

## RECENT VIEWS CONCERNING ELECTRICAL CONDUCTANCE IN SOLUTIONS

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In 1801 Nicholson and Carlyle discovered that solutions conduct, and ever since that time the question as to how they conduct has been more or less of an open one.

Let us first briefly consider two of the older theories of conductance. The first one which we will consider is the theory advanced by Grotthuss. According to this one, the substances existed in the molecular state in the solution. On the passage of the current the molecules first lined up, then split off and then rearranged. This procedure was continued as long as the current was passed. Clausius showed this to be incorrect, for the reason that Ohm's Law holds for liquid as well as metallic conductors, and if this is so, no electrical energy is used up in breaking up the substance, but on the other hand, the ions must already exist in the solution. The reason for a substance break-

ing up on going into solution he ascribed to the collisions due to molecular motion in the solution. Fortunately for Clausius, at the same time Williamson was working on the subject of etherification and came to the same conclusion independently. This theory of Clausius dominated chemistry for many years, in fact until Arrhenius came forward with the one which is familiar to you all. This theory may be stated thus:

When a substance is dissolved in water and conducts the electric current, it is dissociated into ions more or less completely, depending on the dilution, and that the degree of this dissociation may be calculated from (1) the conductance of the solution, (2) the lowering of the freezing point or raising of the boiling point, and (3) the osmotic pressure.

Let us now consider first some of the reasons, in a general way, why this theory is favored, after which we will take up some of the objections, and then consider some of the very recent work.

#### THINGS IN FAVOR OF THE THEORY

1. Many aqueous solutions conduct and many non-aqueous do not.
2. When a current is passed through a solution of an electrolyte there is an immediate production of decomposition products.
3. Many or most electrolytes show too great a lowering of the freezing point, raising of the boiling point, and too great an osmotic pressure.
4. All or nearly all strong bases when neutralized by strong acids show the same heat of neutralization.
5. The instantaneous interaction of chemicals when electrolytes and the slow or lack of action when they are not.
6. Some gases, when dissolving in water, do not obey Henry's Law.
7. The hindering of a reaction by adding something that will give like ions.
8. Most substances dissociate more as the dilution is increased.
9. Faraday's Law.

#### OBJECTIONS TO THE THEORY

1. Non-aqueous solutions do conduct.
2. In some solutions the conductivity does not increase on dilution.
3. In some the dilution makes the conductivity increase, some increase then decrease, some decrease, and some decrease then increase.
4. There are instantaneous reactions in non-aqueous solutions.
5. Neutralization of non-aqueous solution does not always give the same heat of reaction.
6. The degree of dissociation as calculated by the three different methods do not always agree.

7. The hindering of a reaction by adding something which does not give like ions.

8. Faraday's Law holds for non-aqueous solutions.

9. The equation for degree of ionization calculated on the basis of concentration does not always hold, even for typical salts.

These are only a few of the reasons, and many more might be given on each side.

Let us now consider some of the recent work, more in detail.

The work of Walden of Rega apparently showed that there was a direct parallelism between the dissociation power as indicated by the conductivity and the dielectric constant. Without a doubt, this was true for the one solute that he used, but it has been equally well established by work done at Wisconsin and by some unpublished work done in our laboratory, that this relation does not hold in all cases.

Creighton of Halifax on the other hand gives results in a recent paper which show that for aniline in acetophenone the Nernst-Thomsen rule does hold. Also Davis of Dalhousie College found the same relations for rosaniline hydrochloride in organic solvents, as Walden did for his solute.

Thornton of the University of Durham, says in explanation of some high values for the dielectric constant obtained for some liquids such as water, that it is an effect depending on the electrical conductivity.

To get his results Walden assumed that the conductivity of the solvents which he had especially purified was due to ionization. This is likely not the case for the reason that the conductivity is dependent upon the mode of purification. In this connection I will recite the recent work of Corvallo, published in C. R., in which he states that he obtains ether so pure that its conduction is very likely due to impurities.

Viscosity is recognized as having considerable influence on the conductivity of a solution. Lloyd of Alabama has recently showed that he gets entirely different maxima at  $50^{\circ}$  C. than he does at  $100^{\circ}$  C. for the same solutions, and this difference he attributes to changes in viscosity. Pratolongo of Milan determined the conductivity of a solution of citric acid with hydrochloride, arsenious, or phosphoric acids dissolved in it, and found that each addition reduces the specific conductivity. This effect is ascribed in part to an increase of the viscosity of the solution by these additions.

Some very interesting results have been obtained by the prolonged passage of an electric current through ammonia or

ethyl alcohol, when it was found that the conduction increases with the length of time of the passage of the current. Methyl alcohol does not behave in a like manner. This work was done by Corvallo and published in C. R. 156.

The work of Kahlenberg of Wisconsin with instantaneous precipitations of anhydrous copper chloride from anhydrous copper oleate solutions by means of a dry solution of hydrochloric acid in benzene is doubtless familiar to you all. These solutions are all non-conductors and the resulting liquid with the precipitate in is a non-conductor. However, recent work by Cady and Lichtenwaller of Kansas has shown some interesting things in this connection. To take a typical example they passed dry hydrochloric acid gas into copper oleate solution, and while neither one alone was a conductor, nor was the resulting mixture a conductor, they found that just previous to the precipitation, which they say was not instantaneous, that the liquid showed considerable conductivity. At this time I do not care to comment on this work further than to say that it seems to throw light on one of the apparent exceptions to Arrhenius' theory.

The state which a substance is in, apparently has considerable influence on whether the solution conducts or not, even in organic solvents. This was shown by Lloyd of Alabama, who found that when Molybdenum pentachloride is dissolved in an organic solvent giving green solutions, that they have a conductivity of the same order as water solutions of common salts. Differing in this respect, however, that the molecular conduction decreases with dilution. When this same salt dissolves, giving red-brown solutions, they do not conduct appreciably.

With these few considerations, I want, in a way, to ask your pardon for the disconnectedness of the material presented, which, however, is rather forced on the writer by the disconnectedness of the views.