrhenius theory were true this transference number should not change with the concentration. The interionic attraction theory, however, predicts that these transference numbers should vary and, furthermore, for very dilute solutions at least, how much they should change. Fig. 6 shows the results that have been obtained in this field by Dr. Longsworth. Here the measured transference numbers are plotted against the square root of the concentration and the curved lines have been drawn through these points. The change of the transference number predicted from Onsager's equation, 8, is represented in each case by the straight line starting from the value of the limiting transference number, at zero concentration. It will be seen that the curves passing through the observed points merge naturally into the theoretical line, with the exception of that for silver nitrate which substance is, in several respects, abnormal.

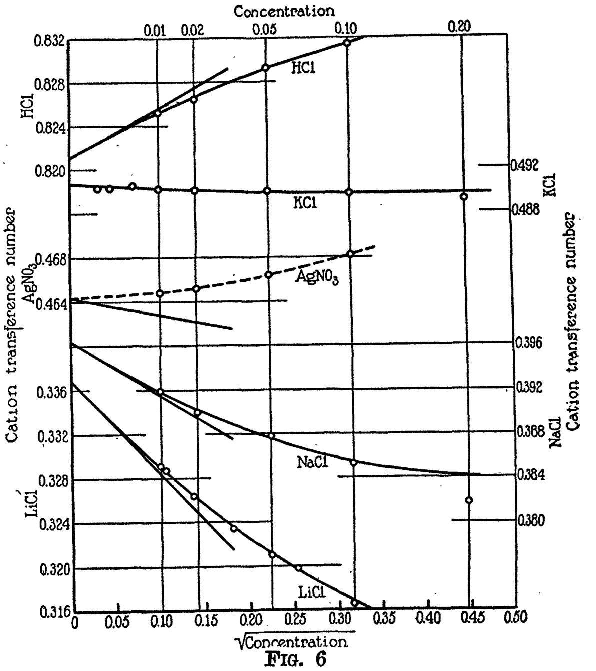

FIG. 6

It is thus evident that the measurements of concentration cells, of conductances and transference numbers on strong electrolytes can all be readily interpreted by the new interionic attraction theory. It was in this region, of strong electrolytes, that the older Arrhenius theory was least successful.

There is, however, a large class, the so-called "weak" electrolytes, for which the assumption of complete dissociation is not adequate. For these there is evidence to indicate that the ions are in equilibrium with an appreciable concentration of undissociated electrolyte in agreement with Arrhenius's original picture. Such an equilibrium may be indicated by

$$\mathrm{HA} \rightleftarrows \mathrm{H}^+ + \mathrm{A}^- \qquad (2)$$

in which HA represents a weak acid and A^- the negative ion produced by its dissociation. As has already been mentioned, Arrhenius believed that the degree of dissociation, α, could be computed from the relation

$$\alpha = \Lambda/\Lambda_0 \tag{1}$$

in which Λ_0 is the limiting equivalent conductance. With the aid of the law of mass action this yields

$$K = \frac{\alpha^2 C}{1-\alpha} \tag{10}$$

a familiar expression known as "Ostwald's dilution law," in which K is the ionization constant. This relation was found to hold quite well for many weak acids and bases, and was really the main quantitative support for the older form of the theory of dissociation. However, as will be shown below, a part, at least, of the success of Ostwald's dilution law was due to a compensation of two errors.

