

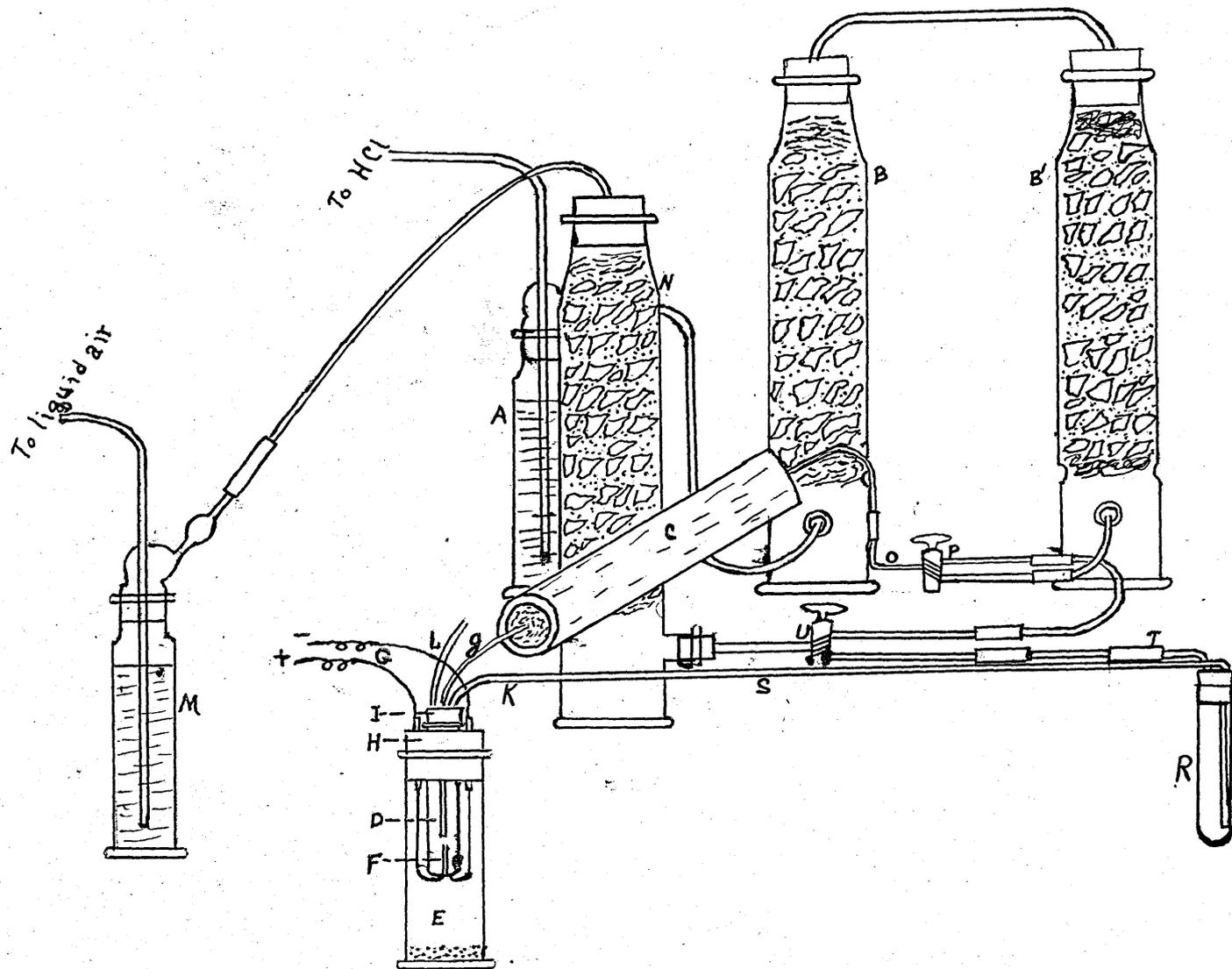
CHEMICAL REACTIONS AND ELECTROLYTIC CONDUCTIVITY
IN NON-AQUEOUS SOLUTIONS.

Presented in Partial Fulfillment of the Requirements for the Master of Science Degree to the Graduate Faculty of the University of Kansas

By

H. O. Lichtenwalter.

May 15th., 1913.



