ELECTROMIGRATION IN A CATION EXCHANGE RESIN

by

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science with a Major in Chemistry.

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Approved by Robert E [illegible]

June 4, 1962

I Introduction

The purpose of this research was to investigate the phenomenon of electromigration of ions in a cation exchange resin. When a potential is applied across a solution of ions in series with an ion exchange resin column, the cations will migrate through the resin toward the cathode and the anions will migrate toward the anode. The cations as they migrate through the resin should form bands because of their different ionic mobilities and their different exchange rates on the resin. The object of these experiments was to design and build the apparatus necessary to achieve the separation of the cationic species and to obtain data on the separation process.

II Historical

Experimental research on the electrochemical properties of ion exchange resins has been done by Bauman and Eichhorn (1) , Juda and McRae (2) , and Kuwabara , Seiyama and Sakai (4).

Bauman and Eichhorn carried out equilibrium experiments on the ion exchange resin, Dowex 50. They concluded that the ion exchange resin is equivalent to a highly ionized salt solution. Juda and McRae explored the electrical conductance of ion exchange resins. Kuwabara, Seiyama and Sakai have done electrochemical studies with ion exchange membranes including studies of the separation of ionic species.

Studies of the migration of ions in an electric field along strips of paper have been carried out by McDonald , Urbin and Williamson (7). They also used this technique to separate proteins.

The first work on the separation of ions in ion exchange resin columns by ionophoresis was done by G. Manecke (6) and was suggested to him by his experiments on ionic movement in ion exchange membranes (5). Manecke's apparatus consisted of a chamber containing the solution of ions to be separated. At either end of this chamber were two tubes ,eight centimeters long and 1.5 square centimeters cross sectional area, connected to the middle chamber through glass fritted disks. The tube located at one end contained a quaternary ammonium base anion exchange resin and at the other end a sulfonic acid cation exchange resin. Platinum electrodes of one square centimeter cross sectional area were connected at each end of the apparatus. Distilled water was allowed to flow over these electrodes. A potential of 120 volts was applied across the electrodes and a direct current of five to twenty milliamperes flowed through the circuit. The ions were separated into bands because of their different mobilities.

Spiegler and Coryell (9) and (10) have also worked on the separation of ions in an ion exchange resin. Their procedure was to apply an electrical potential to electrodes in contact with a column of cation exchange resin , which was continuously flushed with distilled water. The separation of the ions was observed by use of radioisotopes to tag the layer of cations. Spiegler and Coryell proved that the electrode reactions occurring in their apparatus were:

$$\text{anode}: 4R^- + 2H_2O = 4\,HR + O_2 + 4e^-$$
$$\text{cathode}: 4e^- + 4NaR + 4H_2O = 4R^- + 4Na^+ + 4OH^- + 2H_2$$

They also showed that the electromigration phenomena are analogous to those observed in solution except that there are no thermal convection effects. Experimental straight line current versus voltage curves were obtained by Spiegler and Coryell in the operation of their apparatus.

III Apparatus

The apparatus used in this project was similar to that used by Manecke in his experiments. The two different experimental set-ups used are pictured in Figures 1 and 2. The apparatus was made of Pyrex glass tubing. The first set-up, Figure 1, required a warm-up time of about one hour before any electrode reactions or ion migration began. This was probably due to the high resistance of the distilled water in the cathode chamber and to the consequent difficulty in starting ion migration. The length of the apparatus was shortened in the second set-up, Figure 2, to decrease the resistance between the platinum electrodes. Hydrochloric acid was added to the cathode chamber, to the anode chamber, and to the ion exchange resin column. The hydrochloric acid serves as a supporting electrolyte. The warm-up time of the second design of the apparatus was less than five minutes.

The ion exchange resin used in this experiment was Dowex 50wx8 which is a styrene type sulfonic acid resin in hydrogen form.

