C. PHYSICS

XLII. ON SPACE CHARGE IN ELECTROLYTES.

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An experimental investigation of conducting electrolytes was made, in an attempt to determine the existence or non-existence of appreciable amounts of space-charge. The method of attack was electrical, rather than chemical, in nature. It is doubtful whether the problem can be attacked by a chemical method, for theoretical considerations, as well as the present investigation, show that any effects due to space-charge in liquids are extremely small. Electrical methods for examining such effects in a liquid can be shown to be enormously more sensitive than the methods of analytical chemistry.

A substance is electrically neutral if in every small part of it the quantity of negative electricity is exactly equal to the quantity of positive electricity. Thus an ionized liquid or gas is electrically neutral when the differences between the number of negative and positive ions in each volume element, multiplied by the charge per ion, is zero. If, on the other hand, there is an excess of charges of either sign in any volume element of the substance, the substance is not electrically neutral, but is said to possess space charges; its volume density of electrification is different from zero. Space-charge in a conducting substance manifests itself in its effect on the gradient of the electrical potential in the substance; it produces variations in the field intensity in different parts of the conductor.

Conducting gases and electrolytes possess so many properties in common that a survey of the work done on space-charge effects in gases throws much light on the investigation of the same phenomenon in electrolytes. Zeleny and Child found experimentally that the field intensity in a conducting gas between parallel electrodes was greatest near the electrodes and nearly constant for some distance midway between them. This variation is attributed to the movement of the gaseous ions in the electric field. Thus in the space adjacent to an electrode the number of ions approaching the eletrode was greater than the number receding, since the former contained ions generated in all of the gas, whereas the latter contained only the ions generated in the narrow layer near the electrode. The space charge resulting from the excess of negative ions near the anode, and from the excess of positive ions near the cathode, disturbed the field so that its intensity was increased near the electrodes and diminished in the space midway between them. It was also found that the intensity was greater at the cathode than at the anode. Zeleny showed that this was due to the fact that the negative gaseous ions have a greater speed than the positive ions, and there is thus an excess of positive electricity in a conducting gas which increases the field intensity at the cathode and diminishes it at the anode. Mie calculated the field distribution for various values of the current in ionized air at atmospheric pressure. He neglected effects due to diffusion because of their small order of magnitude. His results agree with those obtained experimentally by Zeleny and Child.

The effects of polarization on conduction through high vacua and in thermionic tubes has also been thoroughly investigated. In thermionic tubes, where only negative ions are present, the effects of space-charge on the current and field are matters of considerable importance in their design and operation.

At least three quite different methods have been used in studying space-charge effects in gases. Zeleny and Child measured the potentials assumed by an insulated wire placed parallel to the electrode and in different parts of the field. This method is open to the objection that for points near the electrodes, the insulated wire assumes a quite different potential from that of the gas at the same point when the wire is absent. For points remote from the electrodes, however, the method is considered fairly reliable. Graham improved this method in his experiments with Geissler discharges by using two insulated wires, held at a fixed distance apart and placed in different parts of the discharge.

The most direct means for investigating space-charge is that used by Zeleny. He removed portions of the conducting gas from different parts of the field and determined with a quadrant electrometer the nature and relative amounts of the charges in these portions. His results are in agreement with theory, but they do not admit of an exact evaluation of the charge at a point in the gas. Thompson, and later, Astom, examined the field in Geissler discharges by a method which consists essentially of passing a narrow beam of cathode rays lateral to the Geissler discharge. The cathode rays are deflected by an amount proportional to the field intensity at the point of passage, the deflection being measured on a fluorescent screen. The results obtained by this method corroborate the conclusion that an insulated wire placed close to an electrode does not afford a reliable means of measuring the field distribution in that locality.

