

"After all," says Gilman, "a great teacher is not to be measured by his learning but by his example."

The life of the scholar and teacher may not be exciting and eventful, but in its dignity, its serenity, it may leave little to be desired. As I think of Dana and Porter and Woolsey and Newton, the thing that impresses me most is not their learning, although that was great, but their simplicity, their elevation of soul, their sweetness of spirit, their purity of life. Happy the boy or girl who comes under such influences and who profits by it! Happier still that teacher who can worthily exert it!

THE THEORY OF ELECTROLYTIC DISSOCIATION.

BY LOUIS KAHLENBERG, PH. D.

Professor of Physical Chemistry, University of Wisconsin.

The teacher of natural science is frequently confronted with the question as to how much prominence should be given to this or that scientific theory. It is well recognized that theories are the changeable, the ephemeral part of science; that they are really only tools by means of which the truth, the facts which are eternal, may frequently be discovered, unearthed, and temporarily correlated. Facts carefully established by experiment and observation, and gathered together in the form of carefully made general statements become verbal expressions of the laws of nature. These generalizations so reached are the real treasures of science; they constitute the solid stones of which the temple of science is built; and it is through these that science serves mankind in the broadest and highest sense of the word. It is clearly very essential that the teacher should at all times distinguish very carefully between what is hypothesis and what is fact. The latter once carefully established stands firm and unchangeable, while the theory is only useful in so far as it enables one to group known facts together and to discover new truths. As soon as a theory becomes inadequate

to do this, its period of usefulness is over and its doom is sealed. The pathway of the progress of science is strewn with defunct theories and hypotheses. The spectacle of the birth, growth and death of scientific theories often appalls the less thoroughly versed, for they see in it, as they fancy, the instability of science. Much of this misconception would soon disappear if teachers would always insist that their pupils distinguish at all times between facts and opinions or assumptions, and never for a moment elevate the latter in their minds to the dignity of the former. In this attitude of mind toward fact and theory the teacher of science must ever lead by strong force of example, if he would truly succeed in his vocation, and especially if he would seek during his spare hours to add something of value to the sum total of human knowledge. The one who becomes so imbued with a theory that he raises it in his mind to the dignity of a fact is sure to fall into serious errors; for while hypotheses frequently aid the investigator by stimulating inquiry and by suggesting new relations and new ways of doing things, they also very often by their equally strong hints that such and such things are impossible stifle inquiry along certain lines, prevent new discoveries from being made, and so become a real bar to true progress. However, the investigator who ever bears in mind the difference between facts and theories is not in the least worried by the continual coming and going of the latter; and the teacher of science who leads his pupils to distinguish between established truths and hypotheses need have no apprehension that he has misled his pupils by acquainting them with a theory that soon after has to be entirely discarded. Yet it is true that it is best not to bring to the notice of students—at least of students of high school grade—scientific theories that have not a broad foundation of facts to stand upon, or theories of which it is evident at the time of instruction that their period of usefulness is practically over.

There is practically no one theory of chemistry that has attracted more attention in the last fifteen years than the theory of electrolytic dissociation proposed by Arrhenius in 1887. Though far from universally accepted, it still has many ardent adherents. This theory is so well known that it is entirely unnecessary to give its purport or its history here. It will be recalled that the

hypothesis is based primarily upon the claims of Arrhenius that the molecular conductivity of many solutions (that had been measured at the time of the promulgation of the theory) increases with the dilution; that substances which when dissolved conduct electricity also have "abnormally" low molecular weights in such solutions when tested by freezing- or boiling-point methods; and that the so-called degree of dissociation may be calculated from the electrical conductivity or the results of the molecular weight determinations. In his original paper Arrhenius stated that the phenomena of electrolysis, when viewed in the light of thermodynamics, require the assumption of free ions as was pointed out by Clausius, and that the heats of neutralization of acids and bases in dilute solutions, and the various physical properties of salt solutions, which are well known to be, in general, additive in character, support the electrolytic dissociation hypothesis. Through the latter it was sought to gain for the van't Hoff theory of solutions a general application, and at the same time to bring into correlation facts that had hitherto been entirely isolated. Inasmuch as the commonly used aqueous solutions of acids, bases and salts are electrolytes, practically all the well known chemical reactions of neutralization, precipitation by double decomposition, etc., many of which occur instantaneously, were soon viewed as taking place between the so-called free ions. Books explaining chemical changes and changes of solubility on the ionic basis were soon published; of these Ostwald's *Scientific Foundations of Analytical Chemistry* was the most prominent one, from which ideas were taken, modified, elaborated and incorporated into more elementary texts. The claim was even made that the chemistry of atoms and molecules has given place to the chemistry of ions, and that chemical affinity is a back number.

In the face of the enthusiasm shown by adherents of the dissociation theory and the voluminous material they have published, it is no wonder that teachers are often made to feel that they are entirely behind the times, unless they teach their chemistry with the theory of electrolytic dissociation as the back bone of it, and in general explain the chemical, physical and physiological behavior of solutions from the standpoint of the dissociation theory. But the teacher of the secondary school was not alone

in this, university professors and other investigators of note in physics, chemistry and physiology were looked at askance and even pitied because they could not see what Lothar Meyer called "das wilde Heer der Ionen," and follow them in their gambols.