The current flowing in the circuit was measured by

FIGURE I

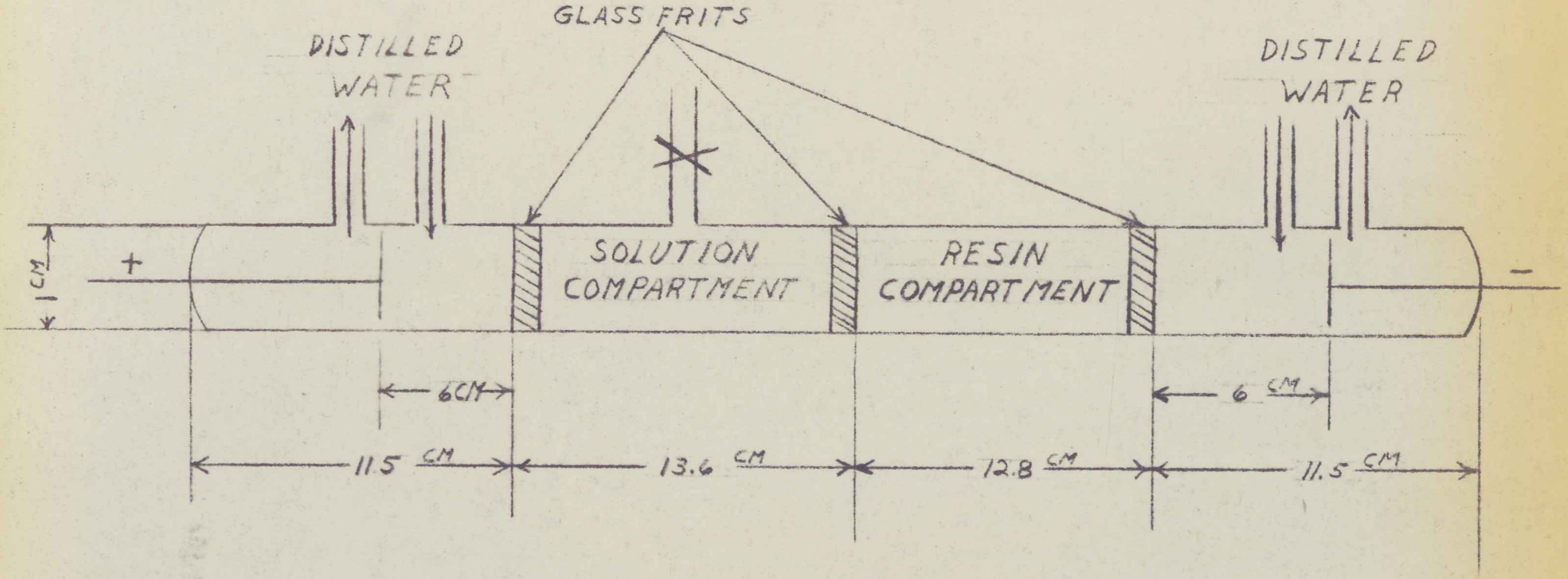
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