In the experimental investigation of space-charge on electrolytes made by Dr. Wm. Schriever, of the University of Oklahoma, and the writer, a method was used similar to that devised by Graham for gases. Two insulated platinum pointers, held at a fixed distance of 1 cm. apart, were placed in different parts of the conducting electrolyte and the potential difference between them was measured with a quadrant electrometer. The electrolyte was contained in a paraffined wooden trough, made in the shape of a rectangular parallelopiped and having the inside dimensions of 37.3 x 4.6 x 6.3 cm. The trough electrodes were rectangular sheets of platinum foil, 5.6 x 4.8 cm., placed parallel to each other, one at each end of the trough. The platinum pointers were made of 0.4 mm. wire sealed into 3mm. glass tubing, the exposed parts of the wire being 4 mm. long. The glass tubes contained mercury which served to complete the metallic circuit between the pointers and the copper wires leading to the electrometer quadrants. Sealing wax was fastened tightly to the glass and copper wires where the latter entered the tops of the glass tubes in order to prevent charges from escaping from the electrolyte to the copper wire over the surfaces of the tubes, and also to keep the mercury in the tubes clean. The pointers were held at a fixed distance apart in a paraffined wooden clamp, and this clamp was attached to a bed-rod in such a manner that it could be moved along the whole length of the trough and fastened in any position. The electrometer was a Dolezalek quadrant electrometer fitted with a quartz suspension. The needle was charged to 135 volts, giving a sensitivity of about 250 mm. per volt on a straight glass millimeter scale placed 1 m. from the suspension mirror.

The potential difference between the anode and cathode of the trough was maintained with Edison secondary cells. This circuit also contained a sliding contact rheostat and a milliameter. A voltmeter was shunted across the trough electrodes. The trough, its contents and all connecting circuits and instruments were insulated. The electrometer and trough were completely enclosed in separate grounded cages made of 14 mesh iron window screen.

The electrolytes used were variously concentrated aqueous solutions of hydrochloric acid between 0.005 N. and 0.3 N, and the electrode voltages ranged between 5.3 and 26. Sufficient solution to cover the electrodes was placed in the trough and a difference of potential applied. The current was allowed to run several minutes and then the potential difference was adjusted to a certain value and kept constant for the remainder of that particular series of observations. The platinum pointers were then placed in the electrolyte in such a position that their end points were approximately on an imaginary line connecting the mid-points of the trough electrodes. Electrometer readings were made with the pointers placed at intervals of 3 cm. along the whole distance between the trough electrodes, and thus the field along the longitudinal axis of the column of electrolyte was explored. In order to eliminate from the average results, effects which might be attributed to progressive changes in the solute concentration and to electrode polarization, the pointers were moved from anode to cathode for all odd numbered trials and in the reverse direction for even numbered trials.

The following interpretations are made from the results of a total of 32 trials, involving four differently concentrated solutions and 12 different electrode potentials. It seems safe to conclude that the field in the electrolyte was uni-directional and normal to the electrodes in the regions invaded by the pointers, since the dielectric constant of the liquid is high, the region explored by the pointers was close to the axis of the liquid, and raising and lowering of the pointers through small vertical distances seemed to have no appreciable effect on the electrometer readings. The fields in the very dilute solutions had characteristics similiar to those in conducting gases containing space charges; the intensity was greater near the electrodes. The maximum intensity, however, was in every case near the cathode, which is the region towards which the faster moving ion migrates. In gases the maximum intensity occurred in the region toward which the slower moving ion migrates. These results are as yet only qualitative but they indicate that there are appreciable non-uniform electrical distributions in dilute hydrochloric acid which can be explained on the basis of space-charges in the conducting electrolyte.

References consulted are: Townsend, "Electricity in Gases", Chapters 3 and 11; Getman, "Outlines of Theoretical Chemistry", pp. 398-403, 494-497; Nernst, "Theoretical Chemistry", pp. 362-402; Zeleny, Phil. Mag. 46, p. 1898; Van Der Bilj, "Thermionic Vacuum Tube, Chapters 1, 4, 5.