CHEMICAL REACTIONS AND ELECTRICAL CONDUCTIVITY IN NON-AQUEOUS SOLUTIONS.

The first observed electrical phenomena on record are those made by Thales, when he noticed the property possessed by amber of attracting such light bodies as paper and feathers under certain conditions. In the seventeenth century, Gilbert showed that a great many substances become electrified upon being rubbed, but that the metals do not possess this property. A century later Galvani observed the contraction of frog's legs when in connection with some source of electricity. Volta^I was the first to find that whenever two metals and a liquid are combined to complete a circuit an electric current is produced. He probably noticed the chemical action which may be produced by passing an electric current through water, but did not appreciate its significance since he makes no mention of it. In 1800, Nicholson and Carlisle observed this decomposition of water into oxygen and hydrogen by the passage of the electric current from the terminals of a voltaic pile. Thus it became known that, under proper conditions, chemical energy is changed into electrical energy and vice versa. Later, Faraday made im-

I

Le Blanc "Textbook on Electro-Chemistry".

portant advances by showing that when an electric current is passed through an electrolyte producing a chemical change, there is a constant ratio between the quantity of electricity passed and the resulting change. The first electro-chemical theory proposed dates back to Sir Humphrey Davy. According to this theory the atoms contain no electric charges, but by contact with other atoms become charged positive or negative, giving charges of opposite sign to these other atoms. In a very short time this theory was followed by one suggested by Berzelius. This dualistic theory of Berzelius gained considerable prominence. Its assumptions were that every atom is charged by both kinds of electricity. These charges were supposed to exist on the atom in polar arrangement and to hold the atoms in the molecule on account of their attraction for each other.

Next Grotthus^I presented the theory that when a current passes through an electrolyte the molecules arrange themselves with the negatively charged end turned toward the positive electrode and the positively charged toward the negative electrode. The attraction exerted on the atoms nearest the electrode causes the decomposition of the respective molecules. Each attracted atom moves to the electrode attracting it and is neutralized by the charge on the electrode, then discharged

I

Ann. de Chim.(I) 58,54 (1808).

as an electrically neutral substance. Each atom thus left free in the solution then combines with one carrying an opposite charge from an adjacent molecule, thus causing the decomposition and recombining of every molecule. Thus each time a charge is neutralized at the electrode every atom must be moved up one place and also each molecule thus formed must turn around to take the position of the preceding.

The above theory was destined to be discarded since by its assumption a potential large enough to effect the decomposition of the terminal molecule would be necessary to carry on electrolysis. This does not correspond to facts as it is known that a very low potential will decompose a copper sulfate solution with copper electrodes. In order to meet such conditions, Clausius^I advanced the theory that when any electrolyte is dissolved in water a portion of it is immediately broken up into simpler molecules. When the current passes, it is not necessary for it to break up the molecules but simply direct the dissociated particles to the electrodes containing an opposite charge. This theory is still accepted by some of the opponents of the modern theory proposed by Arrhenius.

According to this "Theory of Dissociation" as presented by Arrhenius², a large proportion of the electrolyte

^I Pogg. Ann. 101, 347 (1857)

² Z. phys. Chem. I, 651 (1887)

is dissociated into smaller fragments called ions, each fragment from a molecule carrying an electric charge, either positive or negative. These charges exist in equal amounts in a solution, thus making the whole solution electrically neutral. The percentage of the substance existing as ions in the solution increases with dilution until at infinite dilution the electrolyte is supposed to be completely ionized. The conductivity of an electrolyte depends on the extent to which the solution is ionized and the speed with which the ions travel. Hence, by taking the ratio of the equivalent conductivity of a given solution to the conductivity of infinite dilution, it is possible to determine the proportion of ionized electrolyte. It is in regard to the proportion of ionized particles that brings in the principal difference between this theory and the older one of Clausius. The various assumptions made by this dissociation theory may be found in numerous text-books. It is of particular interest, however, to note that the rapid rate with which many chemical reactions take place is considered as being due to interaction among the ions. It is the application of the theory in the explanation of chemical reactions that will be considered in this paper.