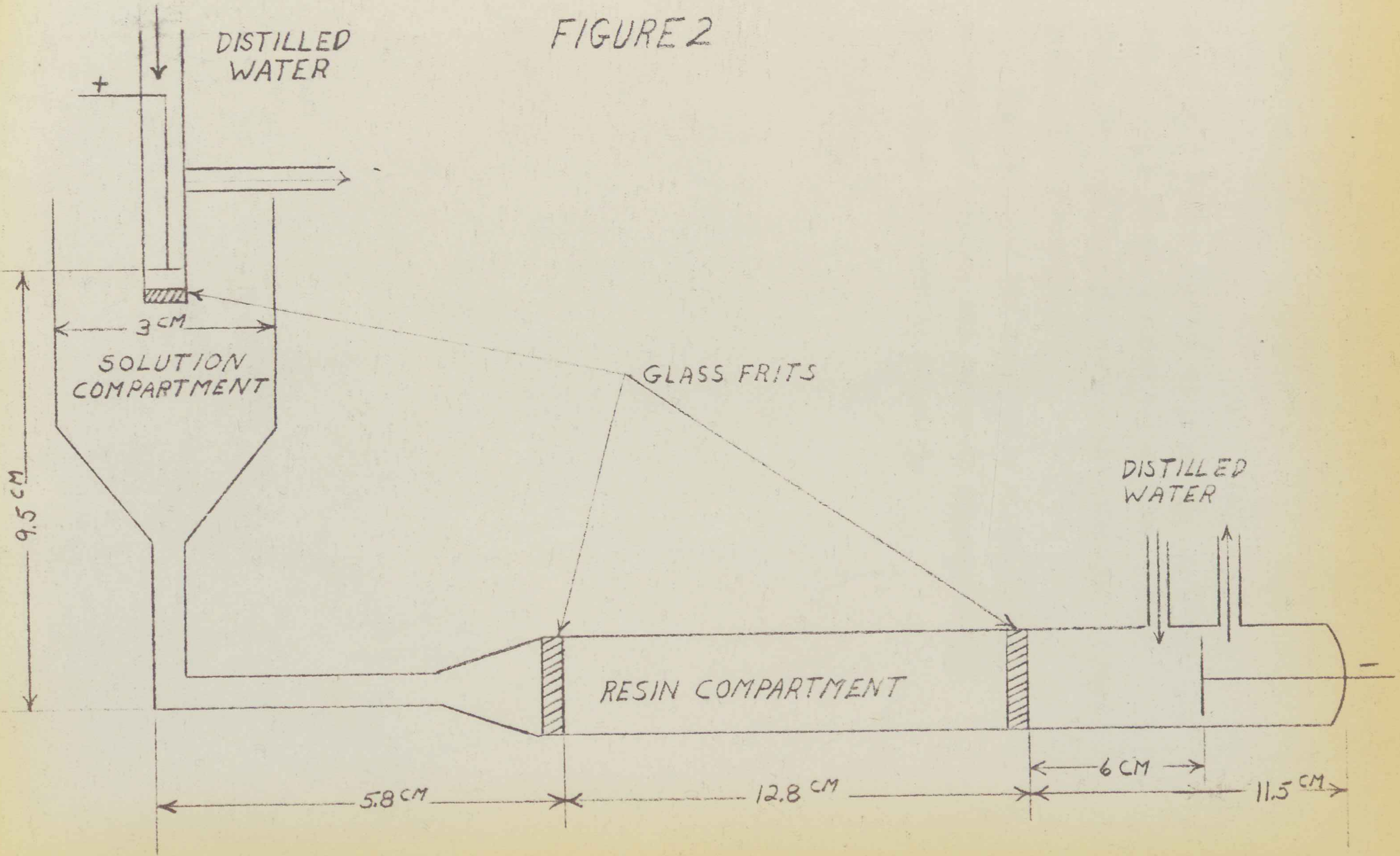
FIGURE 2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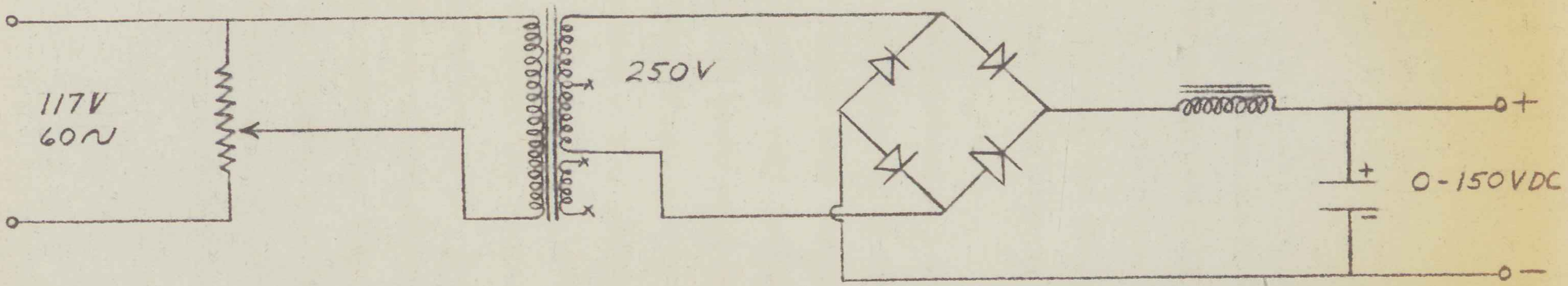
11.5 CM