There are now at hand abundant well established facts that show that the theory of electrolytic dissociation is entirely inadequate, in reality untenable. To rehearse all these here in detail is entirely impossible; they have been fully presented from time to time in a series of articles in the *Journal of Physical Chemistry*, and to these the reader must be referred. In summary, it has been shown that instantaneous chemical reactions, solubility changes, and coloration changes (comparable in every way with those that take place in the common aqueous electrolytic solutions) occur in solutions that are most excellent insulators. On the other hand, the presence of electrolytic conductivity has been found to be by no means necessarily accompanied by chemical action. (Compare the recent article by Kahlenberg and Schlundt on the behavior of solutions in which liquid hydrocyanic acid is the solvent, *Jour. Phys. Chem.*, Oct., 1902.) Thus chemical action takes place quite independent of electrolytic conduction; and, again, the explanation, that, for example, the chlorine in such compounds as chloroform can not be precipitated as silver chloride because the chlorine is not in the ionic state, inasmuch as chloroform is not an electrolyte, is clearly no longer valid. Of this the reader will be convinced by referring to my article in the January number of the *Jour. Phys. Chem.*, 1902. Furthermore, so-called abnormally low freezing-points or abnormally high boiling-points of solutions are by no means always accompanied by electrolytic conduction; while normal freezing-points, normal boiling-points or even abnormally high freezing-points and abnormally low boiling-points are frequently exhibited by solutions that are electrolytes. Again the molecular conductivity does not always increase with the dilution. These statements are true of aqueous as well as of non-aqueous solutions. It is therefore clear that the dissociation theory is no longer tenable. It has become untenable because further investigations have furnished facts that are chemical, physical and physiological in character showing how very inadequate the theory is. With the downfall of the Arrhenius hypothesis, the

original difficulty with the van't Hoff theory of solutions recurs. The latter hypothesis is based upon the analogy between gases and solutions, and is practically inseparably connected with the Arrhenius theory. No doubt these theories have done much toward stimulating research in chemistry and physiology and due credit should be given them on this account. The theory of solutions has, however, directed attention exclusively to dilute solutions. It has thus stood in the way of the study of more concentrated solutions and so has in reality unquestionably been a drawback to true progress toward a thorough understanding of the very important subject of solutions. Similarly the Arrhenius theory has directed particular attention to the phenomena in dilute solutions. The *facts* known at present are sufficient to warrant the expression of the opinion that for a true conception of the nature of solutions and of electrolytic processes it is extremely unfortunate that work should have been directed thus almost exclusively toward dilute solutions.

The act of solution itself is undoubtedly caused by a mutual attraction of solvent and solute, which attraction depends upon the individual nature of the substances under consideration. This mutual attraction is very closely allied to, if not essentially identical with, what is commonly called chemical affinity. This attraction is the so-called osmotic pressure. In the careful study of the act of solution, and of the physical, chemical and physiological properties of solutions nothing becomes more evident than that chemical affinity between solvent and solute really determines all these phenomena. Chemical affinity then should be brought to the forefront in the study of solutions rather than relegated to the background. As for the electrolytic conductivity of solutions, no one can tell whether a given solution will conduct electricity or not without actually trying it. The Arrhenius theory claims to be able to make such predictions, but the facts show that it is entirely unable to do so. We have at present no adequate mechanical explanation of the process of electrolytic conduction; and this is not astonishing, for we also have no such explanation of the conduction of electricity in a wire. It is quite probable that we shall eventually find that these two phenomena are much more intimately related to each other than they seem to be at present.

Moreover, as Fitzgerald said so well in his celebrated Helmholtz memorial lecture, it is not to be charged against any one that he is unable to explain all the phenomena of the universe. The general course that should be pursued in the further study of solutions, I have indicated in the *Jour. Phys. Chem.*, June, 1901.

In being gradually outgrown by the multiplication of facts that are not in harmony with it, the theory of electrolytic dissociation has simply followed the natural course that all scientific hypotheses, founded upon too narrow a basis of induction, must eventually take. Nor need it cause a pang of regret or a sigh to see a worn-out theory go, even though a new one is not at once at hand to supplant it. The older and the more perfect a science is, the fewer theories it has. At any rate, investigations bringing facts that undeceive us as to the real adequacy of a theory, always represent a true step forward; they are always to be welcomed.

The teacher who has not hitherto seen fit to bring the theory of electrolytic dissociation to the notice of his pupils, certainly has no good reason for doing so now, for he can not be classed as being behind the times if he omits mentioning the theory. On the other hand, he who has given his instruction entirely or in part by means of the theory should study with care the new facts that are at hand; should bring these before his pupils, who will not be slow to recognize that the theory is unable to stand in face of the facts. Above all, let the pupils repeat the experiments and then draw the conclusions that follow directly from them. Thus they will learn to love and conserve the truth though theories may fall, and they will at least in a measure experience what the great Scheele did, when he said: "es ist ja nur die Wahrheit, welche wir wissen wollen, und welche Freude bereitet es nicht sie erforscht zu haben."