If a solution of a weak electrolyte contains ions these ions are necessarily subject to the same interionic attractions as have been found to hold for strong electrolytes. Since, due to interionic forces, ion mobilities change with the ion concentrations equation 1, which involves the assumption that they are constant, can not be the correct expression for computing the degree of dissociation α. A correct formula is

$$\alpha = \Lambda/\Lambda_\varepsilon \tag{11}$$

in which Λ_ε is the equivalent conductance of the completely dissociated acid HA at the ion concentration $C\alpha$. The use of Λ_ε instead of Λ_0 corrects for the electrophoretic and time of relaxation effects.[2] In addition, except at zero concentration, the ions are not, as we have seen, normal solutes, and thus have activity coefficients, f_i, generally less than unity. In modern terms, therefore, Ostwald's equation becomes

$$K = \frac{\alpha^2 C}{1-\alpha} \cdot f_i^2 = K' \cdot f_i^2 \tag{12}$$

in which α is computed from equation 11 and K', the "dissociation function" which is not in general constant, is defined by the equation. Equation 12 can be readily transformed into the expression

$$\log K = \log K' + 2 \log f_i = \log K' - 2A\sqrt{C\alpha} \tag{13}$$

the last term coming from equation 6, which may be put into the form

$$-\log f_i = A\sqrt{C\alpha} \tag{14}$$

for very low ion concentrations. For weak electrolytes the product $C\alpha$ is evidently the part of the total concentration C which is present as ions. Thus it is easy to see that, if our reasoning is correct, a plot of the logarithm of the dissociation function, K', against values of $\sqrt{C\alpha}$ should be a straight line with a slope equal to twice the constant, A, of the limiting law of the Debye and Hückel theory. That this is true, at least for dilute solutions of acetic acid, is shown in Fig. 7, which is based on data obtained by Dr. Shedlovsky. The solid line, *e*, has a slope of 2 × 0.506, the latter figure being the Debye-Hückel constant at 25°. The intercept of the straight line with the zero ordinate yields the thermodynamic ionization constant of acetic acid. This limiting value agrees almost exactly with a determination of the same constant made by Harned and Ehlers, using a method, depending upon the measurement of the potentials of concentration cells without liquid junctions, which involves none of the assumptions used in obtaining equation 13. A similar agreement between theory and observation has been obtained with chloroacetic and other acids. The reason why Ostwald's dilution law, equation 10, was moderately successful is now evident. Arrhenius's original expression, equation 1, yields degrees of dissociation, α, which are too low. This error, from our present point of view, was more or less offset by the tacit assumption made by Arrhenius and Ostwald, that the activity coefficients are unity, whereas, for all dilute solutions at least, they are less than unity.

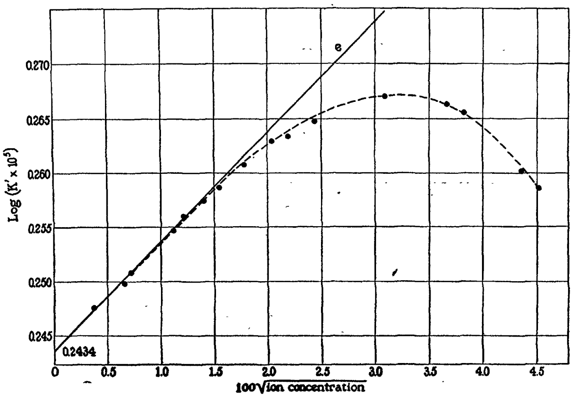

FIG. 7

This short survey of a large field has been confined to work done under the direction of the author at the Rockefeller Institute. A more complete discussion of the interionic attraction theory of electrolytes should include the researches at Columbia University, by Professor LaMer and associates, on electrolytes of higher valence types and on theoretical extensions of the Debye-Hückel theory; the researches of Professors Kraus and Fuoss at Brown University on solutions of

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[2] Values of Λ_ϵ can be obtained as follows. The equivalent conductance $\Lambda_{\epsilon(\mathrm{HAc})}$ of, for example, totally dissociated acetic acid may be obtained from the formula

$$\Lambda_{\varepsilon\,(\mathrm{HAc})} = \Lambda_{\mathrm{H^+Cl^-}} + \Lambda_{\mathrm{Na^+Ac^-}} - \Lambda_{\mathrm{Na^+Cl^-}}$$

Each of the Λ values on the right hand side of the equation must be determined for the concentration $C\alpha$. However, as α must be obtained from equation 11, a short series of trials or approximations must be made to establish the correct values.

electrolytes in non-aqueous solvents; the work on the Wien and Debye-Falkenhagen effects, which deserve extended treatment, and many other researches that might be mentioned. In addition to clearing up a number of outstanding problems the new outlook has, as might be expected, raised quite a number of questions which demand investigation. However, enough of the theory has been outlined to show that it has been a useful tool of research and a powerful stimulator of investigation in what had become a somewhat stagnant field. Such stimulation of research is, of course, the main function of a theory.