means of a direct current milliammeter ,Triplett model 675. A direct current volt-ammeter,Weston model 540, was used to measure the potential applied between the electrodes.

The potential was supplied by a power supply of variable voltage. The schematic diagram of the power supply is shown in Figure 3.

FIGURE 3



IV Experimental Results

The solution used for the separation experiments contained cobalt (II) ions and copper (II) ions. The hydrated cobalt (II) ion is pink in color and the hydrated copper (II) ion is blue. The difference in the color of the two ionic species was used to observe the separation visually.

In the first attempted separation the solution in the anode reservoir was .108 molar with respect to cobalt (II) ions and .114 molar with respect to copper (II) ions. An absolutely well defined separation was not achieved. The initial separation was observed after about two hours of operation. The front part of the migrating ion band became a deep green. The size of the green band gradually became larger. After about five hours of operation, the band was two centimeters wide. The part of the resin column behind the green band was a pinkish-grey color, but there was no sharp boundary between the cupric and the cobaltous ions. The green color of the cupric ion band turned to a dark grey two centimeters behind the front. The grey color lightened and became pink toward the end of the resin column.

The total length of the grey and pink colored part of the resin was about five centimeters.

The rate of movement of the ion front was measured for two hours beginning at the third hour of operation. The velocity was .035 centimeters per minute during the two hour period, but was not constant throughout the period. At the beginning it was .062 centimeters per minute and near the end it was .015 centimeters per minute. The current flowing in the circuit was also measured during this period of operation. It dropped from 13 milliamperes at the beginning to 6 milliamperes at the end of the period. The decrease in the velocity of the ion front and the decrease in the current is caused by the depletion of ions in the vicinity of the electrodes and the consequent increase in the resistance of the solution and resin column.

A better defined separation between the cobaltous and cupric ions was obtained when the solution in the anode chamber was .0325 molar in cobalt (II) ions and .0341 molar in copper (II) ions. The color of the cupric ion band was a lighter green , but the separation between the cobaltous and cupric ion bands was easily seen. The current flowing in the circuit was measured as a function of the applied voltage during this run. Figure 4 is a plot of current versus voltage for the system with 0.2N hydrochloric acid initially present in the cathode chamber and with the solution in the anode reservoir slightly acidified. Figure 5 is the plot of current versus voltage with 0.2N hydrochloric acid initially in both the cathode and anode chambers. Results similar to those shown in Figure 5 were obtained when the acid concentration of the cathode chamber was increased above 0.2N. The discontinuity shown in Figure 5 is a true discontinuity because it was impossible to obtain any experimental points between 60 and 100 volts. This discontinuity of the current versus voltage curve seems to indicate a threshold of some sort.

The electrode reactions occurring during the operation of this equipment were:

anode : $2Cl^- = Cl_2 + 2e^-$

cathode : $2H^+ + 2\ e^- = H_2$.