Like other theories that represent such great advancement, it met with strong opposition for many years. However, it soon stimulated inquiry into the nature of solutions and

the relation of chemical reactions to electrical conductivity. First, aqueous solutions were studied almost exclusively. From the results thus obtained many facts have been observed that lend strong support to the theory. Naturally, the investigations were extended to non-aqueous solutions^{II} having the purpose in view of ascertaining the nature of chemical reactions occurring in such, also the corresponding electrical conductivity. During recent years such investigations have become quite extensive. Especially has a large amount of work with non-aqueous solutions, conducted by Kahlenberg^I and others in his laboratory, been done. The results of this work have led these men to set forth reasons for not accepting the dissociation theory. For instance, Kahlenberg² conducted double decompositions in non-aqueous solutions and states that instantaneous reactions occur without any conductivity, hence no ionization. It is with a view of studying similar double decompositions that this investigation has been undertaken. He chooses benzene as a solvent and copper, nickel and cobalt oleates as the solutes. After drying the benzene very carefully, he finds the conductivity to be practically negligible. After drying the oleates over phosphoric anhydride and sodium, their solutions in benzene also were found to be

^{II} H.P. Cady, Jour. Phys. Chem. I, 707 (1897).

^I Kahlenberg, Jour. Phys. Chem. 6, I (1902); Sammis: *Ibid.*, 10, 593 (1906); Gates, 15, 97 (1911)

² *l.c.*

non-conductors. He then passes dry Hydrochloric Acid into this solution and observes that a large precipitate forms and still no conductivity is observed. From this he draws the conclusion that instantaneous double decomposition has occurred without the presence of ions.

Since the above work was done Professor H.C.Allen^I, of this University, has repeated the experiments and found also that the dry benzene was practically a non-conductor. However, when he introduced the dry oleates into the benzene, a marked increase was observed in the conductivity and when hydrogen chlorid was passed in this solution, a precipitate formed, but by no means instantaneously. From the moment the hydrogen chlorid was added, the conductivity increased until reaching a maximum at the instant the precipitate appeared when it became so great as to deflect the galvanometer off the scale. As the precipitation became complete, this deflection grew much smaller. The apparatus used was similar to that described by Kahlenberg in the above reference and corresponds in most respects to the description, which will follow, of the apparatus used in this investigation.

In addition to the above knowledge concerning the solutions of salts of unsaturated acids, it was thought desirable to learn whether salts of the saturated acids would give similar

I

"Instantaneous Chem.Reactions in Benzene and Toluene", Kans. Univ. Sci.Bulletin, 1905.

reactions, also to study salts of unsaturated acids with two double bondings as well as others with one double bonding besides the oleates.

One of the first difficulties encountered was in finding salts which are soluble in hydrocarbons. It was found that benzene, toluene and petroleum ether can equally well be used as solvent, being almost perfect insulators. The following salts were found to be soluble in one of the above:- Silver melissinate¹, Copper melissinate², Lead stearate, Barium linoleate³, Lead erucate and copper oleate⁴.

These salts were prepared from the respective acids obtained from Kahlbaum or Schuchardt. A slight excess of sodium hydroxide was added to the acid first forming the sodium salts. The calculated amounts of sulphates or acetates of the respective metals were then added to these sodium salts giving the desired products. These precipitates were carefully washed with water and dried in a water oven for several days. They were then dissolved in benzene or toluene and placed in bottles with a liquid alloy of metallic potassium and sodium, and left there for several weeks until becoming perfectly dry.

¹ Archiv.d.Pharmacie 246,170 . ² Ann.der.Chem.183,354

³ Lewkowitsch p.II2 .

⁴ Ann. 244, 266(1888).

It was found that such an alloy of potassium and sodium serves very well to dehydrate the solutions. In order to obtain such an alloy that would remain liquid at ordinary temperature, the metals were heated together in proportions of at least 50 per cent potassium^I. Such a liquid alloy continually keeps a clean metallic surface exposed to the solution.

The hydrogen chloride was prepared in a Kipp generator by concentrated sulphuric acid and ammonium chloride. The generator was connected to a gas washing bottle(A)² containing concentrated sulphuric acid. After passing through this, the Hydrochloric Acid was conducted through two towers (B and B^I) about 40 cm. in height. These towers were filled with alternate layers of pumice stone and phosphoric anhydride. From the tower the Hydrochloric Acid was led through an electric resistance heater(C) and into the cell (D) used to measure the conductivity.