OBITUARY

DUNCAN STARR JOHNSON[1]

IN the recent death, in the seventieth year of his age, of Duncan Starr Johnson, the Division of Biology and Agriculture of the National Research Council has suffered the first loss from its long list of distinguished chairmen. Professor Johnson spent practically all his active life as a scientist at the Johns Hopkins University, where at the time of his death he was professor of botany and director of the botanical garden.

Though his research lay largely in the field of plant morphology, with occasional excursions into ecology, he was singularly catholic in the breadth and accuracy of his knowledge of the field of plant science. Few men could have done what he did in conducting—at first single-handed, later with the cooperation of Professor Livingston—a department of botany of such distinction that graduate students were drawn from far and near, many of whom have taken honored places in American science.

As chairman of the Division of Biology and Agriculture for 1931–32, Professor Johnson showed the same characteristics that made him a great teacher. His most conspicuous qualities were an unswerving integrity and independence and a devotion to accuracy that sometimes seemed almost extreme. Duty to him was a sacred word, and he followed his ideals without a trace of compromise. To him and to men like him American science owes much. The Division of Biology and Agriculture mourns his loss as a friend, as an exemplar of the true scientific spirit and as one who served it with scrupulous regard to his obligations as chairman.

RECENT DEATHS

FRANK TWEEDY, topographer and topographical engineer to the U. S. Geological Survey from 1884 until his retirement in 1926, died on June 28 at the age of eighty-three years.

LEON CHESTER MARSTON, JR., who was recently appointed assistant professor of entomology at Pennsylvania State College, died on June 22. He was thirty-two years old.

A CORRESPONDENT writes: "Paul Vere Roundy died suddenly at his home on June 21, following many months of ill health. He was born in 1884 and was appointed a member of the U. S. Geological Survey in 1908. In the ensuing twenty-eight years he served as geologist and paleontologist, working especially in the oil fields of Oklahoma and of California and in the phosphate reserve of Florida. He was also known through his work on the ostracods and conodonts, which was interrupted by his untimely death in his fifty-third year."

SCIENTIFIC EVENTS

ACTIVITIES OF THE INTERNATIONAL UNION OF BIOLOGICAL SCIENCES

IN the Executive Committee of the International Union of Biological Societies the following changes have been necessary: Professor Sir Albert Seward, our eminent president for the last period, not being reeligible, has been succeeded by Professor E. D. Merrill, of Harvard University; the vice-president, Professor Godlewski, by Professor D. M. S. Watson, of London, and the general secretary, Professor de Selys Longchamps, who has retired, by the undersigned. We have to thank most cordially Professor Seward for the very able way in which he conducted the work on behalf of our union and Professors Godlewski and de Selys for their activity.

In addition to the countries which had already joined the union (The Argentine, Belgium, Czechoslovakia, France, Great Britain, Italy, Japan, Jugoslavia, Morocco, the Netherlands, Poland, Portugal, South Africa, Spain and Switzerland) we were much pleased in welcoming Sweden and the United States of America; negotiations with a number of other countries have not yet been concluded.

The union granted subventions to the Central Bureau for Fungus Cultures at Baarn, to the Concilium Bibliographicum at Zurich, to the International Office for Nature Protection at Brussels and to the Année Biologique at Paris; it subscribed to the *Zoological Record,* London.

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[1] Memorial adopted by the Division of Biology and Agriculture of the National Research Council on April 24, 1937.