FIGURE 4

CURRENT VS. VOLTAGE

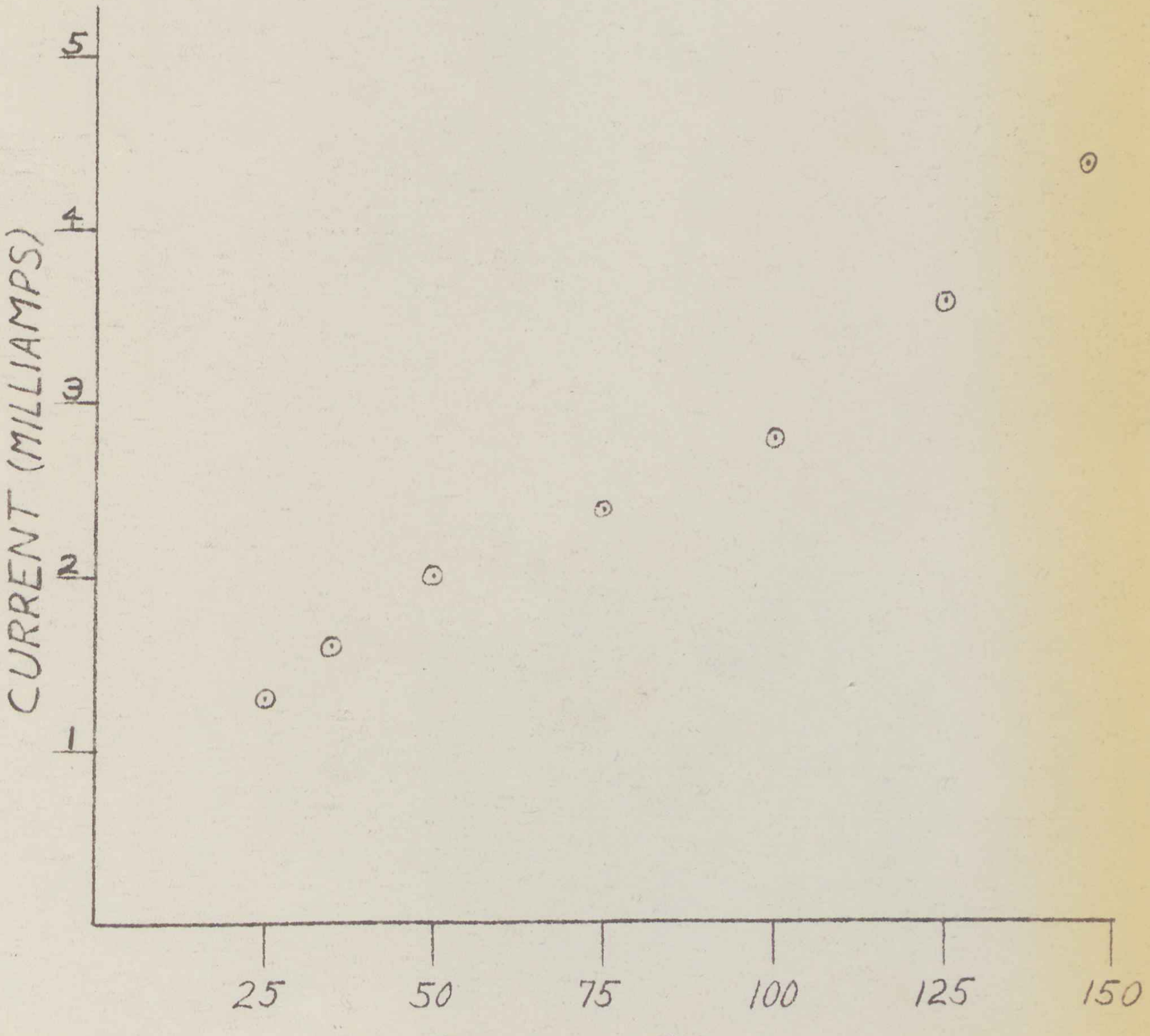