The cell was enclosed in a larger jacket (E) in which phosphorus pentoxide was placed to keep the outer portion of the cell perfectly dry. It was one of the same type as the Arrhenius resistance cell. The electrodes(F) were of platinum and placed about one millimeter apart. They were connected by platinum wires (G) sealed through the bottom of the cell, to lead wires connected to the galvanometer and current. These

^ILandolt - Börnstein p.304

²Letters used in the description of apparatus refer to the drawings on first page.

lead wires passed through openings in the rubber stopper (H) which closed the casing around the cell. Sulphur was used to insulate the wires from the rubber. In the top of the cell was placed a three-holed rubber stopper through which three glass tubes entered the cell. Through one of these tubes was admitted the Hydrochloric Acid. One (K) was used to carry in the air, used to dry the cell, also to introduce the solution. The third (L) was connected with a phosphorus pentoxide tube in series with a calcium chloride tube. The escaping gases from the cell passed out through this last tube. When conductivity measurements were taken, the cell was connected in series with a direct current generator of 110 volts and with a sensitive galvanometer. No other resistance - except that of the lead wires and of the galvanometer - was introduced except in instances that will be mentioned later. The sensitiveness of the galvanometer was determined by connecting it with a potentiometer and measuring the deflection when the E.M.F. was varied, but always at known value. It was found that when an electromotive force of one volt was applied, it would require 86,547,000 ohms resistance in order that the galvanometer would show a deflection of 1 division (m.m.). The resistance of the galvanometer coil was found to be 1245 ohms. The galvanometer cell and entire system were insulated by placing them on sulphur. This proved to be the best insulator that was available. It was used to insulate every place where there was a chance for leakage of current.

Hard rubber and other substances were tried, but in every case where they were used the instrument showed marked effects of leakage.

Before making conductivity measurements, dry air was passed through the cell until the deflection of the galvanometer was negligible. A flask of liquid air was connected in series with a wash bottle (M) filled with sulphuric acid and a tower (N) filled with pumice stone and phosphorus pentoxide similar to the one mentioned above. From this tower the air was led through the electric resistance heater, then through the cell. Thus, the cell was thoroughly dried by passing this hot air through each time before use. The tower connected with the Hydrochloric Acid generator and the one through which the air was passed connected to the same glass tube (O) by a two way stop-cock (P), thus enabling the operator to pass in either Hydrochloric Acid or air at will.

The solutions used were centrifuged whenever necessary in order to settle out any particles. They were then placed in a tube (R) fitted with a two-holed rubber stopper. These connected with a tube (S) passing to the conductivity cell and one (T) connected with the drying tower through which the air passed. By means of a two way stop (U) cock the air could be passed

through the tube thus forcing the solution into the cell.

Before taking readings of the conductivity of the solution, the cell was in each instance dried so thoroughly that when the 110 volts was applied the galvanometer would show a deflection of only about one division or less. The toluene and benzene, dried over sodium-potassium alloys, the same as were the solutions, were placed in the cell and showed scarcely any deflection - a small part of a scale division. The Hydrochloric Acid was also tested and did not conduct scarcely any better than the air. This was again swept out by air before using the cell further.

When a toluene solution of copper oleate was introduced, the conductivity was so great that the galvanometer was thrown off the scale (40 divisions) . A shunt of 200 ohms was placed across the galvanometer, thus carrying approximately one-seventh of the current through the instrument - and the reading was found to be about 9 divisions. Hydrogen chloride was then admitted and the deflection was so large as to again pass off the scale, with only this portion of the current. A rather rapid precipitation of copper chloride occurred. The deflection soon began to decrease and finally became negligible. The shunt was then disconnected from the galvanometer and still the deflection was less than a division after the precipitate had settled. Instead of drying the copper oleate

used here by the method described above, it was placed in the toluene with potassium, then heated in an Erlenmeyer flask fitted with a condenser tube. This was found to dry the solution in a short time when heated to boiling. This method was used because it was found when dried by the slower process nearly all the copper was thrown out of solution forming a dark layer just above the sodium-potassium.

With a benzene solution of lead erucate the deflection was again so great as to throw the galvanometer off the scale. When a shunt of 40 ohms was placed across the instrument, the deflection was 14 divisions. When introducing Hydrochloric Acid, it went off the scale but gradually lowered to a negligible deflection. In this case, also, a precipitate was observed. Another sample gave similar results.

