

A New Form for the Electrolytic Dissociation Theory

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Some time ago (1906) I advanced the proposition that a simple electrolytic dissociation is not accompanied by change of colour. I have now tried to establish this hypothesis by new experiments.

It seems to me that experiments with chromium salts are especially adapted for elucidating this question, because the changes between normal and complex salt in the case of these compounds take place only slowly, so that in using them it is possible to work with solutions which are demonstrably free from complex salts, a condition not so easily obtainable in the case of other metallic salts. I have therefore made a number of experiments with chromium chloride, chromium nitrate, and chromium sulphate, and I find that pure normal chromium salts in solution always have exactly the same absorption of light, no matter what the concentration and the acid is, but as soon as the formation of complex salts can be demonstrated, the colour is changed.

However, it is only in the case of the strong electrolytes that the colour is not changed with the concentration. The colour of the weaker electrolytes depends upon the concentration. I suppose that in the solutions of the weaker electrolytes there is always a greater or smaller quantity of undissociated salt, corresponding in structure to complex salts, and that this salt not only causes the changes in colour but also reduces the electric conductivity.

These colour-relations found in connection with electrolytic dissociation can best be explained by changing Arrhenius's hypothesis in the following manner: We suppose that the strong electrolytes always are completely separated into ions, and that this is the reason why they always have the same colour in all concentrations. If changes of colour take place in solutions of an electrolyte, the ions have more or less entered into combination with each other, the dissociation is not complete.

If this hypothesis is correct, then the decrease in molecular conductivity and in molecular depression of the freezing-point that accompanies the increase in concentration must be due to the action of the electric charges of the ions on each other. The molecular conductivity is diminished not because the number of ions is decreased but because the ions move more slowly. Sutherland has tried to explain the diminution of the molecular conductivity in such a way, but, as it seems to me, without having been quite successful in his attempt. For the explanation it is necessary to have the kinetic theory of liquid, which we still lack. Yet it seems to me there can be no doubt that the electrolytic friction must increase with the ion-concentration, both because the positive and the negative ions will more frequently collide than the neutral molecules and also because the electric field around the ions, increasing with the concentration, will create about the ions a water-mantle of increasing thickness.

It accords well with this new form for the dissociation theory that the "degree of dissociation" which has been calculated from the molecular conductivity is, in the case of strong electrolytes, approximately determined by the valency of the ions (Ostwald-Walden's rule), by the dielectric constant of the solvent (Walden), and by the concentration of the salt. The fact that the so-called "degree of dissociation" depends upon the electric constants of the substances without admitting of any specific influence by chemical affinity becomes quite natural when this quantity in reality is the decrease in electrolytic friction due to the electric forces among the ions. And the fact that the law of mass action does not apply to the influence of the concentration on the degree of dissociation of strong electrolytes will no longer be an inexplicable anomaly. In the case of the dissociation of weak electrolytes, as is well known, the law of mass action has been found to be applicable, but by means of the conductivity we here measure a real dissociation, since the ion-concentration in the solution is so small that we can consider the electrolytic friction as constant.

This new form for the dissociation theory explains just as well as the old Arrhenius form the analytical reactions and the phenomena of electrolysis. The only thing that is not explained so well by the new as by the old theory is the agreement between the decrease in the molecular conductivity and the decrease in the molecular depression of the freezing-point with the increase in concentration. (The agreement between the degrees of dissociation, which are calculated from freezing-point, boiling-point, distribution, electromotive force, etc., is a necessity, since all these quantities can be deduced from osmotic pressure.) But the agreement between the degree of dissociation calculated from the conductivity and that calculated from the freezing-point is not always perfect (e.g., in the case of sodium chloride), and, besides, the approximate agreement may possibly, some time in the future, be explained by the fact that both the decrease in the molecular conductivity and the decrease in the molecular depression of the freezing-point are due to the electric forces at work among the ions.

For all these reasons the new form seems to me to represent a valuable alteration of the Arrhenius dissociation theory.