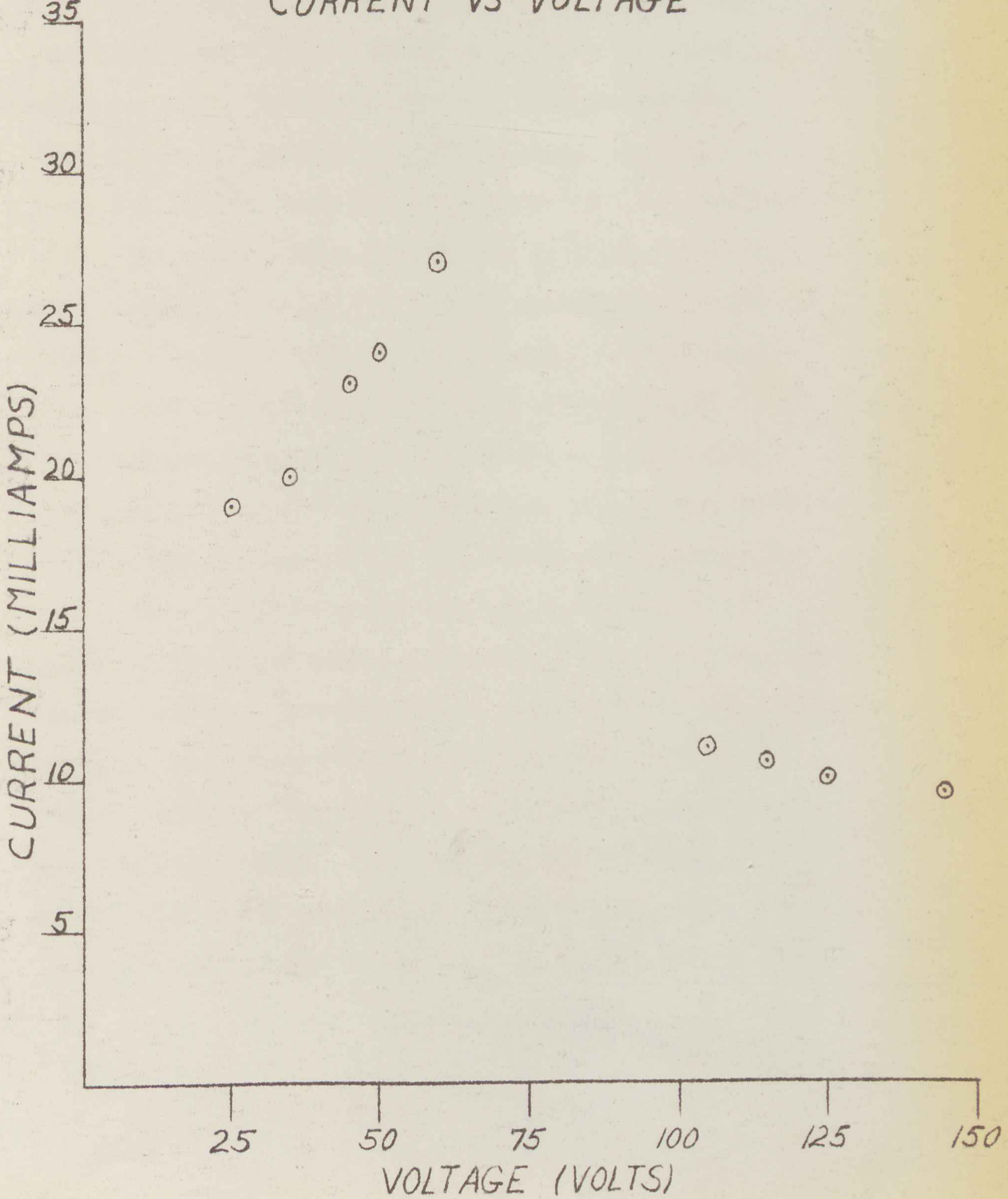