The first of the saturated salts used were the mellisates. The copper salt was dried in same way as the copper oleate for the same reason. The silver salt was kept in a dark place while drying. When a benzene solution of the copper mellisate was used the deflection was again great enough so that it was necessary to put in a shunt of 300 ohms. It now read 54 divisions. When Hydrogen chlorid was passed, the deflection at first was too great to read on the scale, but soon came down to a few divisions. No precipitate was observed. The silver mellisate gave similar results, except that the

conductivity was less. A toluene solution of lead stearate was used and it gave a deflection of about 13 divisions. On passing Hydrochloric Acid, this was increased to 17 divisions. No precipitate formed.

Barium linoleate was then tried in a benzene solution. This salt was used because it contains two double bondings. When dried in the air, as mentioned above, the solution was found to give a deflection of about 7 divisions, which increased to 21 divisions when Hydrochloric Acid was introduced. However, no precipitate was formed. Upon suggestion, this salt was again prepared but instead of drying in the air before final dehydration over sodium and potassium, it was dried as well as possible between filter paper and immediately placed in solution over sodium and potassium and heated as the above salts. When introducing this solution into the cell the deflection was so great that it was necessary to insert a shunt of 200 ohms across galvanometer. The reading on the scale was then 7 divisions. When Hydrochloric Acid was admitted the deflection was too large to read at first. A large precipitate rapidly formed and after this settled the deflection decreased to 3 divisions. The difference in the results obtained with this salt suggest that when dried in air it becomes saturated - the two double bondings becoming satisfied by oxidation - and under these conditions one would expect results as above which were

similar to those with the saturated salts.

It is seen from the above that in no instance did precipitation occur between the Hydrochloric Acid and the saturated salts - melissinates and stearates . However, their benzene and toluene solutions showed some conductivity which increased when Hydrochloric Acid passed through the solution. The salts with one double bonding - oleates and erucates - precipitated in every instance and showed considerable conductivity. Likewise with the linoleate where we have two double bondings.

An increase in conductivity was observed in each solution when hydrogen chlorid was added, showing ionization to some extent at least. After saturating the solution with hydrogen chlorid, it was partly swept out by passing air through the cell. By thus diluting the solution the deflection increased for some time, then decreased, thus showing maximum conductivity when not completely saturated with the acid.

In no instance was the reaction found to be instantaneous although rather rapid, especially with the linoleate.

The decrease in the conductivity soon after the solutions were introduced suggested that the polarization was quite appreciable. In order to test for this, we passed the current of 110 volts through the cell containing the solution for a short time. Then, by means of a specially constructed switch set in sulphur, the current was broken and at the same

time, the cell was connected to a condenser with a capacity of one microfarad, thus charging the latter. The condenser was also connected - through a condenser key - to the galvanometer. By this condenser key the condenser was discharged through the instrument. It gave considerable deflection. On comparing this deflection with that given by the charge stored in the condenser by a standard Weston cell, it was found that the solutions gave rise to a back E.M.F. of a large fraction of a volt. This polarization again shows that the solutions have electrical properties similar to those of any ordinary electrolyte.

Kahlenberg states that reactions like the above cannot be explained by the dissociation theory. While the conductivity with the above unsaturated salts is perhaps insufficient to account for the rapid reactions, it is great enough to indicate that the reactions may be due to ionization. Professor H.P. Cady has suggested another explanation which would seem very reasonable and is strengthened by the above results. This explanation assumes that the reactions with the salts of the unsaturated acids take place in two steps. First, the salt would combine with the hydrogen chlorid and form addition products. Second, intramolecular rearrangement occurs with the precipitation of the chlorid and the formation of the acid, If such addition products are formed with salts of unsaturated acids, we would expect results such as were obtained, since they would not be

formed in saturated salts. If this is true, we would then conclude that ionization in the latter was insufficient to cause precipitation, while, in the unsaturated, the precipitation did occur due to the combined effects of ionization and the formation of addition products.

In view of the appreciable conductivity observed with each solution that gave a precipitate, every one of the above reactions is in accord with the dissociation theory, especially if, in addition, the explanation, which has just been mentioned, is accepted.

This work was suggested and carried out under the direction of Professor H. P. Cady. This opportunity is taken to thank him for the guidance he has given me throughout the work.