FIGURE 5

CURRENT VS VOLTAGE



V Summary

The discontinuity in the current versus voltage curves at higher hydrogen ion concentrations may be caused by the depletion of ions in parts of the solution. The hydrogen ions may be attracted toward the cathode very quickly. This may cause an increase in the apparent resistance of the solution and a consequent decrease in the current flowing in the circuit. Also at the higher hydrogen ion concentrations most of the current flowing in the circuit is carried by the hydrogen ions. This may slow down the movement of the ionic bands through the resin and may also hinder the separation of the ions into bands. The problem of the separation into bands and the movement of the bands may be investigated by running distilled water and then solutions of varying concentrations of hydrochloric acid through the cathode chamber. This procedure will eliminate the decreasing current and the decreasing velocity of the band which was observed above. This separation technique should work using other supporting electrolytes. This problem of using other supporting electrolytes should also be investigated.

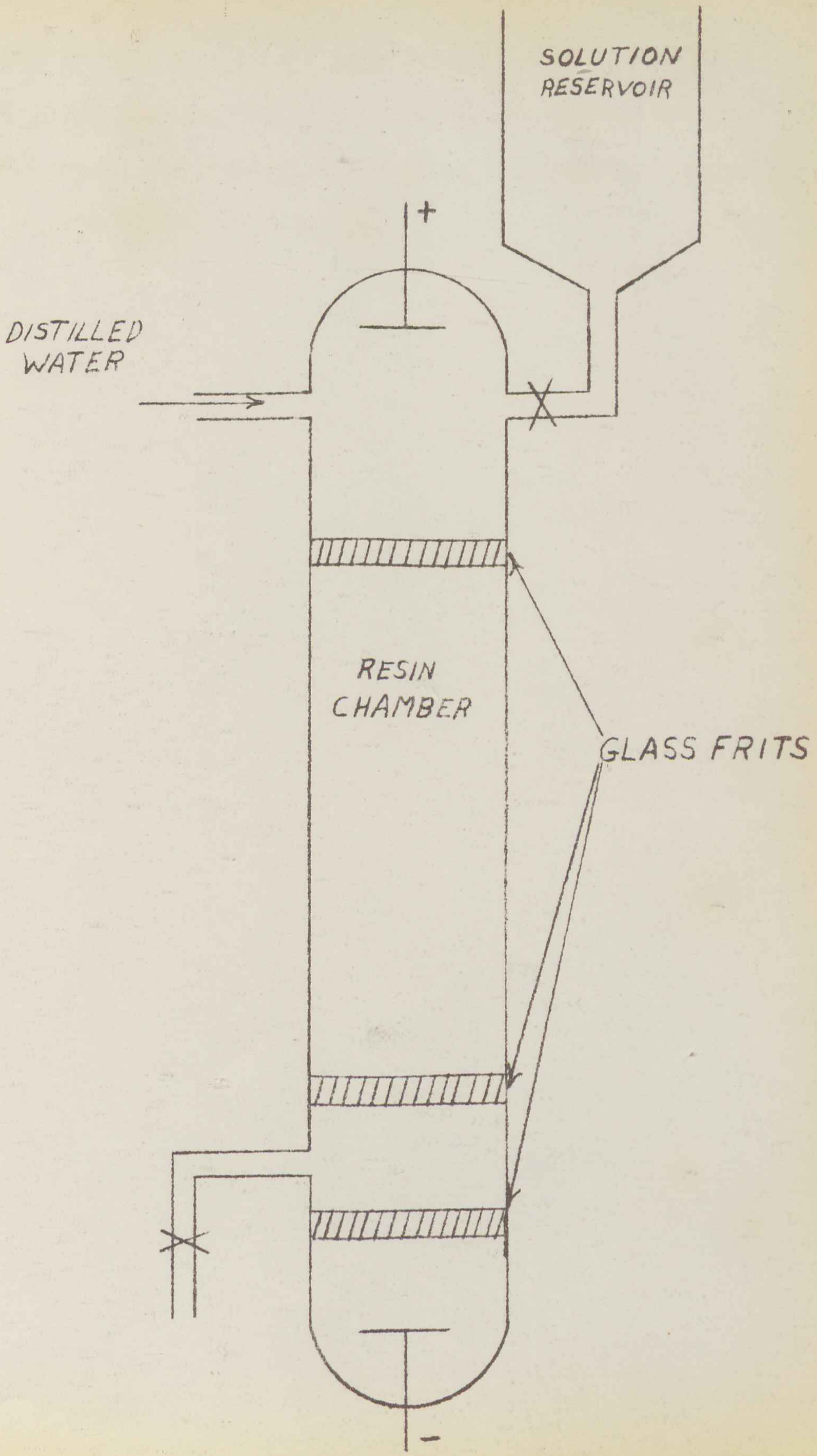
The current versus voltage curve shown in Figure 4 was expected to be a straight line. A straight line was not obtained because the system WAS not static or at equilibrium during the time that measurements were made. This will cause some scattering of the experimental points.

The length of the resin column used in any one separation should depend upon the amount and concentration of the solution to be separated. In the separation run above, the failure to get a good visible separation between the cupric and cobaltous ions was caused by the limited amount of time and the limited length of the resin column used. A better separation would have been obtained if a longer resin column had been used. The ion exchange resin has a limited capacity to exchange hydrogen ions for metal ions. The capacity of the ion exchange resin limits the amount of ions a column of certain length and diameter will be able to separate.

The order of migration of ions was found to be the same as the order in simple solution. The cupric and cobaltous ions have the same charge ,plus two, but the cupric ion is smaller than the cobaltous ion. The smaller cupric ion should have a higher velocity and this was born out in the experiments. The green band observed migrating in front of the pink band was the cupric ion band. The green color was caused by the yellow colored resin and the blue colored cupric ion adding to give the green color. The order of migration of the ionic bands should be investigated with various other ions to determine whether the ions migrate in the same order as they would in a simple solution free of convection currents.

The use of this phenomenon ,in connection with a chromatographic type set-up,as an analytical tool is possible. A design of this type of equipment is shown in Figure 6. This type of set-up would have distilled water flowing through the resin column. The glass fritted disks shown in Figure 6 should be fine enough so that they will pass water only under suction. As the ionic bands move out of the resin and into the cathode chamber, samples could be taken to be analyzed spectrophotometrically. This use as an analytical tool may be limited to some

FIGURE 6


SOLUTION RESERVOIR
+
DISTILLED WATER
RESIN CHAMBER
GLASS FRITS
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extent by the length of time necessary to obtain a separation. The use of the chromatographic technique may speed up the separation process and make the phenomenON more useful.

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